

**Project name: Rapid Small-Scale Column Testing to Treat
PFAS in Potable Groundwater Supply from UW15
Groundwater Well**

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To: Joe Grande
Water Quality Manager
Madison Water Utility
119 E Olin Ave
Madison WI 53713

From: Francisco Barajas

Date:
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CC: Angel Gebeau, AECOM
Chris Curran, AECOM

Treatability Study Technical Memorandum

Introduction

AECOM prepared this technical memorandum with the findings from a treatability study designed to determine the effectiveness of reducing per- and polyfluoroalkyl substances (PFAS) in groundwater samples from the Madison Water Utility (MWU) Unit Well (UW)15 using granular activated carbon (GAC) and ion-exchange resins (IXR). Due to the employment of laboratory scale, small columns, rapid small scale column tests (RSSCTs) allow for data collection under a fraction of the time that is needed in a pilot-scale test while maintaining a high level of data accuracy. The RSSCT is based on method ASTM D6586 and provides two important pieces of information: 1) comparison of relative performance between different test conditions; and 2) the specific throughput and carbon usage rate, which may be used to estimate GAC bed life for a large-scale system.

Test Goals

The RSSCT study had the main goal of demonstrating the effectiveness of two different GAC and two different IXR media at removing key PFAS compounds by adsorption. The GAC products were FiltraSorb® 400 (F400) from Calgon Carbon Corporation and AV1240LDX from AqueoUS Vets. The IXR were PFA 694E from Purolite and PSR2+ from Dow Chemical Company.

The RSSCT test goals:

1. Evaluate the relative performance among different sorbent products while tested under controlled laboratory conditions.
2. Evaluate the time to breakthrough for 33 PFAS compounds (WI33) in all media tested.
3. Evaluate the water volume treated per mass of sorbent product (specific throughput rate).
4. Confirm overall water characteristics and their impact on treatability including volatile organic compounds (VOCs) and dissolved inorganic species.

The client objective for the future system is to reduce PFAS concentrations to non-detect for PFOA and PFOS to meet the Environmental Protection Agency's (EPA) health advisory values of 0.004 and 0.02 parts per trillion (ppt) for PFOA and PFOS, respectively, and to achieve a Health Hazard Index less than 1 per the Wisconsin Department of Health guidance. The Health Hazard Index measures a risk of combined PFAS compounds. The Health Hazard Index is determined by adding the sum of various species of PFAS divided by their respective health guidance levels. If that sum is greater than 1 then the water is assumed to have a PFAS risk that requires public notification. The performance of the sorbent media was evaluated based on a breakthrough criterion of 20 nanograms per liter (ng/L) of total PFAS concentration in the columns' effluents. At full scale, the lead vessel

media will be replaced at a total PFAS concentration of 20 ng/L such that the lag vessel effluent should remain below detection limits. The information collected from this RSSCT will be useful for the future feasibility study and preliminary design.

Test Approach

Treatment technologies for PFAS removal in water matrices based on separation have been studied and developed. GAC has been established as an effective sorbent for adsorption of organic contaminants, including PFAS. MWU requested IXR be tested as well to review performance for PFAS adsorption and N-nitrosodimethylamine (NDMA). Evaluating the performance of these media under laboratory-scale flow-through conditions that simulate large-scale implementation can reveal valuable information needed for media selection and pilot-scale test design.

The treatability study evaluated four media for PFAS reduction, as shown in **Table 1**.

Table 1. Media Selected for the Treatability Study

MEDIA TYPE	SORBENT PRODUCT	SUPPLIER	MESH SIZE	MEAN DIAMETER (µm) ¹	WATER SOURCE
Bituminous GAC	F400	Calgon	12 x 40	937	Spiked and Non-spiked
Bituminous GAC	AV1240LDX	AqueoUS Vets	12 x 40	912	Spiked
Ion Exchange Resin	PFA 694E	Purolite	16 x 50	675	Non-spiked
Ion Exchange Resin	PSR2+	Dow	16 x 40	700	Non-spiked

¹ µm – micrometer, measured via laser diffraction.

An aliquot of the site water was spiked with the PFAS compounds of Perfluorooctanoic acid (PFOA), Perfluorooctane sulfonic acid (PFOS) and Perfluorohexanesulfonic acid (PFHxS) to achieve a total concentration of 40, 40 and 80 ng/L, respectively. The aliquot was also spiked with two VOCs: Trichloroethylene (TCE) at 1 µg/L and Tetrachloroethylene (PCE) at 5 µg/L. Columns containing F400 and AV1240LDX media were tested with this spiked site water. Columns testing the F400, PFA 694E and PSR2+ media were tested with the non-spiked site water.

The overall approach for the RSSCT to achieve the test goals consisted of the following elements:

- Experimental (test) design to indicate the number of column treatments and test conditions, as well as the number of sampling events.
- Procedures for the overall study which include site sample collection, shipping, baseline characterization, RSSCT subtasks, and RSSCT sample collection and shipping.
- Analytical methods to be used with emphasis on PFAS analysis.

The tests lasted for 8 days of RSSCT operation time to allow breakthrough. A schematic of the RSSCT is provided in **Figure 1** (next page).

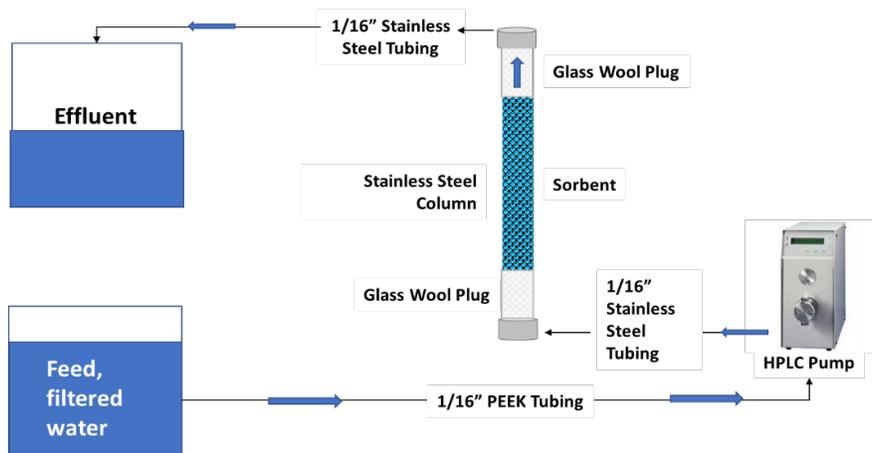


Figure 1. Schematic of RSSCT apparatus

Nearly two-hundred liters of water were collected in high-density polyethylene (HDPE) drums and shipped overnight to AECOM's Process Technology and Treatability Laboratory located in Austin, Texas. Upon receipt, the samples were inspected for leaks, logged, and stored.

The RSSCT targeted to simulate large-scale application of media in a typical pressurized media vessel. Table 2 shows the RSSCT experimental matrix, and the number of samples analyzed.

Table 2. Experimental matrix for RSSCT

TREATMENT COLUMN	GROUND WATER TESTED	SORBENT TYPE	INFLUENT SAMPLES, BASELINE	EFFLUENT SAMPLES	TOTAL
1	Spiked	F400	3	9	12
2	Spiked	AV1240LDX		9	9
3	Non-spiked	F400	3	9	12
4	Non-spiked	PFA 694E		9	9
5	Non-spiked	PSR2+		9	9
TOTAL			6	45	51

Design Parameters

RSSCTs rely on scaling down the adsorption phenomena observed in large-scale media systems. This scaling is carried out down to laboratory column sizes that are a few centimeters (cm) long and usually no more than 1 centimeter in diameter. To achieve representative sorption and flow conditions, the media is ground, sieved, washed, and dried until a particle size is obtained which will not interfere with the geometry of the small column (called *small scale* particle size). The simulated large-scale empty bed contact time (EBCT) was defined first to obtain the design parameters for the small-scale columns. Table 3 shows these parameters. Different EBCTs and flowrates were selected for the different sorbent types (GAC vs. IXR); however, these parameters were similar for columns with the same sorbent type.

Table 3. Small- and Large-Scale Design Parameters for RSSCT

WATER SOURCE	MEDIA PRODUCT				
	SPIKED		NON-SPIKED		
DESIGN PARAMETERS	F400	AV1240LDX	F400	PFA 694E	PSR2+
Large Scale EBCT (min)	10	10	10	3	3
Particle size (large scale, cm)	0.094	0.091	0.094	0.068	0.070
Scaling factor (small/large particle)	0.012	0.012	0.012	0.029	0.027
Small Scale particle size (cm)	0.0104	0.0101	0.0104	0.0114	0.0115
Small Scale EBCT (min)	0.12	0.12	0.12	0.09	0.08
Small Scale Carbon bed length or depth (cm) target	1.43	1.46	1.43	0.91	0.85
Nominal number of bed volumes to process	100,000	100,000	100,000	150,000	150,000
Small Scale Flowrate (L/min)	1.92	1.98	1.92	1.75	1.73
Minimum test duration (days)	8.6	8.6	8.6	8.9	8.5
Volume of water tested per column (L)	23.8	24.3	23.8	22.6	21.2

EBCT: empty bed contact time
 cm: centimeter
 mL/min: milliliter/minute
 L: liter
 min: minutes

The simulated large-scale EBCT was selected based on industry standard values for GAC and IXR to treat groundwater. The scaling factor was obtained using the constant diffusivity model which relates the particle sizes for the small- and large-scale systems, as described in the methodology from ASTM D6586.

The flow rate for each column allowed a rapid sample collection (under 5 hours) to obtain the necessary minimum sample volumes for PFAS (250 mL), VOC (40 mL) and total organic carbon (TOC) analyses (40 mL). For the IXR columns, sample volume increases were needed to allow for NDMA analysis (250 mL), the sample collection time was extended proportionally. The column setup was optimized to minimize the effluent flowrate and thus, the amount of water used for testing.

Baseline Sampling

A baseline characterization was performed for the bulk spiked and non-spiked water samples. The baseline characterization parameters were: PFAS, VOC, TOC, NDMA, pH, oxidation reduction potential (ORP), electric conductivity (EC), dissolved oxygen (DO), total suspended solids (TSS), total dissolved solids (TDS), and turbidity.

RSSCT Setup and Monitoring

RSSCT columns were set up under controlled laboratory conditions. All materials used for sampling, handling, tubing, column body, and column accessories were PFAS-compatible such as HDPE, silicone, stainless-steel and polypropylene. Laboratory tasks were conducted in compliance with the AECOM PFAS sampling protocols. These protocols are based on Michigan’s Department of Environmental Quality (MDEQ) PFAS Sampling Guidance and facilitate high-quality and reliable data for PFAS concentrations by minimizing the risk for cross-contamination. Water samples were stored under refrigeration until shipping to Eurofins Environment Testing in Chicago, Illinois, where Eurofins shipped the sample splits for PFAS and VOC analysis to Eurofins Sacramento and Eurofins Eaton South Bend, respectively. The steps for column setup and operation were based on those described in method ASTM D6586. A summary of the test procedure is as follows:

1. Representative samples from the media product were collected according to method Test E300. The media was then crushed and sieved to yield the desired particle size. This was followed by washing with distilled deionized water, drying at 150 °C for 4 hours, and stored in an amber glass jar until ready for use. The crushed media material was characterized to determine particle size distribution via laser diffraction.
2. Prior to the RSSCT column packing, the size reduced media was mixed with distilled deionized water to create a slurry with 1:1 water to media ratio.

3. The media slurries were packed into stainless-steel columns. Glass wool was packed at the bottom and top of the columns. The weight and height of the media beds were measured.
4. Then, the RSSCT columns were connected to high-performance liquid chromatography (HPLC) pumps, which provided precise and consistent flowrate and pressures.
5. Effluent samples were collected daily and stored under refrigeration until shipping to Eurofins.
6. Flowrate, pH, ORP, EC, DO and turbidity were monitored frequently.

Sampling and Analysis

All analytes were reported by Eurofins Laboratories at their location in Chicago, Illinois. Our experienced sampling team recommended using EPA Method 537 modified (list of 33 compounds) with DNR accreditation to yield the best understanding of the PFAS characterization. The analytical methods for the RSSCT are shown in Table 4.

Table 4. Analytical methods for RSSCT samples

ANALYTE	METHOD	PERFORMED BY	
PFAS	EPA MOD 537.1, DNR list of 33 compounds	Eurofins Sacramento	
VOC	EPA 524.2 Regulated DW VOC	Eurofins South Bend	
TOC	SW 9060A	Eurofins Chicago	
NDMA	EPA 8270E		
Alkalinity	SM 2320B		
Anions	EPA 300.0 chloride, nitrate, sulfate		
Perchlorate	EPA 314.0		
Arsenic	EPA 6020		
Uranium	EPA 6020A		
Chromate	EPA 218.6		
pH/ORP/EC/DO	HACH Benchtop Meter		AECOM
Turbidity	Hannah Instruments Turbidity Meter		
TSS	ASTM D5907-18		
TDS	EPA 160.1		

PFAS: Poly- and Perfluoroalkyl Substances
 TOC: Total Organic Carbon
 VOC: Volatile Organic Compounds
 NDMA: N-nitrosodimethylamine
 ORP: oxidation reduction potential
 EC: electric conductivity
 DO: dissolved oxygen
 TSS: Total Suspended Solids
 TDS: Total Dissolved Solids

Samples were shipped in several batches. The first batch focused on samples collected to pinpoint PFAS detection in the effluent. Once PFAS concentrations were detected, more samples were shipped for further analysis to fill the data gaps to characterize breakthrough.

Results

Results were obtained for baseline characterization and effluent samples. The columns operated for 8.5 days. **Table 5** shows the total water volume run through each column and the equivalent bed volumes.

Table 5. Water volume and bed volumes through each column

WATER SOURCE	SPIKED		NON-SPIKED		
	F400	AV1240LDX	F400	PFA 694E	PSR2+
Run Length (d)	8.5	8.5	8.5	8.5	8.5
Run Volume (L)	23.8	24.3	22.9	21.2	21.6
Bed Volume (BV)	100,299	100,055	96,767	140,898	143,852

Baseline Characterization

The baseline characterization performed in the spiked and non-spiked influent samples provided the time zero concentration levels for PFAS and TOC present in the water, as well as other water quality parameters. Total PFAS, total regulated PFAS, VOC and water quality parameters are shown in **Table 6**.

Table 6. Water quality parameters in baseline samples.

SAMPLE	RAW WATER	SPIKED INFLUENT	NON-SPIKED INFLUENT
pH	8.05	NA	NA
ORP (mV)	426	NA	NA
EC (µS/cm)	769	NA	NA
DO (mg/L)	6.79	NA	NA
Turbidity (NTU)	0.39	NA	0.22
Total PFAS (ng/L)	41.1	220	39.6
Total Regulated PFAS (ng/L)	5.7	63.5	5.2
Trichloroethylene (TCE) (µg/L)	0.21	1.98	NA
Trichloroethylene (µg/L)*	NA	4.05	NA
Tetrachloroethylene (PCE) (µg/L)	0.21	0.52	NA
Tetrachloroethylene (µg/L)*	NA	17.9	NA
N-Nitrosodimethylamine (NDMA) (µg/L)	NA	NA	<3.8
Total Organic Carbon (TOC) (mg/L)	<0.47	1.42	1.42
Total Hardness (mg/L)	311	NA	NA
Calcium (mg/L)	80.7	NA	NA
Iron, total (mg/L)	<0.82	NA	NA
Iron, dissolved (mg/L)	<0.82	NA	NA
Manganese, total (mg/L)	<0.0023	NA	NA
Manganese, dissolved (mg/L)	<0.0023	NA	NA

NA = not analyzed

*Measured via GC-FID in-house

PFAS Concentrations

Total raw water PFAS concentration was 41.1 ng/L. After filtration through a 1 µm filter, the non-spiked influent water total PFAS concentration’s average was 39.6 ng/L over three sampling events. The spiked influent had an average total PFAS concentration of 220 ng/L with concentrations of 51 ng/L, 64 ng/L and 86 ng/L for PFOA, PFOS and PFHxS, respectively. Detection limits for PFAS by the analytical methodology were as low as 0.50 ng/L.

Figure 2 shows the effluent concentrations of Total PFAS against the specific throughput. Specific throughput is defined as the volume of water treated, in liters, divided by the mass of sorbent media, in kilograms. The number of bed volumes are related to the specific throughput via multiplication with the sorbent mass and division with the sorbent bed volume. The F400, PFA 694E and PSR 2+ columns, which were fed with the non-spiked influent, had Total PFAS concentrations that remained below the influent concentration, indicating removal of PFAS by these GAC or IXR products with no complete media exhaustion within the test period. As an observation, the F400 and AV1240LDX columns that were fed with the PFAS-spiked influent, remained under the average spiked influent PFAS concentration and the AV1240LDX GAC’s total PFAS concentration surpassed more than 50% of the spiked influent’s total PFAS concentration. For the non-spiked columns, the F400 GAC’s total PFAS concentrations almost reached the non-spiked influent’s PFAS concentration.

The figure also shows the predicted rate at which the effluent criteria of 20 ng/L Total PFAS is exceeded for each sorbent, and when sorbent change-out would be required. This threshold concentration was not surpassed in the IXR loaded columns but was exceeded in the carbon loaded columns for both spiked (F400 and AV1240LDX) and

non-spiked (F400) RSSCTs. Nevertheless, the F400 loaded columns performed relatively well under both tests' conditions, especially when compared against the AV1240LDX loaded column.

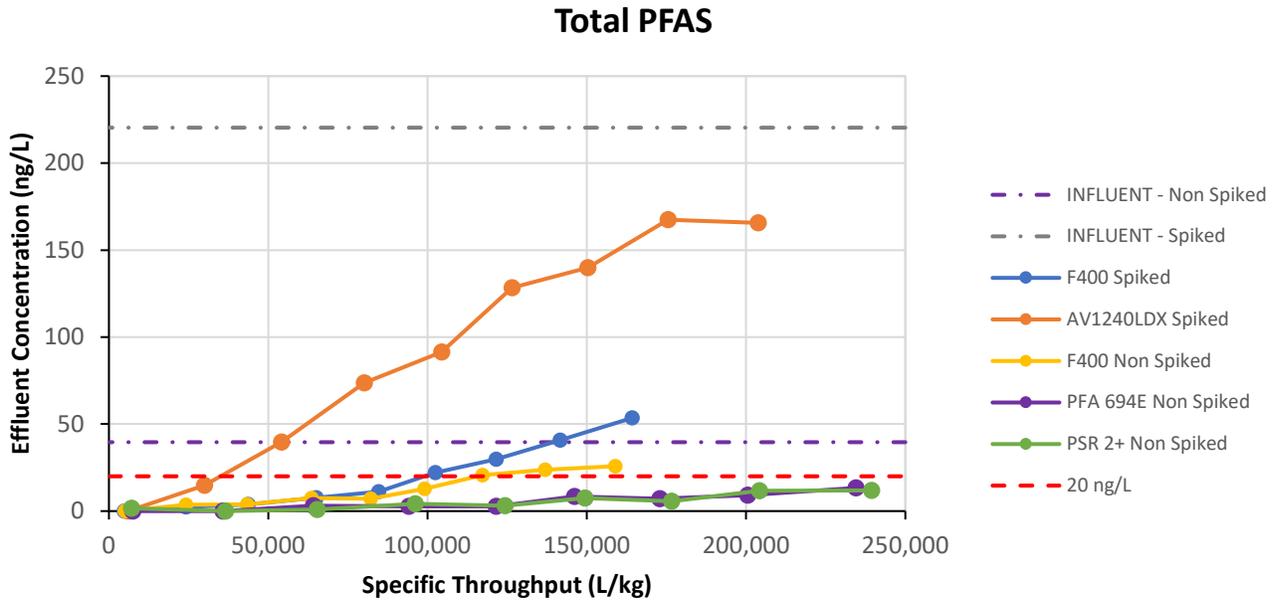
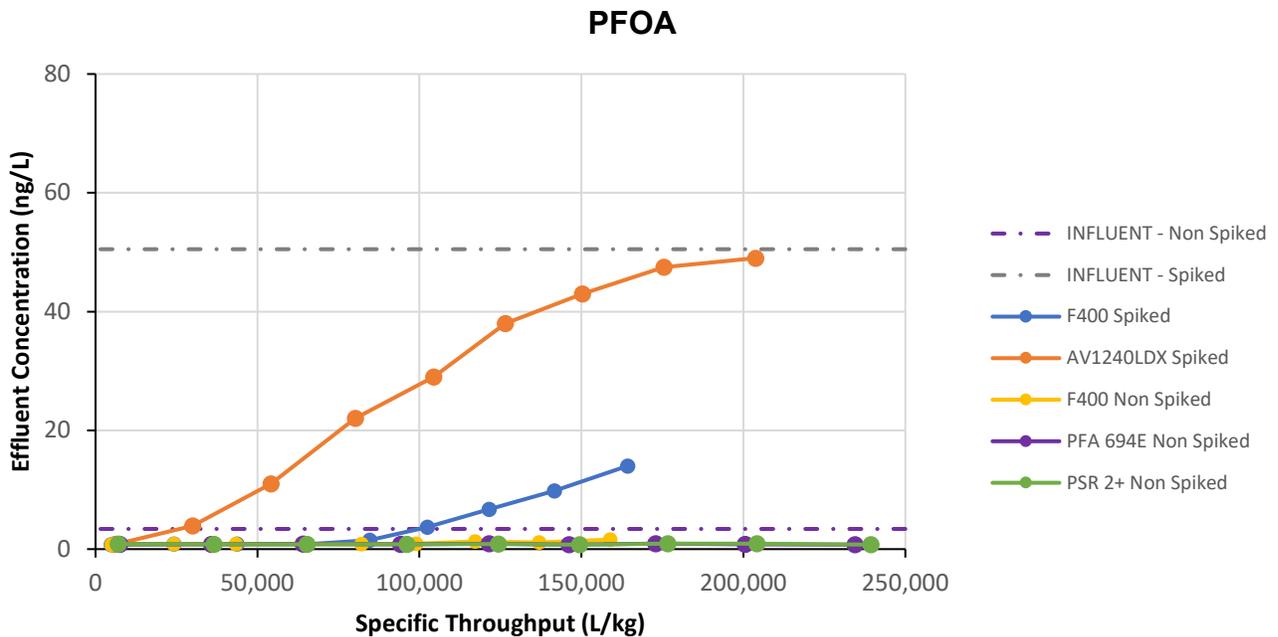


Figure 2. Effluent concentrations for total PFAS from RSSCT columns. Dashed red line indicates the effluent criteria concentration of 20 ng/L for total PFAS, and the other dashed lines indicate the influent concentrations

Effluent concentrations for PFOA and PFOS were key components of total PFAS concentrations which affected sorbent media saturation. **Figure 3** shows the trends observed for these compounds across the specific test throughput. PFOA effluent concentrations follow the same trend as total PFAS, while PFOS shows a better removal, even in the AV1240LDX loaded column.



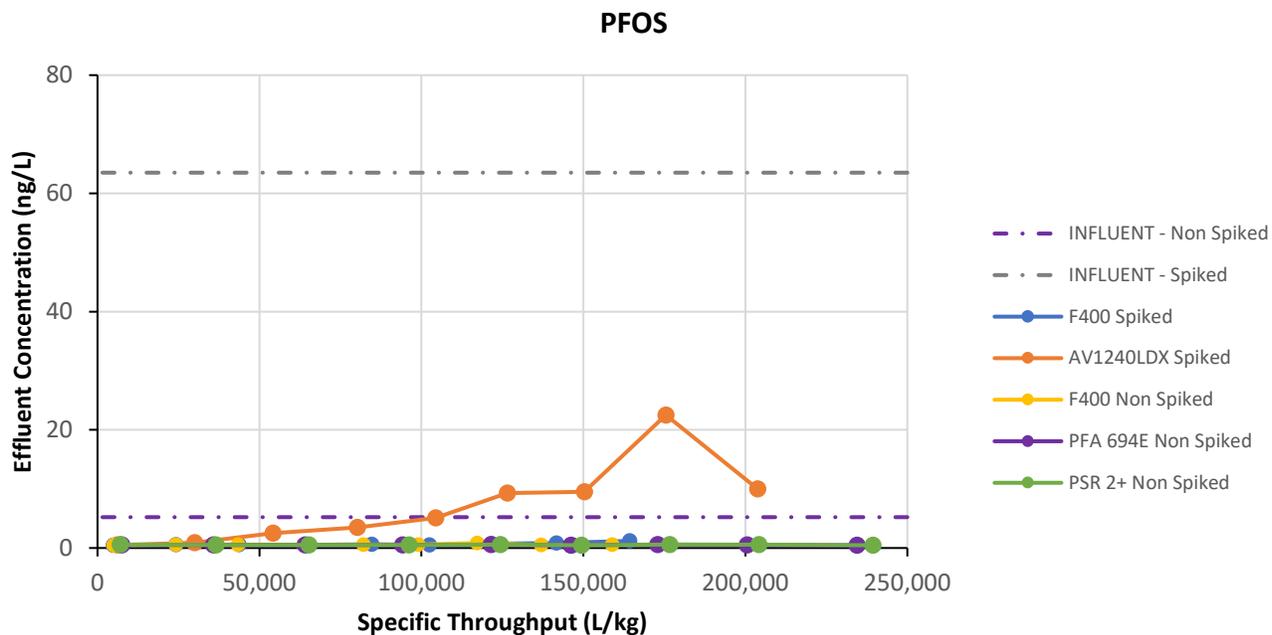


Figure 3. Effluent concentrations for PFOA and PFOS from RSSCT columns. The dashed lines represent the average influent concentration.

Table 7 shows the concentration values for each RSSCT for those PFAS compounds that were detected in one or more effluent samples. All PFAS compounds tested, but not shown, were non-detects for the influent samples and all effluent samples.

The table also shows TOC concentrations in the influent and effluent samples. Importantly, TOC interferes with PFAS removal efficiency and reduces bed life. In spiked RSSCTs, TOC was at an average influent concentration of 0.85 mg/L; removal of TOC by the F400 GAC RSSCT was superior to the AV1240LDX RSSCT, as shown for the lack of TOC detection in the former, and lack of removal in the latter. TOC in the non-spiked influent water was, on average, higher than in the spiked water at 1.9 mg/L. However, some TOC concentration variability was observed in individual influent measurements, especially in the non-spiked water. The standard deviations of these measurements were 1.3 mg/L for the non-spiked influent water and 0.22 mg/L for the spiked water.

Table 7. Individual PFAS concentrations from RSSCT columns. Red font indicates total PFAS effluent concentrations above 20 ng/L or Hazard Index value greater than 1.

COLUMN 1 (F400 Spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	PFBA (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFBS (ng/L)	PFPeS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	FOSA (ng/L)	Total PFAS (ng/L)	Hazard Index	TOC (mg/L)
Average	Influent	2.3	4.4	4.9	2.0	51	2.7	2.6	86	64	<1.19	220	7.90	0.85
0.25	2,927	<2.2	<0.45	<0.53	<0.23	<0.77	<0.18	<0.27	<0.52	<0.49	<0.89	0	0	0.58
1.24	14,741	2.4	<0.50	<0.59	<0.25	<0.86	<0.20	<0.30	<0.58	<0.55	<0.99	2.4	<0.01	<0.47
2.25	26,651	2.4	1.5	<0.59	<0.25	<0.86	<0.20	<0.30	<0.58	<0.55	<1.00	3.9	<0.01	<0.47
3.33	39,699	2.3	4.4	0.76	<0.23	<0.80	0.23	<0.28	<0.54	<0.51	<0.92	7.7	<0.01	<0.47
4.34	51,664	<2.7	5.9	1.9	<0.28	1.5	0.62	<0.34	1.3	<0.61	<1.1	11.2	0.11	<0.47
5.26	62,569	2.4	7.0	3.4	0.56	3.7	1.4	0.33	3.3	<0.53	<0.96	22.1	0.27	<0.47
6.25	74,202	<3.4	6.1	4.8	0.91	6.7	2.3	0.58	6.6	<0.75	1.8	29.8	0.59	<0.47
7.31	86,506	2.5	6.6	5.2	0.98	9.8	2.9	1.1	11	0.86	<0.99	40.8	0.81	<0.47
8.50	100,299	2.7	6.1	6.3	1.5	14	3.4	1.3	17	1.2	<1.0	53.5	1.19	0.67

COLUMN 2 (AV1240LDX Spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	PFBA (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFTeA (ng/L)	PFBS (ng/L)	PFPeS (ng/L)	PFHxS (ng/L)	PFHpS (ng/L)	PFOS (ng/L)	PFDoS (ng/L)	FOSA (ng/L)	Total PFAS (ng/L)	Hazard Index	TOC (mg/L)
Average	Influent	2.3	4.4	4.9	2.0	51	<0.26	<0.69	2.7	2.6	86	0.55	64	<0.92	<1.19	220	7.90	0.85
0.25	2,968	<2.2	<0.46	<0.54	<0.23	<0.79	<0.25	<0.68	<0.19	<0.28	<0.53	<0.18	<0.50	<0.90	<0.91	0	0	0.48
1.24	14,726	<2.4	3.6	1.5	<0.25	3.9	0.39	<0.72	0.56	<0.30	4.0	<0.19	0.92	<0.96	<0.97	14.9	0.35	0.48
2.25	26,572	<2.4	5.1	3.7	0.84	11	0.69	<0.72	1.9	1.0	13	<0.19	2.5	<0.96	<0.97	39.7	1.02	0.51
3.33	39,355	2.2	4.9	5.0	1.5	22	1.0	<0.67	2.7	1.9	29	<0.17	3.5	<0.89	<0.90	73.7	2.03	0.52
4.34	51,261	<2.4	4.0	4.8	1.6	29	1.1	<0.72	2.6	2.2	41	<0.19	5.1	<0.95	<0.96	91.4	2.77	0.59
5.26	62,121	2.6	5.3	5.6	2.2	38	1.2	<0.69	3.4	2.7	58	<0.18	9.3	<0.92	<0.93	128	3.86	0.61
6.25	73,805	<3.1	5.1	5.7	2.3	43	1.4	<0.94	3.0	2.8	67	<0.25	9.5	<1.3	<1.3	140	4.35	0.60
7.30	86,142	2.9	5.1	5.3	2.3	48	1.4	<0.73	3.1	3.3	74	0.29	23	<0.96	<0.99	167	5.45	0.59
8.50	100,055	3.0	5.2	5.1	2.3	49	1.4	1.4	3.3	3.4	79	0.24	10	1.0	1.3	166	5.02	0.79

COLUMN 3 (F400 Non-spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	PFBA (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFTeA (ng/L)	PFBS (ng/L)	PFPeS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	FOSA (ng/L)	Total PFAS (ng/L)	Hazard Index	TOC (mg/L)
Average	Influent	<2.3	4.5	4.5	1.9	3.4	<0.26	<0.64	2.4	2.2	14	<0.47	<1.02	39.6	0.63	1.9
0.25	3,002	<2.1	<0.43	<0.51	<0.22	<0.70	<0.24	<0.75	<0.18	<0.26	<0.50	<0.55	<0.86	0	0	1.9
1.24	14,699	2.6	<0.50	<0.59	<0.26	<0.87	<0.28	<0.74	<0.20	<0.31	<0.58	<0.55	1.1	3.7	0.06	1.3
2.25	26,387	2.8	1.1	<0.59	<0.25	<0.90	<0.27	<0.75	<0.20	<0.31	<0.58	<0.55	<1.0	3.9	<0.01	<0.47
3.33	38,705	2.5	4.0	0.78	<0.26	<0.87	<0.28	<0.74	0.22	<0.31	<0.59	<0.55	<1.0	7.5	<0.01	<0.47
4.34	50,000	<2.4	4.9	1.7	<0.25	<0.86	<0.27	<0.80	0.58	<0.30	<0.58	<0.59	<0.99	7.2	<0.01	<0.47
5.26	60,296	<2.6	6.7	3.2	0.60	<0.93	<0.29	<1.1	1.1	0.33	0.93	<0.84	<1.1	12.9	0.04	0.48
6.25	71,374	3.8	7.0	4.6	0.95	<1.3	<0.42	<0.74	1.6	0.50	2.2	<0.54	<1.5	20.7	0.06	0.51
7.31	83,360	2.8	6.7	5.1	1.2	1.2	0.32	<0.78	2.2	0.98	3.5	<0.58	<0.98	23.8	0.15	0.50
8.50	96,767	<2.6	6.3	6.0	1.4	1.6	0.50	<0.64	2.3	1.5	6.2	<0.47	<1.0	25.8	0.24	0.81

COLUMN 4 (PFA 694E Non-spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	PFBA (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFOA (ng/L)	PFHpA (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	FOSA (ng/L)	Total PFAS (ng/L)	Hazard Index	TOC (mg/L)
Average	Influent	<2.3	4.5	4.5	3.4	1.9	14	<0.51	<1.02	39.6	0.63	1.9
0.25	4,460	<2.3	<0.47	<0.55	<0.81	<0.24	<0.54	<0.51	<0.93	0	0	2.2
1.24	21,468	<2.3	<0.47	<0.55	<0.85	<0.24	<0.54	<0.54	<0.93	0	0	1.6
2.25	38,524	2.4	0.63	<0.58	<0.82	<0.25	<0.57	<0.52	<1.0	3.0	<0.01	0.52
3.33	56,572	<2.3	1.7	<0.56	<0.89	<0.24	<0.55	<0.56	1.1	2.8	0.06	0.51
4.34	73,039	<2.5	2.8	<0.61	<0.76	<0.26	<0.60	<0.48	<1.0	2.8	0	0.57
5.26	87,814	2.6	4.2	0.52	<0.93	<0.22	<0.51	<0.59	1.1	8.4	0.06	0.59
6.25	103,929	<2.6	4.5	0.79	<0.83	<0.27	<0.63	<0.52	1.8	7.1	0.09	0.56
7.25	120,498	2.6	5.5	2.5	<0.75	0.40	0.61	<0.47	1.1	9.0	0.07	0.61
8.50	140,898	2.6	5.7	3.1	<0.81	0.40	0.61	<0.51	0.89	13.3	0.06	0.80

COLUMN 5 (PSR2+ Non-spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	PFBA (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFOA (ng/L)	PFHpA (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	FOSA (ng/L)	Total PFAS (ng/L)	Hazard Index	TOC (mg/L)
Average	Influent	<2.3	4.5	4.5	<0.86	1.9	14	<0.55	<1.02	39.6	0.63	1.9
0.25	4,211	<2.4	<0.50	<0.59	<0.80	<0.25	<0.58	<0.51	1.6	1.6	0.08	2.3
1.24	21,988	<2.3	<0.46	<0.55	<0.82	<0.24	<0.54	<0.52	<0.93	0	0	1.5
2.25	39,246	<2.3	0.87	<0.56	<0.79	<0.24	<0.55	<0.50	<1.0	0.87	0	0.61
3.33	57,755	2.2	2.0	<0.54	<0.87	<0.23	<0.53	<0.55	<0.91	4.2	<0.01	0.50
4.34	74,710	<2.5	3.1	<0.59	<0.74	<0.26	<0.58	<0.47	<1.0	3.1	0	0.60
5.26	89,812	2.4	4.4	0.71	<0.93	<0.22	<0.50	<0.59	<0.86	7.5	<0.01	0.63
6.25	106,151	<2.6	4.7	1.0	<0.91	<0.27	<0.62	<0.58	<1.1	5.7	<0.01	0.68
7.25	122,690	<2.6	5.5	1.4	<0.75	<0.27	4.8	<0.48	<1.0	11.7	0.12	0.60
8.50	143,852	2.4	5.4	2.8	<0.86	0.39	<0.50	<0.55	0.88	11.9	0.05	0.83

RSSCT Metrics

The RSSCT results obtained (as described in the method ASTM D6586) are shown in **Table 8** based on Total PFAS effluent concentration breakthrough. The criteria selected was based on reaching 20 ng/L of total PFAS in the effluent. Because bed volumes across the RSSCTs varied, sorbent performance must be evaluated on a specific throughput basis, which normalizes the volume of water treated per mass of sorbent. Specific throughputs for the F400 and AV1240LDX loaded columns were obtained from the graph shown in Figure 2. Specific throughputs for the IXRs PFA694E and PSR2+ are minimum values as none of the effluent concentrations reached the threshold of 20 ng/L. Therefore, the exact water volume, bed volumes, and RSSCT operation time were not identified for the IXRs during the testing period and would have required a longer run time.

Table 8. Summary of Results from RSSCT based on 20 ng/L total PFAS in the effluent.

PARAMETER	UNITS	F400 Spiked	AV1240LDX Spiked	F400 Non-spiked	PFA694E Non-spiked	PSR2+ Non-spiked
RSSCT Bed Life	min	7,566	2,116	8,677	>12,236	>12,236
Treatable Bed Volumes	-	61,075	17,185	70,042	>142,493	>150,333
Total Volume of Water until Breakthrough	L	14.5	4.2	16.6	>21.2	>21.6
Specific Throughput	L/kg	100,000	35,000	115,000	>234,824	>254,118
Sorbent Usage Rate	g/L	0.010	0.029	0.009	<0.004	<0.004

RSSCT: rapid small-scale column test

L: liters

g: grams

min: minutes

>: Total PFAS 20 ng/L was not reached during testing so final values are greater than the numbers provided.

Monitoring Parameters

pH from the effluent samples slowly and steadily increased, for the test duration, with values ranging from 8.15 to 8.81 (**Table 9**). Influent pH values increased only up to 8.18 and 8.20 for the non-spiked and spiked influents, respectively. For GAC full-scale systems, a small rise in pH is expected, followed by a plateau or stabilization. A pilot-scale study would be able to evaluate long-term trends in pH fluctuations. ORP effluent readings for the spiked columns effluents remained stable between 350 to 425 mV, while the non-spiked effluents on the first day were between 50 to 100 mV and then jumped up to the same range of 350 to 425 mV for the rest of the test. The electric conductivity readings for the non-spiked effluent samples were stable around 800 µS/cm. The F400 spiked column started at 1600 µS/cm and dropped down to about 800 µS/cm by day one. Starting on day 6, the spiked F400 effluent began to climb again. The AV1240LDX spiked column effluent also was higher than the non-spiked columns effluents, initially but stabilized to around 800 µS/cm as well. All column effluents' dissolve oxygen

measurements remained stabled around 8 mg/L to 9 mg/L, except for a notable increase to about 9.6 mg/L at the 24-hour mark of the test, before dropping back down to the 8 to 9 mg/L range. Turbidity remained low at below 0.8 NTU for all column effluents. Lastly, flowrates were monitored daily and held constant for the test duration for all five columns. (**Appendix A**).

Table 9. Individual water quality parameters from RSSCT columns.

COLUMN 1 (F400 Spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	pH	ORP (mV)	EC (µS/CM)	DO (mg/L)	TSS (mg/L)	TDS (mg/L)	TURBIDITY (NTU)
0.0	Influent	8.05	426	769	6.79	0	424	0.39
0.12	1,534	8.25	368	917	8.57	0.7	436	0.62
1.11	13,180	8.34	366	1060	9.20	NA	NA	0.56
2.12	25,039	8.44	357	748	8.61	NA	NA	0.29
3.20	37,742	8.20	362	809	8.79	NA	NA	0.22
4.22	49,846	8.37	354	743	8.78	NA	NA	0.17
5.11	60,360	8.49	346	744	8.94	NA	NA	0.21
6.12	72,331	8.55	332	744	8.85	NA	NA	0.27
7.13	84,054	8.73	362	780	8.72	0.38	433	0.69
8.50	100,055	8.81	405	765	8.62	NA	NA	0.24

COLUMN 2 (AV1240LDX Spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	pH	ORP (mV)	EC (µS/cm)	DO (mg/L)	TSS (mg/L)	TDS (mg/L)	TURBIDITY (NTU)
0.0	Influent	8.05	426	769	6.79	0	424	0.39
0.12	1,534	8.25	368	917	8.57	0	442	0.48
1.11	13,180	8.34	366	1060	9.20	NA	NA	0.75
2.12	25,039	8.44	357	748	8.61	NA	NA	0.35
3.20	37,742	8.20	362	809	8.79	NA	NA	0.23
4.22	49,846	8.37	354	743	8.78	NA	NA	0.22
5.11	60,360	8.49	346	744	8.94	NA	NA	0.20
6.12	72,331	8.55	332	744	8.85	NA	NA	0.20
7.13	84,054	8.73	362	780	8.72	0	425	0.32
8.50	100,055	8.81	405	765	8.62	NA	NA	0.25

COLUMN 3 (F400 Non-spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	pH	ORP (mV)	EC (µS/cm)	DO (mg/L)	TSS (mg/L)	TDS (mg/L)	TURBIDITY (NTU)
0.0	Influent	8.05	426	769	6.79	0	424	0.39
0.12	1,461	8.28	84	743	8.55	0.36	431	0.25
1.11	13,164	8.30	370	762	9.52	NA	NA	0.18
2.12	24,892	8.33	358	751	8.36	NA	NA	0.23
3.20	37,184	8.16	410	772	8.78	NA	NA	0.45
4.22	48,614	8.18	356	750	8.87	NA	NA	0.32
5.11	58,622	8.39	353	745	8.69	NA	NA	0.30
6.12	69,973	8.47	339	747	8.60	NA	NA	0.31
7.13	81,253	8.73	369	781	8.62	1.17	432	0.28
8.50	96,767	8.78	376	751	8.64	NA	NA	0.29

COLUMN 4 (PFA694E Non-spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	pH	ORP (mV)	EC (µS/cm)	DO (mg/L)	TSS (mg/L)	TDS (mg/L)	TURBIDITY (NTU)
0.0	Influent	8.05	426	769	6.79	0	424	0.39
0.12	2,186	8.22	102	750	8.45	0.9	428	0.18
1.11	19,229	8.23	372	776	9.08	NA	NA	0.23
2.12	36,322	8.28	352	749	8.19	NA	NA	0.45
3.20	54,338	8.16	379	759	8.76	NA	NA	0.32
4.22	71,052	8.28	357	753	8.77	NA	NA	0.30
5.11	85,403	8.36	352	756	8.66	NA	NA	0.31
6.12	101,854	8.44	343	747	8.39	NA	NA	0.28
7.13	118,431	8.75	365	781	8.58	0.9	428	0.29
8.50	140,898	8.77	359	790	8.70	NA	NA	0.25

COLUMN 5 (PSR2+ Non-spiked)

ELAPSED TIME (D)	BED VOLUMES PASSED	pH	ORP (mV)	EC (µS/cm)	DO (mg/L)	TSS (mg/L)	TDS (mg/L)	TURBIDITY (NTU)
0.0	Influent	8.05	426	769	6.79	0	424	0.39
0.12	2,105	8.22	66	754	8.37	0.9	428	0.19
1.11	19,701	8.22	367	891	9.11	NA	NA	0.49
2.12	37,006	8.27	343	747	8.06	NA	NA	0.26
3.20	55,449	8.15	377	745	8.74	NA	NA	0.36
4.22	72,681	8.28	354	754	8.70	NA	NA	0.35
5.11	87,349	8.37	356	756	8.64	NA	NA	0.32
6.12	104,085	8.45	343	757	8.59	NA	NA	0.31
7.13	120,624	8.75	361	778	8.59	0.9	428	0.27
8.50	143,852	8.74	352	767	8.64	NA	NA	0.30

VOCs Results

TCE and PCE concentrations were both at 0.21 µg/L in the raw water (**Table 6**). These concentrations were lower than what the raw water concentration objective of 5 µg/L PCE and 1 µg/L TCE was expected to be. Therefore, TCE and PCE were spiked to the influent of the “Spiked” columns in the attempt to maintain the presence of these chlorinated ethenes. Due to the challenges of conserving volatile compounds like TCE and PCE in the RSSCT setup, in-house analysis of these compounds via GC-FID were frequently conducted in the influent reservoir of the Spiked RSSCT columns. Spiking of PFAS, PCE and TCE was conducted on August 3rd, 2022, at 6:11 am before the RSSCT operation. A second spike of PCE and TCE was conducted that same day at 1:10 pm because in-house measurements of the influent indicated that PCE and TCE concentrations were not high enough. Concentrations of TCE and PCE analyzed via EPA 8260 method were below the method’s detection level (<0.20 µg/L) in the non-spiked influent container, whereas the spiked influent water had TCE and PCE concentrations that averaged 0.52 and 1.98 µg/L, respectively. All effluent samples from the spiked water RSSCT columns show concentrations of TCE and PCE below their analytical method detection limits.

In-house screening analysis of TCE and PCE via GC-FID for the spiked RSSCTs influent were conducted by sampling the headspace volume in the spiked influent water container. These measurements confirmed that some of the TCE and PCE partitioned into the headspace of the influent container, affecting the equilibrium concentration of these chemicals in the liquid phase. By using the Henry’s law constant, temperature, vapor phase volume, and liquid phase volume, the dissolved concentrations of TCE and PCE were calculated at various time events. Figure 4 shows the estimated aqueous concentrations of TCE and PCE in the spiked influent water container. The results show an overestimation of the aqueous concentration with respect to the EPA 8260 method results. However,

even though this was just a screening method, the samples were analyzed immediately after collection, which minimizes the probability of sample leaking or volatilization. Thus, this screening method fulfilled its objective of demonstrating that TCE and PCE were maintained in the spiked influent container during the RSSCT study.

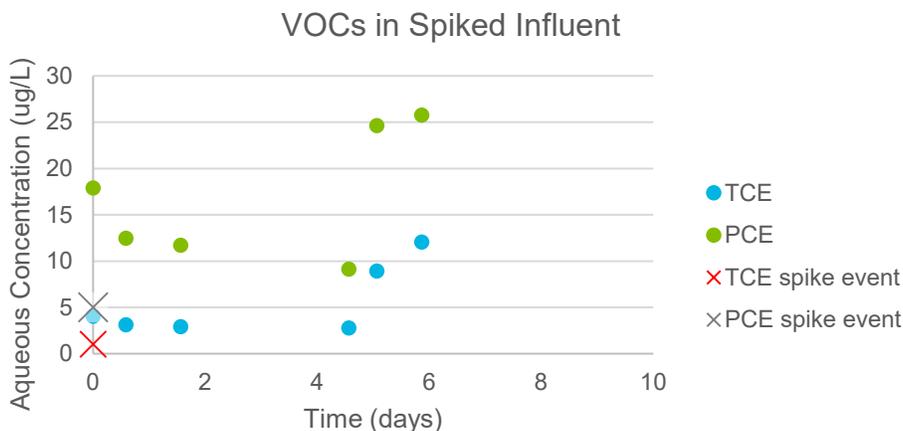


Figure 4. TCE and PCE aqueous concentrations (estimated via GC-FID) in the spiked influent water container during the first six days of RSSCT operation.

Lastly, NDMA was analyzed in the non-spiked RSSCT tests. NDMA was reported below detection level for the raw water and both IXR (PFA 694E and PSR2+) final effluents.

General Chemistry Results

A raw water sample and the final effluent from each of the five columns were analyzed for arsenic, chromate, uranium, perchlorate, bicarbonate alkalinity, nitrate, sulfate, and chloride (Table 10) for ion exchange performance modeling that may occur during the full-scale design. There were no significant changes from the raw water sample to the effluents of each column, except for perchlorate. Both IXR final effluents were non-detect for perchlorate while the GAC final effluents and raw water perchlorate values were between 0.29 to 0.31 µg/L. However, the influent concentration of perchlorate was 0.33 µg/L, which indicates that no formation of perchlorate occurred during the RSSCT treatment.

Table 10. Individual water quality parameters from RSSCT columns.

ANALYTE	UNITS	RAW WATER	F400 SPIKED END EFFLUENT	AV1240LDX SPIKED END EFFLUENT	F400 NON-SPIKED END EFFLUENT	PFA694E NON-SPIKED END EFFLUENT	PSR2+ NON-SPIKED END EFFLUENT
Arsenic	µg/L	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23
Chromate	µg/L	0.56	0.66	0.66	0.64	0.59	0.61
Perchlorate	µg/L	0.33	0.29	0.31	0.29	<0.058	<0.058
Uranium	µg/L	0.76	0.80	0.80	0.78	0.86	0.88
Chloride	mg/L	49.9	46.6	46.2	48.5	46.0	44.5
Bicarbonate Alkalinity	mg/L	304	299	306	312	311	307
Nitrate	mg/L	2.6	2.8	2.8	2.6	2.5	2.6
Sulfate	mg/L	30.3	28.6	28.1	29.4	28.1	27.1
Total Dissolved Solids	mg/L	424	433	425	432	428	430
Total Suspended Solids	mg/L	0	0.378	0	1.17	0.90	0.29
Trichloroethylene (TCE)	µg/L	1.98	<0.2	<0.2	<0.2	N/A	N/A
Tetrachloroethylene (PCE)	µg/L	0.52	<0.2	<0.2	<0.2	N/A	N/A
N-Nitrosodimethylamine (NDMA)	µg/L	<3.8	N/A	N/A	N/A	<3.7	<3.7

N/A = not analyzed

Conclusions

The bench-scale RSSCT treatability study was successful at evaluating the relative performance of two GAC products (F400 and AV1240LDX) and two IXRs (PFA694E and PSR2+). Two test scenarios were evaluated: first, raw water consisting of low PFAS, PCE, and TCE concentrations which were treated by F400, PFA694E and PSR2+ sorbents; the second scenario consisted of evaluating the use of GACs (F400 and AV1240LDX) in an influent water with increased concentrations of PFAS, PCE, and TCE.

The evaluations indicate that IXR products are effective at treating total PFAS as all effluent samples remained below the test criterion of 20 ng/L total PFAS. The IXRs showed that PFAS could be treated for at least 234,824 and 254,118 L/kg for PFA694E and PSR2+, respectively. F400 was not as effective as IXRs and showed breakthrough above the threshold level after 115,000 L/kg. On the other hand, in RSSCT influents that were spiked with PFAS, TCE and PCE, the two GACs evaluated had clear and different results. The F400 loaded column showed a PFAS retention near 100,000 L/kg, not too far from its counterpart in the non-spiked influent water. In contrast, the AV1240LDX loaded column retained PFAS at only 35,000 L/kg.

No VOCs were detected in the effluent concentrations, even in the spiked influent columns, indicating that VOC removal was not an issue for this water matrix. NDMA was not detected in samples from the non-spiked influent water, and therefore no NDMA was detected in effluent samples.

This RSSCT evaluation did show the impact of PFAS influent concentration in GAC bed life, as evidenced by the shorter F400 bed life when the total PFAS influent concentration is, on average, 210 ng/L against 39.4 ng/L. In conclusion, the RSSCT demonstrated that IXRs can produce the longest retention of total PFAS below 20 ng/L, with F400 showing, at best, 70% of the retention time, and that F400 had a superior performance with respect to AV1240LDX.

Appendix A – Probe Measurements Plots

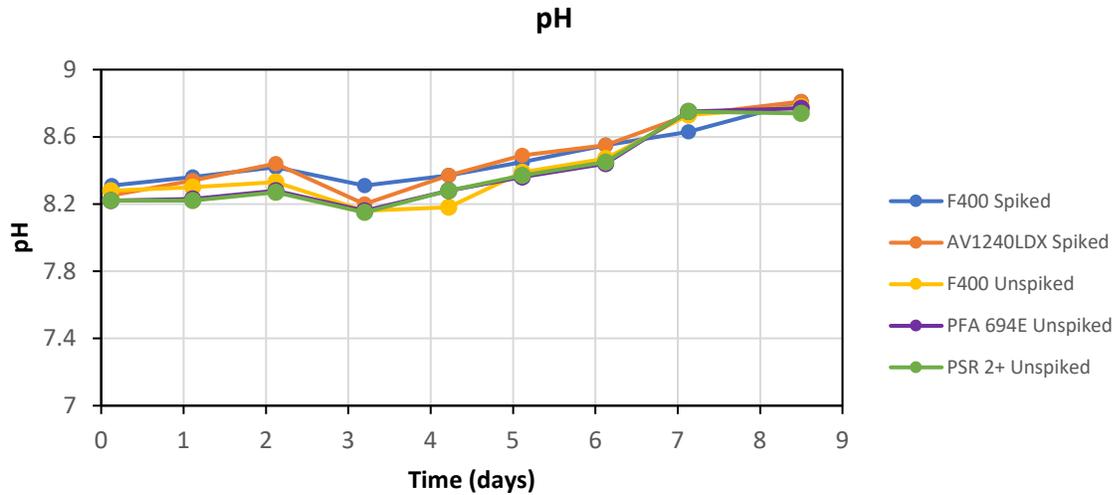


Figure A-1. pH values over time from RSSCT columns.

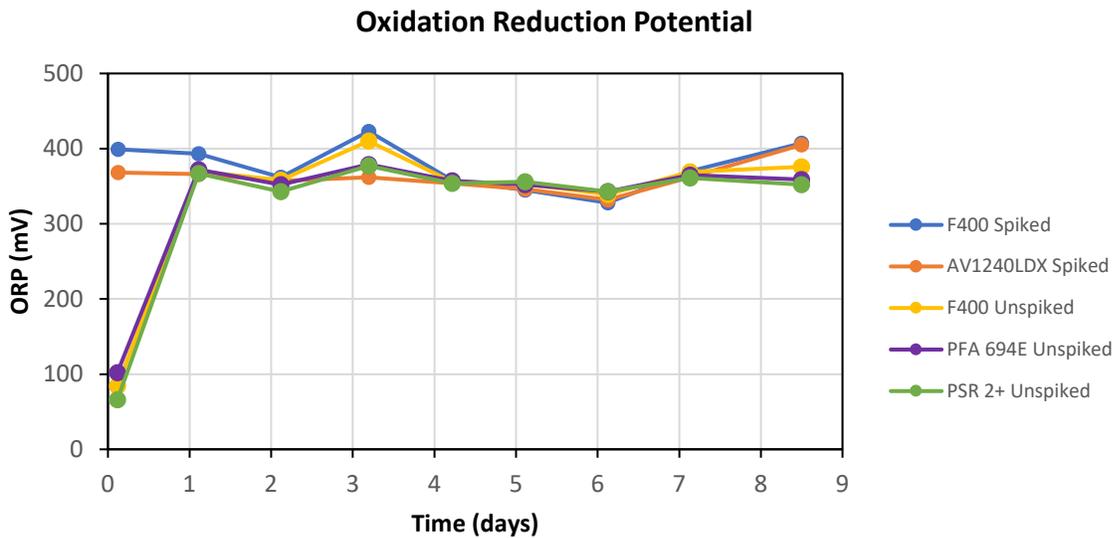


Figure A-2. Oxidation reduction potential values over time from RSSCT columns.

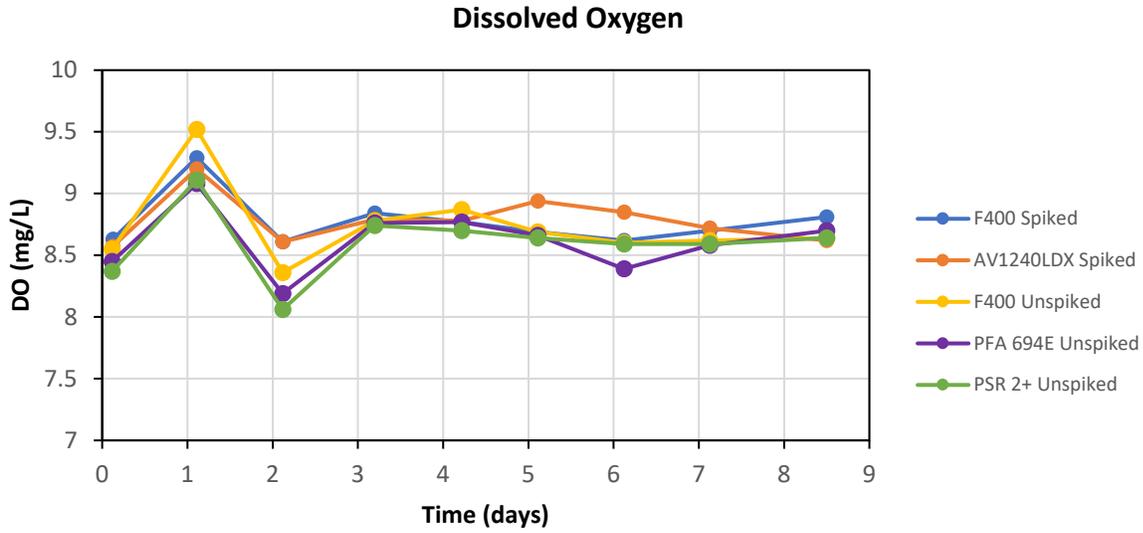


Figure A-3. Dissolved oxygen over time from RSSCT columns.

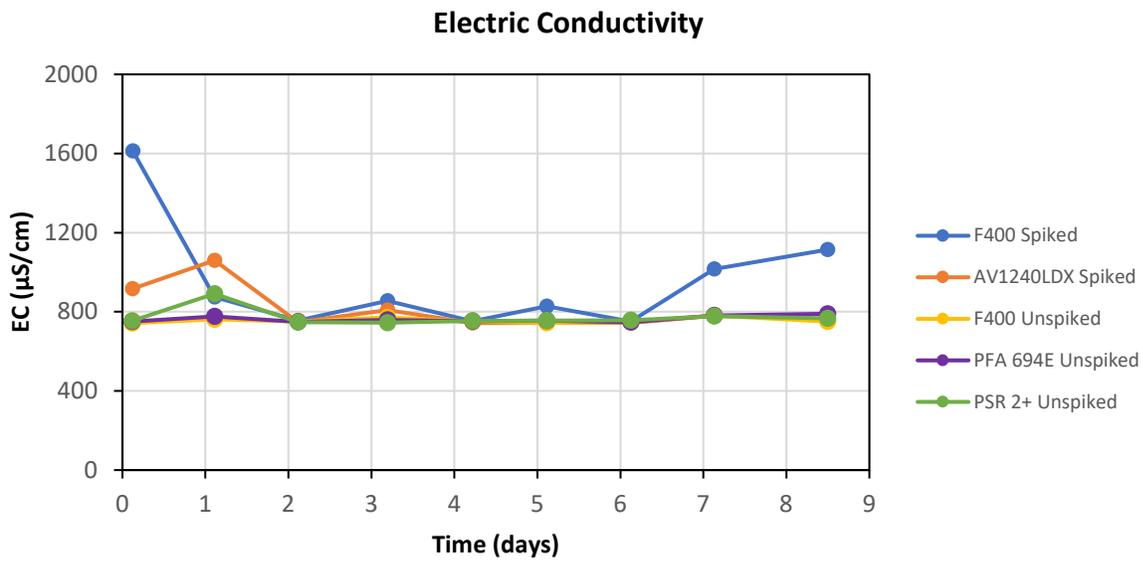


Figure A-4. Electric conductivity values over time from RSSCT columns.

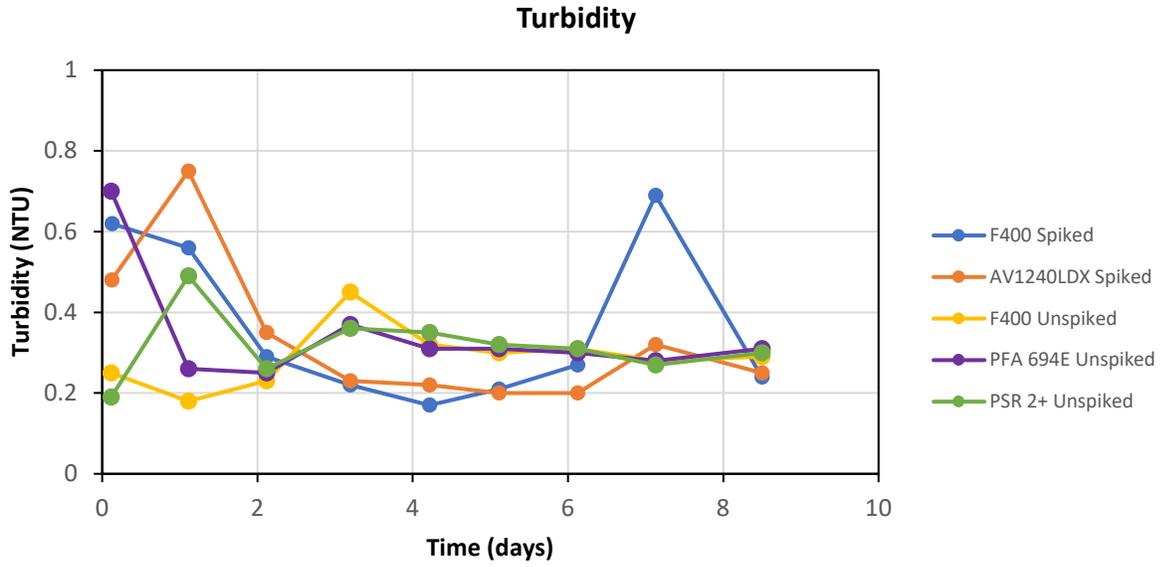


Figure A-5. Turbidity over time from RSSCT columns.

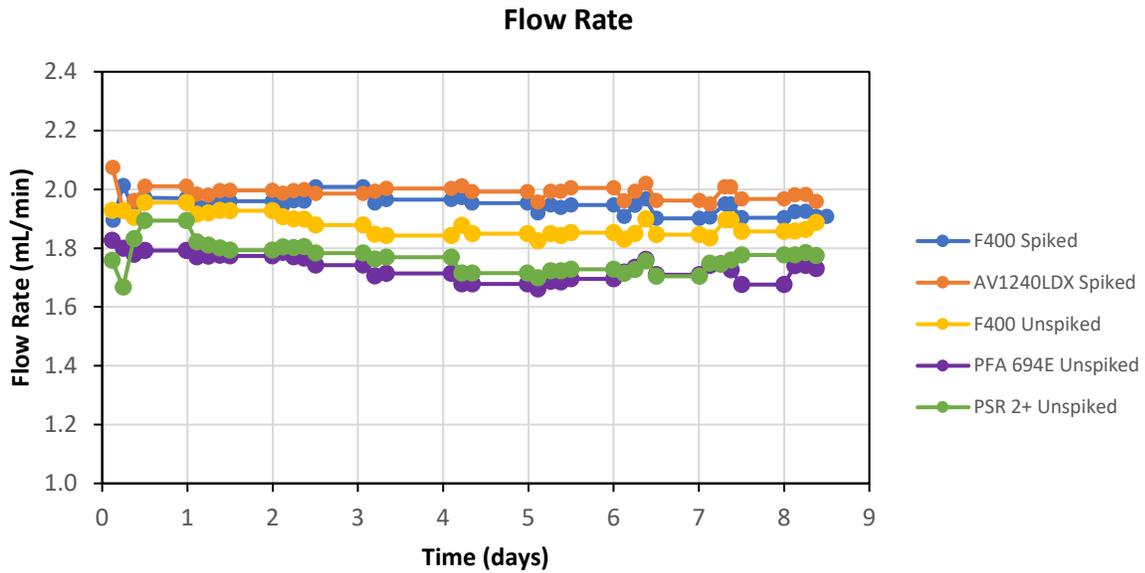


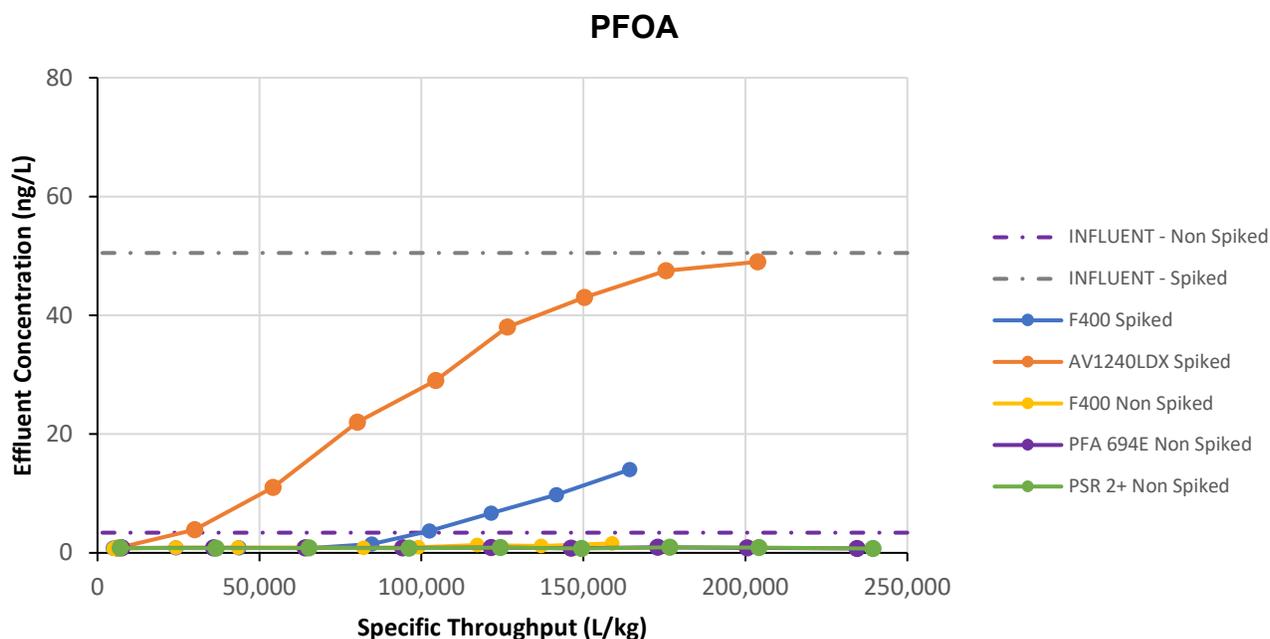
Figure A-6. Flow rates over time from RSSCT columns.

Appendix B PFAS Plots

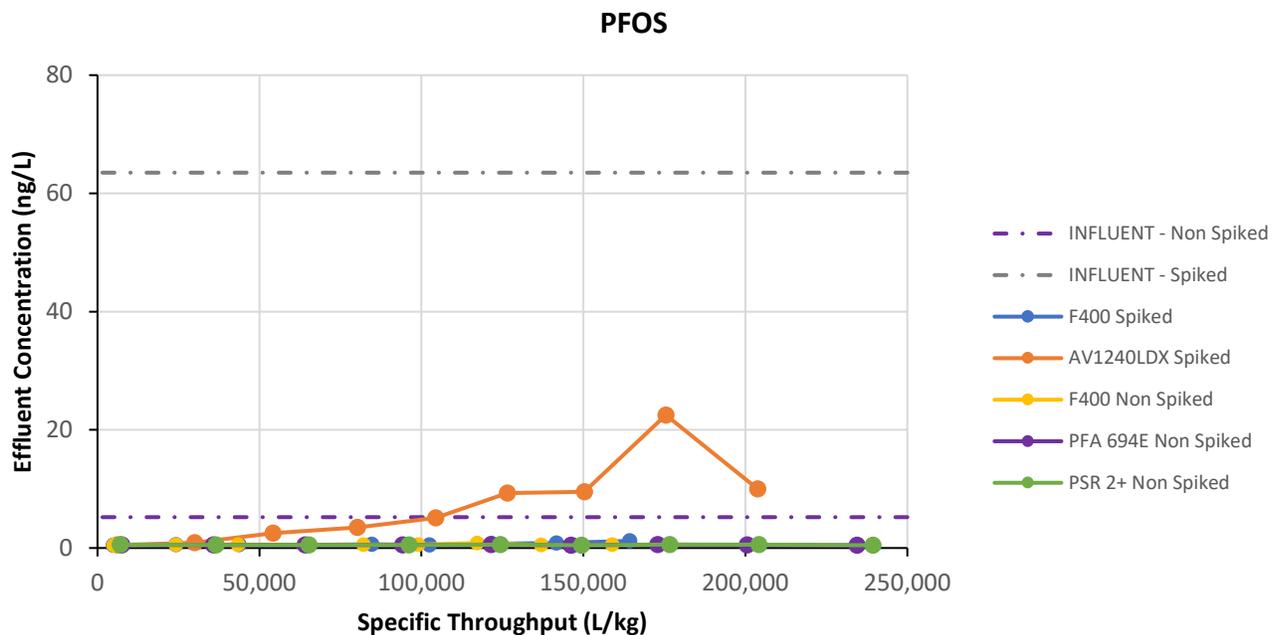
Over the test period, the non-spiked F400 column effluent exceeded the influent’s concentration for Perfluorohexanoic acid (PFHxA) and Perfluorononanoic acid (PFNA). The spiked 400 column effluent had breakthrough, based on detection, of PFHxA, perfluoropentanoic acid (PFPeA), and Perfluorobutanesulfonic (PFBS), PFOA, and PFOS, among others. The other GAC, AV1240LDX had the most PFAS compounds that saw breakthrough based on detection – PFHxA, perfluorotetradecanoic acid (PFTeA), PFNA, PFBS, Perfluoroheptanoic acid (PFHpA) and Perfluoropentanesulfonic acid (PFPeS). The PFOA and PFHxA compounds were elevated above the detection limit by the end of the test for all three GAC-containing columns but approached near the influent level concentration (full saturation of media) for the AV1240LDX column.

All five columns saw breakthrough (based on detection) of Perfluoropentanoic acid (PFPeA) within a specific throughput of 100,000 L/kg. All the GAC columns’ concentrations of PFPeA exceed the influent’s concentration within 50,000 L/kg, whereas the two IXR columns had breakthrough later around 65,000 L/kg. The two IXR column effluents did not breakthrough above influent concentrations for any other PFAS compounds.

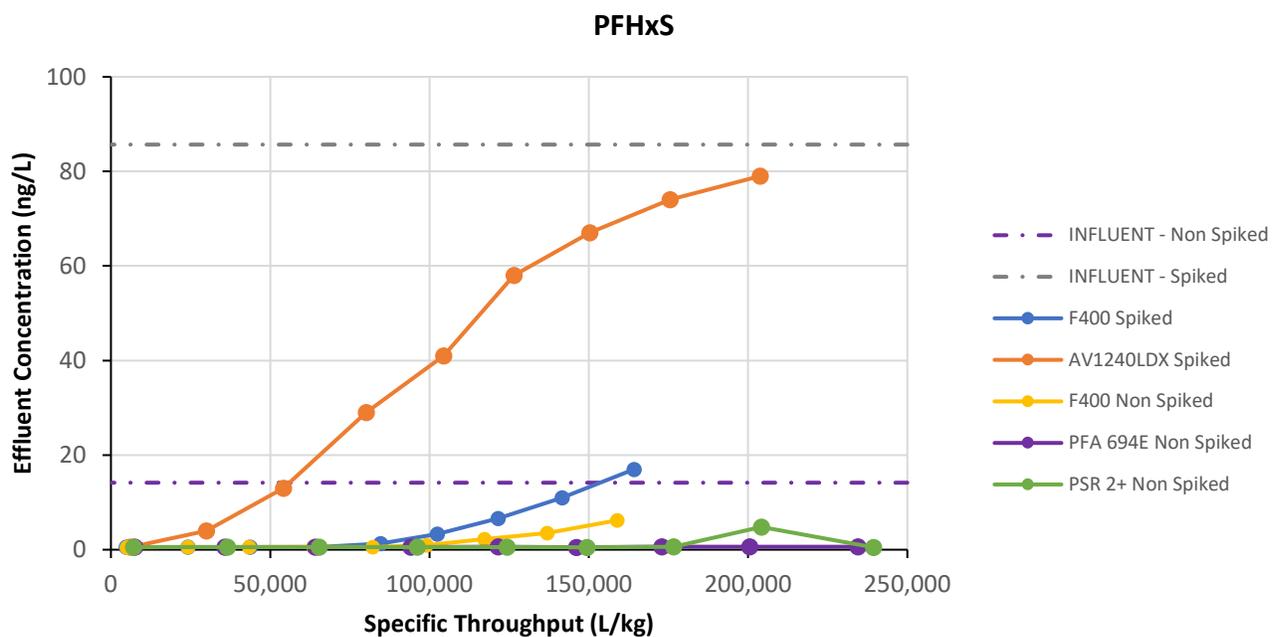
The plots below show the breakthrough plots of individual PFAS compounds that resulted above the detection limit in one or more effluent samples.



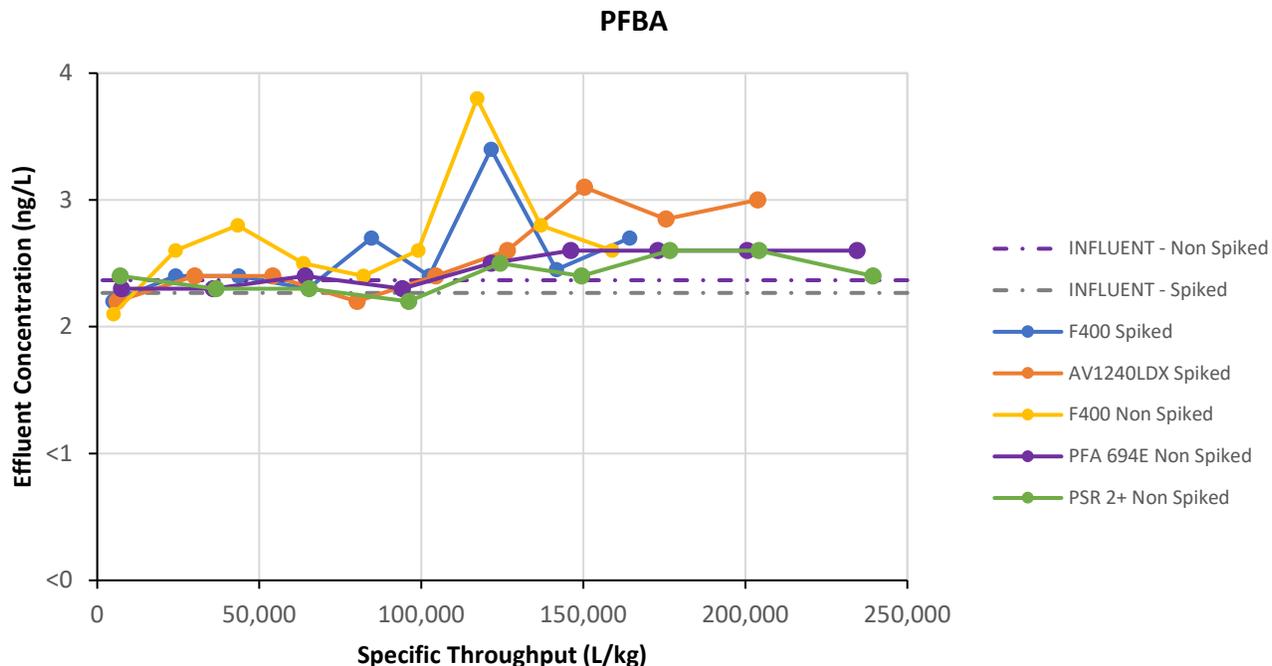
Note: analytical reporting limits varied between 0.74 and 0.91 ng/L.
Figure B-1. PFOA results over time from RSSCT columns.



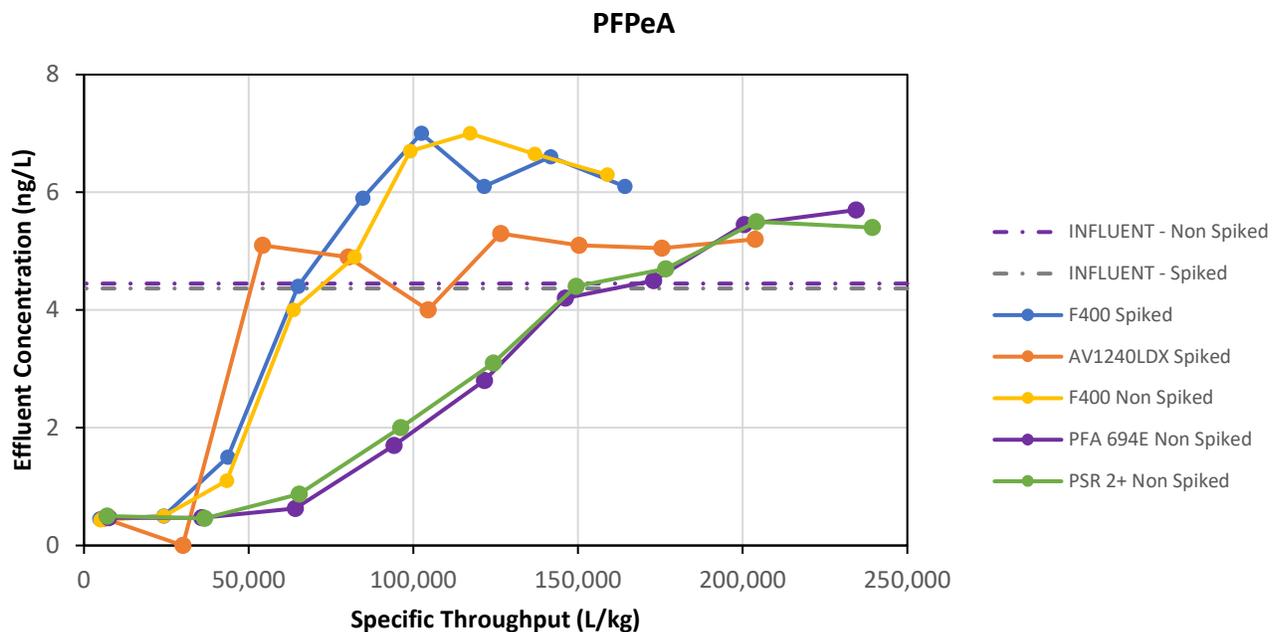
Note: analytical reporting limits varied between 0.47 and 0.84 ng/L.
Figure B-2. PFOS results over time from RSSCT columns.



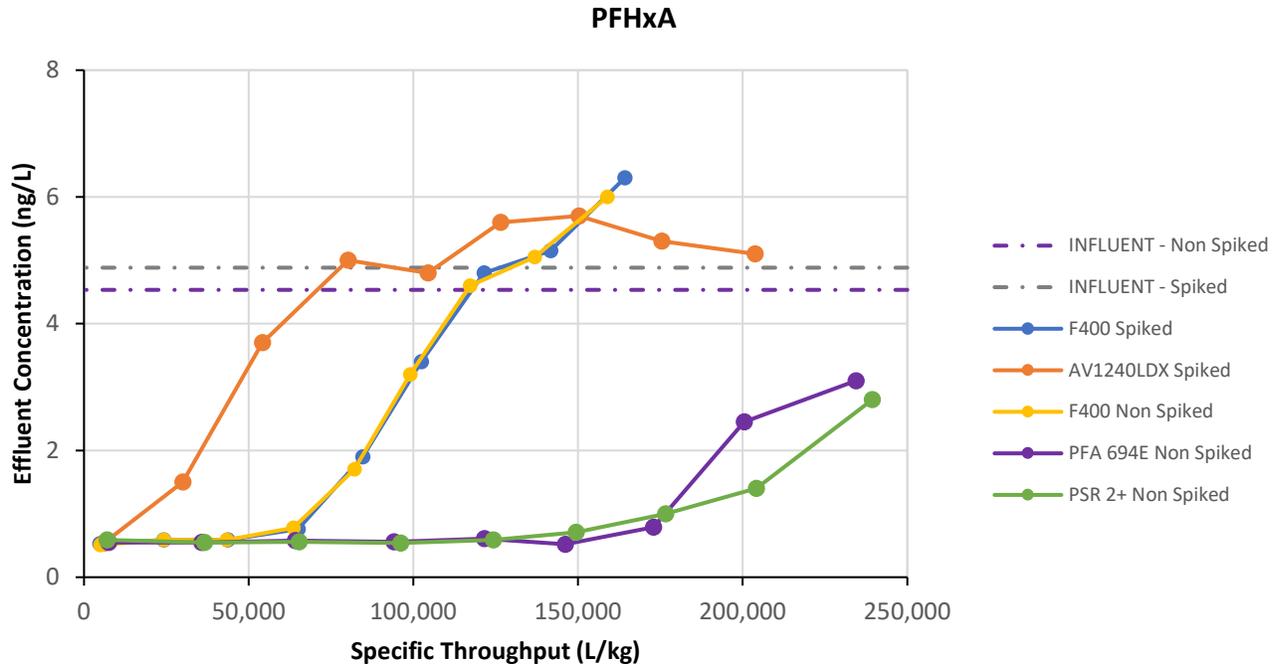
Note: analytical reporting limits varied between 0.50 and 0.63 ng/L.
Figure B-3. PFHxS results over time from RSSCT columns.



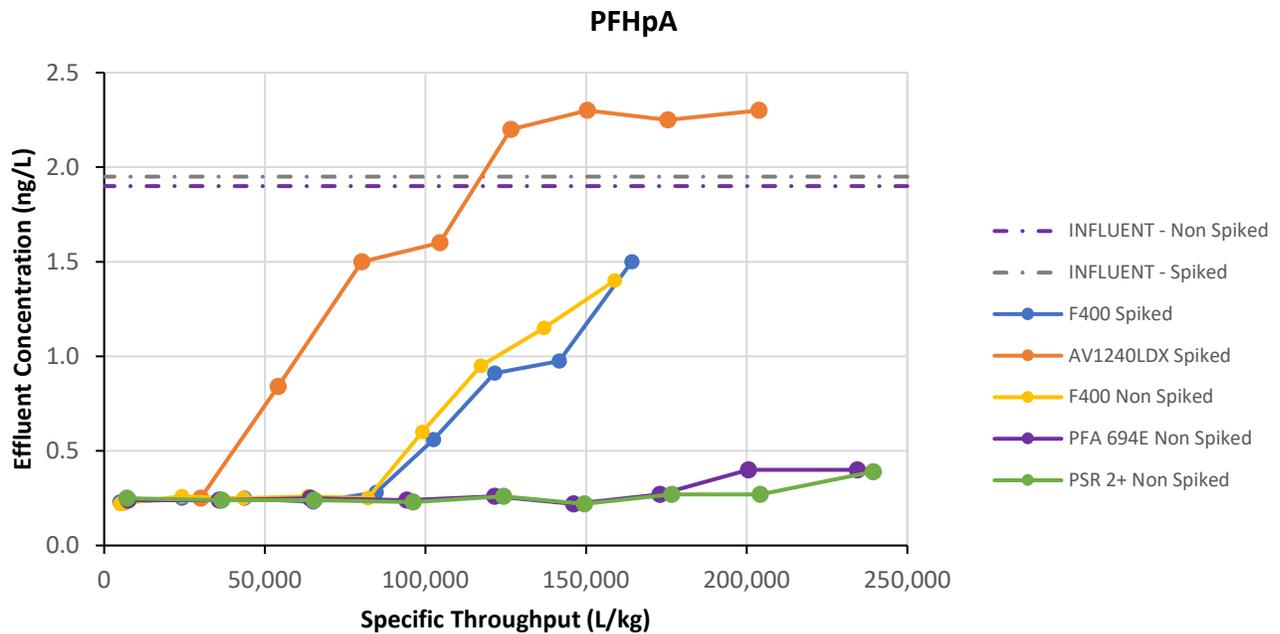
Note: analytical reporting limits varied between 2.1 and 3.4 ng/L.
Figure B-4. PFBA results over time from RSSCT columns.



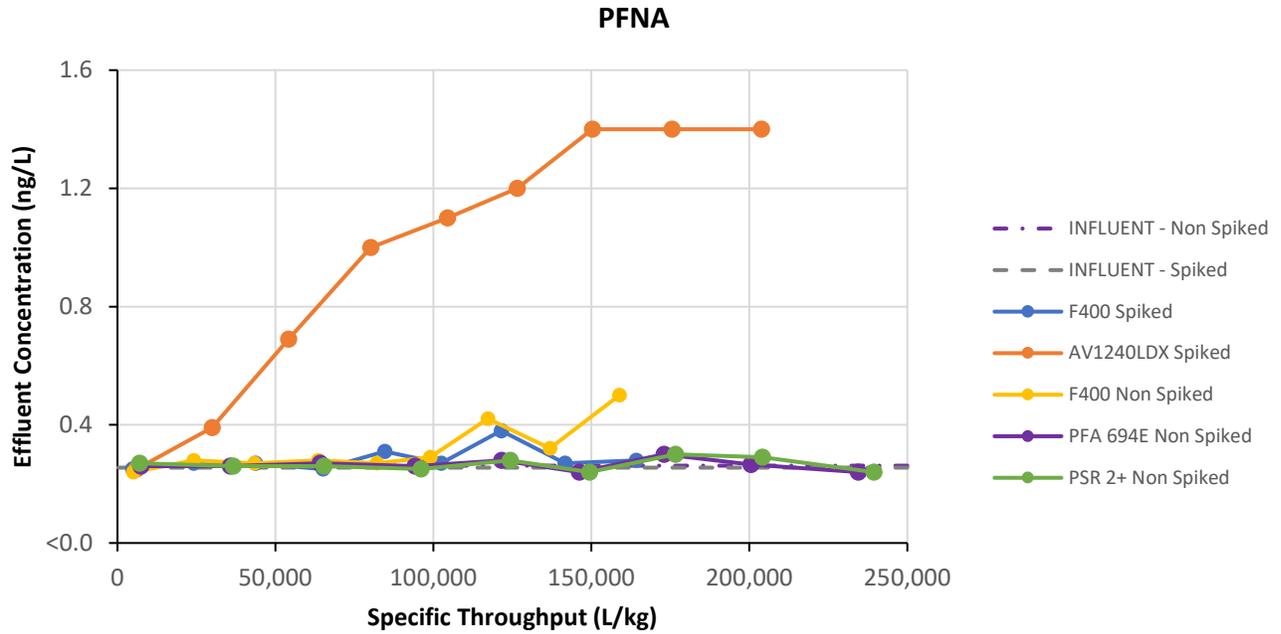
Note: analytical reporting limits varied between 0.43 and 0.50 ng/L.
Figure B-5. PFPeA results over time from RSSCT columns.



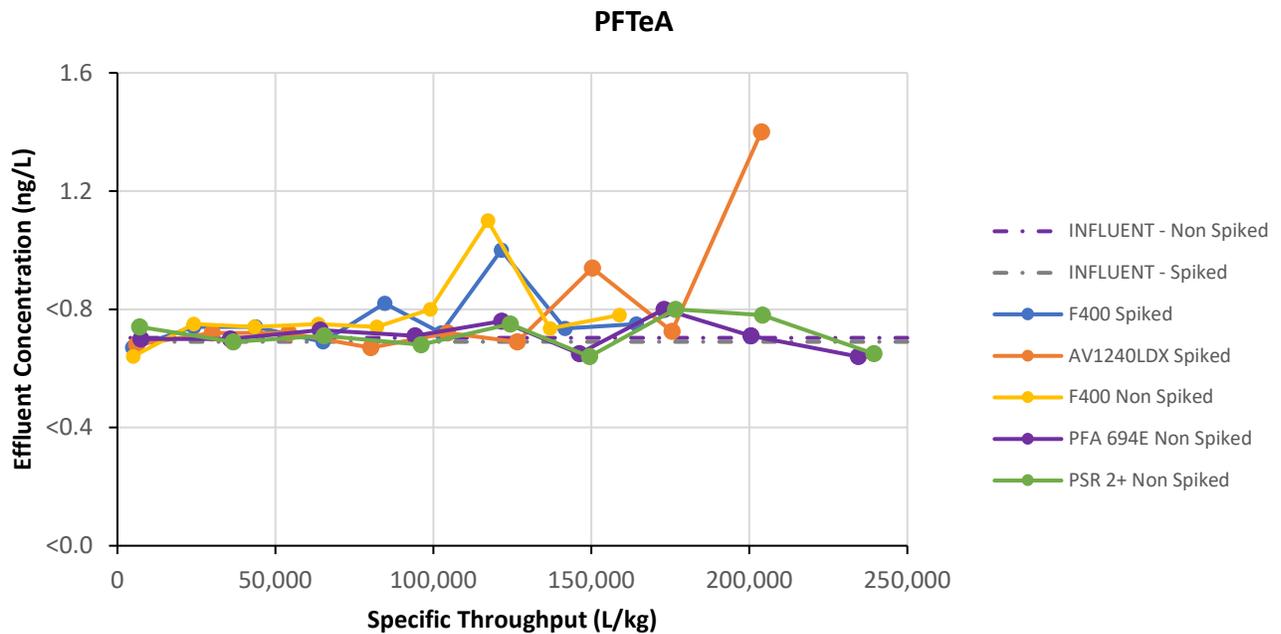
Note: analytical reporting limits varied between 0.51 and 0.61 ng/L.
Figure B-6. PFHxA results over time from RSSCT columns.



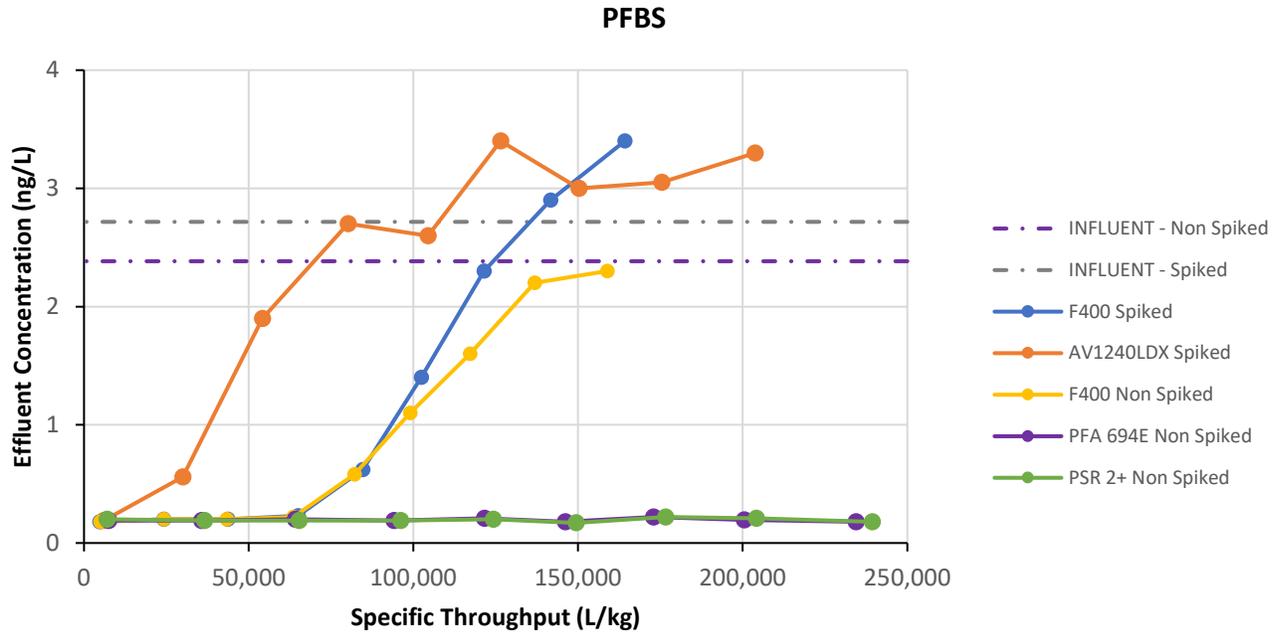
Note: analytical reporting limits varied between 0.22 and 0.28 ng/L.
Figure B-7. PFHpA results over time from RSSCT columns.



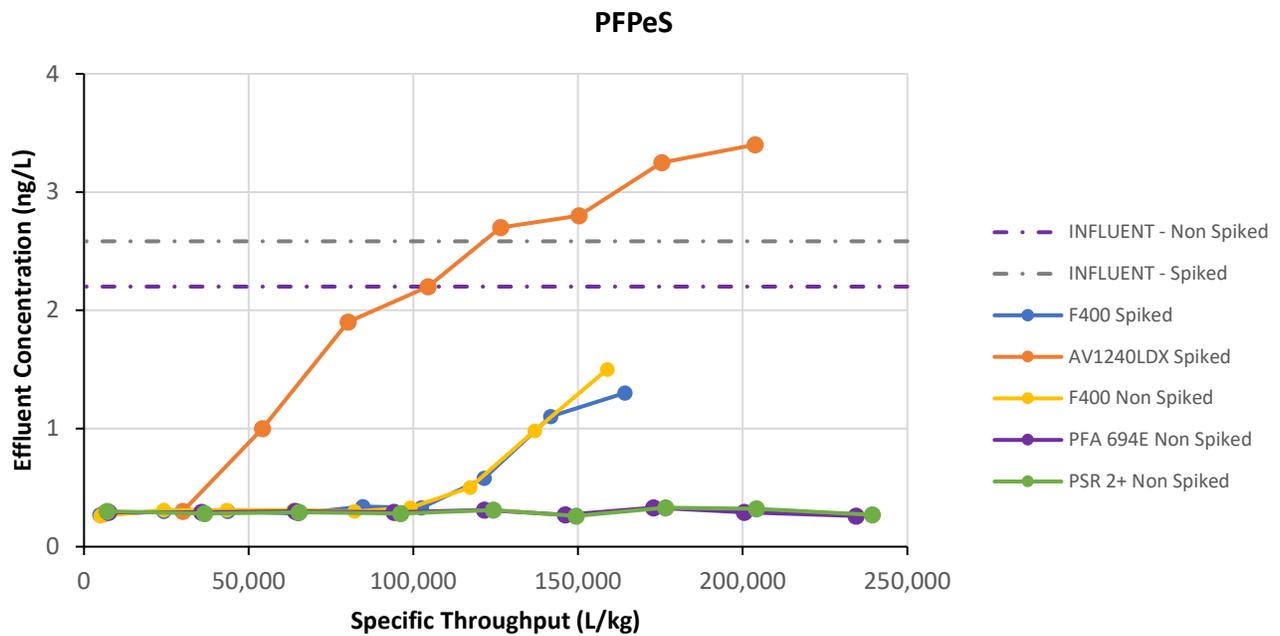
Note: analytical reporting limits varied between 0.23 and 0.42 ng/L.
Figure B-8. PFNA results over time from RSSCT columns.



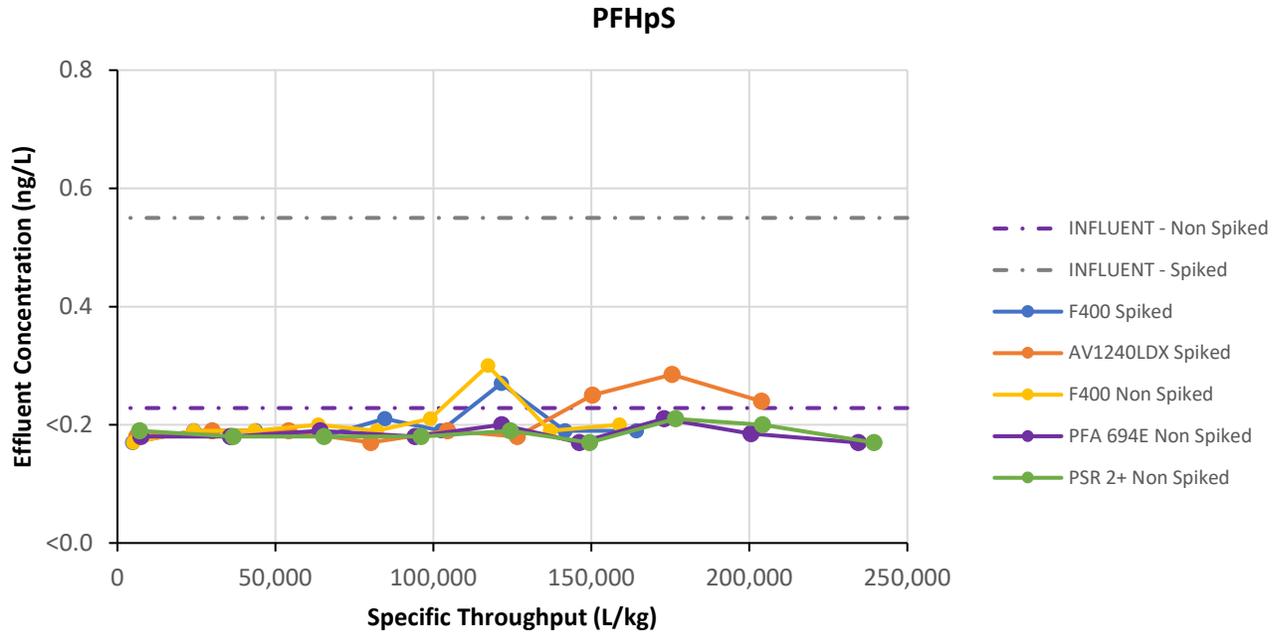
Note: analytical reporting limits varied between 0.64 and 1.10 ng/L.
Figure B-9. PFTeA results over time from RSSCT columns.



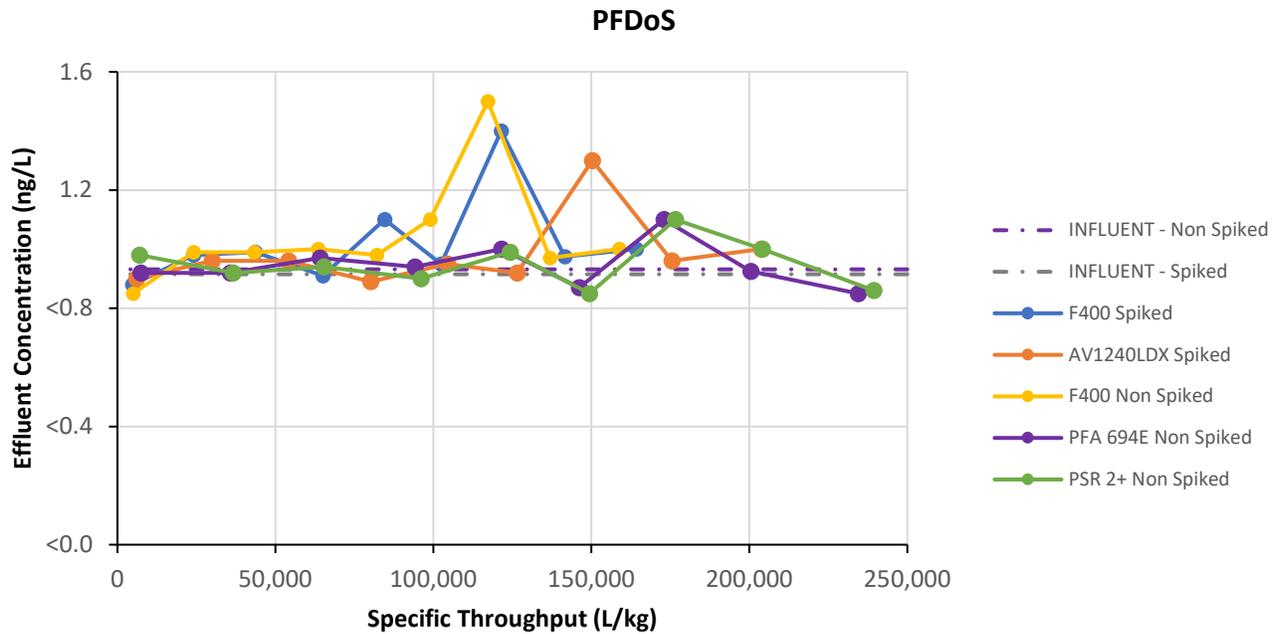
Note: analytical reporting limits varied between 0.18 and 0.22 ng/L.
Figure B-10. PFBS results over time from RSSCT columns.



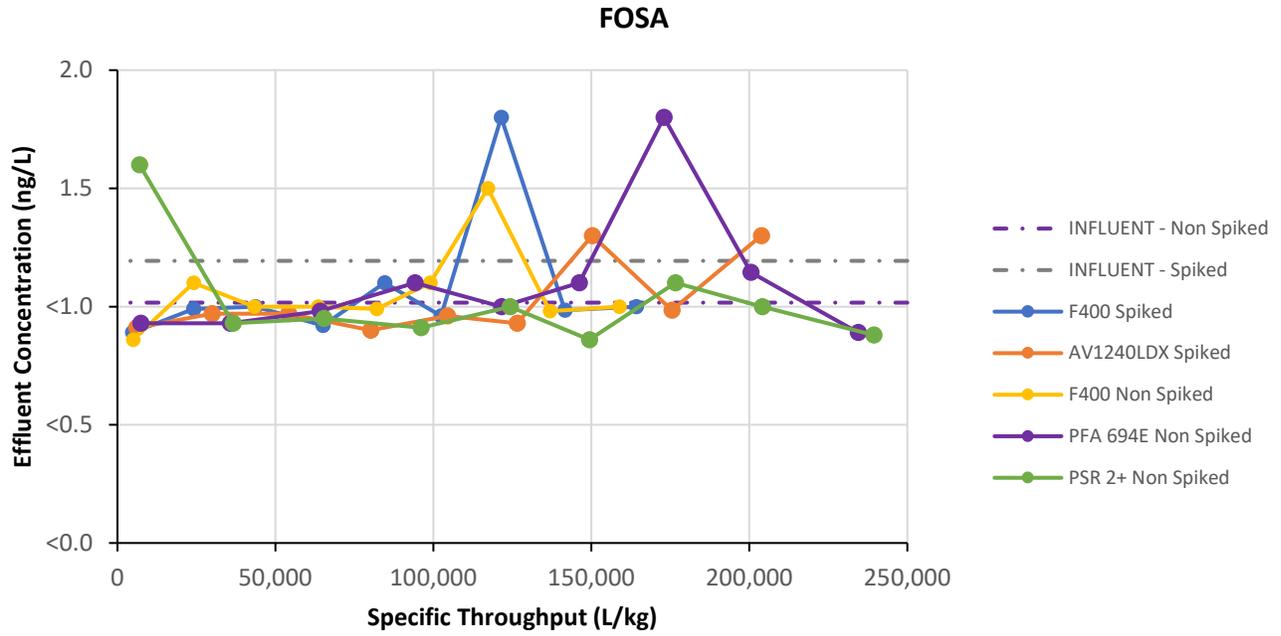
Note: analytical reporting limits varied between 0.27 and 0.34 ng/L.
Figure B-11. PFPeS results over time from RSSCT columns.



Note: analytical reporting limits varied between 0.17 and 0.27 ng/L.
Figure B-12. PFHpS results over time from RSSCT columns.



Note: analytical reporting limits varied between 0.83 and 1.30 ng/L.
Figure B-13. PFDoS results over time from RSSCT columns.



Note: analytical reporting limits varied between 0.86 and 1.30 ng/L.
Figure B-14. FOSA results over time from RSSCT columns.