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Pilot Scale Removal of Per- and Polyfluoroalkyl Substances and Precursors from AFFF-Impacted Groundwater by Granular Activated Carbon

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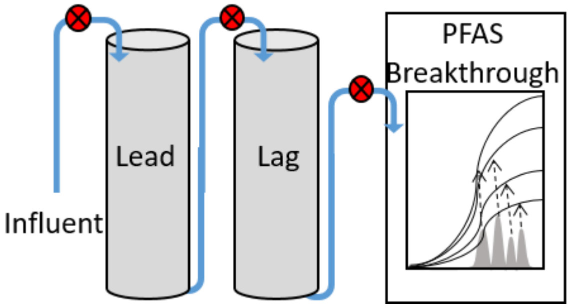

ABSTRACT

The US military, municipal fire stations, airports, and the petroleum-processing industry have used aqueous film forming foam (AFFF) to extinguish hydrocarbon-based fires. Repeat uses of AFFF during firefighting activities resulted in per- and polyfluoroalkyl substances (PFASs) contamination of groundwater. Granular activated carbon (GAC) adsorption is a frequently selected technology for remediating water containing organic contaminants, including PFASs. A pilot study conducted over nine months at a military fire-fighting training area employed two GAC vessels in a lead-lag configuration to evaluate PFAS removal. Breakthrough was quantified for branched and/or linear isomers of 15 PFASs identified by liquid chromatography tandem mass spectrometry (LC-MS/MS) including perfluoroalkyl carboxylates, perfluoroalkyl sulfonates, perfluoroalkyl sulfonamides, and fluorotelomer sulfonates. The total oxidizable precursor (TOP) assay was used to provide information on precursors in the influent and to quantify precursor breakthrough. Individual PFASs quantified by LC-MS/MS accounted for 76% of the PFASs in influent as quantified by the TOP assay. The influent PFAS profile was used to infer the nature of the AFFFs used at the site. Breakthrough of shorter-chain PFAS and branched isomers occurred before breakthrough of longer-chain PFAS and linear isomers. For PFAS with equal perfluoroalkyl chain length, adsorbability for different head groups was in the order $-COO^-$ $< -SO_3^- < -CH_2CH_2SO_3^- < -SO_2NH$. TOP assay results further showed that precursors of perfluoroalkyl carboxylic acids (PFCAs) broke through GAC in addition to commonly measured PFCAs and perfluoroalkylsulfonic acids. Chromatographic retention times of PFAS obtained from a single analysis of influent groundwater can be used to predict the relative order of breakthrough for other PFASs at the pilot scale on GAC.

WATER IMPACT STATEMENT

Groundwater contamination by PFASs requires cost-effective remediation approaches. Granular activated carbon adsorption of PFASs from groundwater contaminated by aqueous film forming foams is controlled by PFAS chain length, isomer configuration, and polar head group. GAC performance can be predicted from chromatographic retention times of PFAS in influent water.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic chemicals that have been used in many industrial and consumer products since the 1950s.[1-3] PFASs occur as mixtures and are hydrophobic, oleophobic, and heat stable.[1] PFASs are manufactured by either electrochemical fluorination (ECF),[4] which produces 25% branched (Br) and 75% linear (L) PFASs,[5-7] or fluorotelomerization-based manufacturing processes which produce only L PFASs,[2] except for PFCAs produced by the telomer olefin process.[5]

Although aqueous film forming foam (AFFF) was developed and deployed by the Navy in the early 1960s,[8] AFFFs have been used at US airports, municipal fire stations and airports, petroleum facilities, and other industries to effectively extinguish hydrocarbon-based fires.[8] The history of AFFFs placed on the Qualified Product List indicates multiple AFFFs were available for use between the 1970s and 1990s when fire fighters on military bases regularly trained with AFFF.[9, 10] Due to the uncontained nature of AFFF use during emergencies and fire-fighter training, perfluoroalkyl carboxylates (PFCAs), sulfonates (PFSAs), and precursors that degrade to PFCAs and PFSAs, along with other AFFF constituents (e.g. hydrocarbon surfactants)[11] and co-contaminants (e.g., petroleum hydrocarbons and chlorinated solvents) have contaminated surrounding soils,[12] sediment,[13] surface water,[14-16] and groundwater.[11, 12, 15, 17-20] As a consequence, surface water and groundwater sources of drinking water have been contaminated with AFFF-derived PFASs.[21, 22]

In 2016, the U.S. EPA established a Lifetime Health Advisory (LHA) of 70 parts per trillion (ng/L) for the sum concentration of PFOA and PFOS.[23] To reduce human and ecological exposure to perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) and other PFASs, remediation systems are being installed. Technologies for treating PFAS are evolving quickly and include sequestration technologies, such as granular activated carbon (GAC)[24-27] and ion-exchange resins.[24, 25, 27, 28] Other treatment technologies include membrane technologies (e.g., reverse osmosis or nanofiltration), and destruction technologies (e.g., chemical oxidation,[29] electrochemical oxidation[30] reductive defluorination,[31] or sonolysis).[32]

Given the availability and familiarity with GAC treatment systems, it is a frequently considered option for remediating PFAS-impacted groundwater. The efficacy of GAC for removing PFOA and PFOS is commonly evaluated by laboratory batch or column systems with the target of achieving concentrations below the U.S. EPA LHA. Most studies evaluate only PFCAs and PFSAs,[27, 28, 33-43] and only one bench-scale study documents the removal of precursors from AFFF-contaminated groundwater.[40] Removal of PFCAs and PFSAs by GAC, but not precursors, at the pilot and full scale has been reported but only for drinking water and municipal wastewater.[24, 35, 41, 44, 45] To the best of our knowledge, there are no published reports that characterize PFAS removal including precursors, at ug/L concentrations in AFFF-contaminated groundwater at the pilot scale by GAC.

At present, analytical methods for individual PFASs based on liquid chromatography with high resolution mass-spectrometry (LC-HRMS) are evolving to include more precursors.[18-20, 46-49] However, LC-HRMS for precursor analysis is not yet routine nor commercially available, so a selective use of LC-HRMS in combination with more readily available LC with tandem mass spectrometry (LC-MS/MS) may be a prudent approach for studies aimed at investigating a wider array of precursors. Although LC-HRMS was applied to study the sorption of precursors from groundwater onto GAC in laboratory batch systems,[40] it has not been applied to pilot- or full-scale systems.

As a complementary approach to the quantification of individual precursors by LC-MS/MS or targeted LC-HRMS, the total oxidizable precursor (TOP) assay provides a quantitative estimate of precursors.[50] The TOP assay, which is commercially available, is a useful screening tool until analytical methods for a more comprehensive array of PFASs becomes available through contract laboratories. The quantity of precursors informs the total PFAS load, beyond PFCAs and PFSAs, that requires treatment. Data from the TOP assay also can be used as a proxy for the breakthrough of oxidizable PFAS precursors on GAC systems. Because the TOP assay does not identify individual precursors, data typically are reported as the net change in PFCA concentrations before and after oxidation. To the best of our knowledge, the TOP assay has not been used to evaluate precursor breakthrough on GAC at any scale. In this study, a pilot-scale GAC system containing two columns in series was operated over a nine-month period at a former military fire-fighter training site. Influent, lead column effluent, and lag column effluent samples were collected weekly or bi-weekly and analyzed for 17 PFASs, including PFCAs, PFSAs, precursors and their branched (Br) and linear (L) isomers by liquid chromatography tandem mass spectrometry (LC-MS/MS). Information on the 17 PFASs in the influent, which included six PFCAs (C4-C9), five PFSAs (C4-C8), and six precursors including 4:2, 6:2, and 8:2 fluorotelomer sulfonates (FTSs) and C5, C6, C8 perfluoroalkyl sulfonamides (FASAs) provided insight on the AFFF(s) used at the site. The TOP assay was applied to a select number of influent and effluent samples to assess GAC breakthrough of total oxidizable precursors as well as individual precursors. Breakthrough curves for the branched and linear isomers of the PFCAs, PFSAs, and FASAs were constructed and modeled with a pore-surface diffusion model to quantitatively compare PFAS adsorbability. The correlation between breakthrough bed volume and chromatographic retention times can be used to predict relative breakthrough of individual PFAS using a similar mechanism of retention (e.g. GAC).

EXPERIMENTAL METHODS

Standards and Reagents. The solvents and chemicals used for this study are described in the Supplemental Information (SI). Native and isotopically labeled standards were the same as those used in Backe et al., but with the addition of FHxSA and FOSA (Wellington Laboratories, Guelph, ON, Canada).[18] For the full list of PFAS analytes and acronyms, see Table S1.

GAC System Design. The pilot-scale system was installed alongside a full-scale GAC treatment system. This pilot-scale GAC system, including the GAC selected, was installed to mimic the operational conditions of the full-scale GAC system and to study PFAS breakthrough (see the SI for more information). Influent to the pilot-scale system was comprised of blended groundwater obtained from seven extraction wells approximately 150 meters (m) down gradient from the fire-fighter training area. The influent contained PFAS and co-contaminants, including solvents (e.g. acetone) and halogenated hydrocarbons (e.g.1,4-dichlorobenzene), at µg/L concentrations (data not shown), and hydrocarbon surfactants.[11] The average total organic carbon (TOC) concentration in the GAC influent was 2.0 mg/L, which is relatively high for groundwater.

Influent was pumped through two 200-L steel drum vessels that were plumbed in series and contained prepacked, reactivated GAC (DSR-A 8x40, Calgon Carbon Corporation, Pittsburgh, PA). GAC properties and system design parameters are summarized in Table 1. Influent was pumped by a low pressure, peristaltic pump at a rate of 8 L/min into the GAC vessels. Interconnecting piping and valves were PTFE-free and fabricated of polyvinyl chloride. The pilot system was operated for nine months from November 2016 through August 2017, except for a one-month shutdown in February 2017. No GAC removal or changeout occurred during the pilot study period.

Sample Collection, Transport, and Storage. Samples of influent, lead vessel effluent, and lag vessel effluent were collected on a weekly basis for the first seven months and then bi-weekly for the following two months, except for the shutdown period. Samples were collected in 30 mL high-density polyethylene (HDPE) containers (VWR, Radnor, PA). Field blanks consisted of laboratory-deionized water shipped in 30 mL HDPE containers that were opened during sample collection. Trip blanks consisted of laboratory-deionized water shipped to the site in 30 mL HDPE containers that were not opened at any time during sample collection and shipping. All field (n=4) and trip blanks (n=4) were below the limit of quantification (LOQ) for all targeted PFAS. The first seven effluent samples from the lag vessel served as blank controls (all were <LOQ for all targeted PFAS), which indicates the PFAS background in the pilot-scale GAC system was negligible. All samples were shipped to Oregon State University on ice and then frozen at -20 °C until analysis.

Sample Extraction. Samples were brought to room temperature and inverted several times for homogenization. A 3 mL aliquot was placed in a 15 mL centrifuge tube along with 0.97-1.0 g NaCl, 10 µL hydrochloric acid, and 0.72 ng of all mass-labeled internal standards (Table S1). Samples were extracted in triplicate with 10:90 2,2,2-trifluoroethanol in ethyl acetate to give a total volume of 1 mL to which 500 µL of methanol was added for a final volume of 1.5 mL for analysis by LC-MS/MS.[18]

TOP Assay. Five pairs of influent and lead vessel effluent were collected at 3,200, 5,800, 9,200, 11,000, and 16,000 bed volumes and analyzed by the TOP assay.[50] Each 15 mL centrifuge tube received 1.5 mL of sample and 1.5 mL reaction solution (60 mM potassium persulfate, 125 mM sodium hydroxide in water). Samples were placed in a water bath between 85-90 °C for 6 h followed by storage at 4 °C until analysis, which was within one week of reaction. Prior to analysis, samples were brought to room temperature, neutralized with 10 μL HCl, and then spiked with 0.72 ng of all isotopically labeled standards and extracted as described above.

PFAS Selection and Analysis by LC-MS/MS. Groundwater from an upgradient location at this site was initially characterized by LC-HRMS and revealed 52 individual PFAS (Table S1).[20] However, when the GAC influent groundwater for this study was screened for these 52 PFAS, only 17 were present above the LOQ. Information on the selection criteria for the 17 PFAS from the independent LC-HRMS analysis can be found in the SI.

Analyses were performed on an Agilent 1100 series (Agilent, Santa Clara, CA) HPLC attached to a Waters Triple Quadrupole Detector MS/MS system (Waters Corporation, Milford, MA). The LC-MS/MS was fitted with two zirconium modified diol (Zr-diol) and one Zorbax Silica (Sil) guard columns (Agilent) and a Zorbax Eclipse Plus C18 analytical column (Agilent).[18, 51] Calibration curves consisted of five to seven standards ranging from 10 ng/L- 5,000 ng/L for all analytes, with the exception of FOSA (50 ng/L – 10,000 ng/L) and 6:2 FTS (10 ng/L- 2,500 ng/L).

All calibration curves were required to be linear ($R^2 \geq 0.99$). Each PFAS was quantified by isotopically labeled standard calibration and assigned a data quality tier of confidence (Table S1).[52] Briefly, quantitative (Qn) analytes are those which contain both authentic analytical and isotopically labeled internal standards, semi-quantitative (Sq) analytes had reference materials but unmatched internal standards, and qualitative (Ql) analytes had neither authentic or internal standards. Instrumental LOQs were 10 ng/L for all analytes (Table S1) with the exception of FHxSA and FOSA which had an LOQ of 50 ng/L. All values reported concentrations >LOQ signal-to-noise values greater than nine. The LOD values for all analytes were defined as 3.3x lower than the LOQ, and with a signal-to-noise value between three and nine. Br and L concentrations were calculated by separately integrating the Br and L peaks.

Each analytical sequence was comprised of one to three weeks of samples, a whole method extraction blank, and several solvent blanks. Whole method extraction process blanks consisted of spiking deionized water with all isotopically labeled standards and extracting as described above. The matrix for solvent blanks was generated by extracting a mixture of 3 mL deionized water as described above. All process and solvent blanks fell at or below half of the limit of quantification (< ½ LOQ). Replicate samples of influent (n=4) were used to calculate a standard error as a measure of precision about the reported concentrations.

Data treatment and breakthrough curves. Breakthrough curves for individual PFAS were developed by normalizing effluent concentrations for individual PFASs with the corresponding influent concentration at each sampling time point and plotting the ratio as a function of bed volumes of water treated at the time of sample collection. Resulting breakthrough curves were fit with the pore-surface diffusion model (PSDM)[53, 54] using the approach described in Summers et al.[55] and in Fotta.[56] Adjustable model inputs included both equilibrium and kinetic parameters. Equilibrium parameters were the apparent Freundlich capacity parameter (K*) and the Freundlich exponent (1/n). K* for individual PFASs was estimated by dividing the bed volumes of water treated at 50% PFAS breakthrough (BV_{50}) by the GAC bed density (ρ_{bed}); i.e., $K^* = BV_{50}/\rho_{bed}$.[57] K* describes the adsorption capacity of the tested GAC for a given PFAS in the tested water. The Freundlich isotherm exponent (1/n) was set to one because percent micropollutant removal in GAC adsorbers is independent of the initial micropollutant concentration when background organic matter is present.[58] Kinetic parameters were tortuosity (τ) and the surface-to-pore diffusion flux ratio (SPDFR). When pore diffusion alone effectively described PFAS breakthrough curves, surface diffusion was eliminated by setting the SPDFR to 10^{-30}. The pore diffusion coefficient was adjusted by varying tortuosity, with the constraint that tortuosity could not be less than one. For steeper breakthrough curves, pore diffusion alone could not effectively describe the data. In that case, the tortuosity was set to its smallest allowable value (i.e., 1.0), and the SPDFR was increased from 10^{-30}. For the PSDM, the average C_0 was determined from the measured PFAS concentrations in 28 GAC influent samples over the nine-month period of the pilot study. For the lag column, K*, τ, and SPDFR (required for Br-PFOA only) values for each analyte are reported in Table 2. For the lag column, K* values were within 10% of those for the lead column. Intraparticle diffusion flux values were within a factor of 2 of those for the lead column, except for PFBA, for which the difference was a factor of 5. The latter result was likely due to uncertainty in the PFBA breakthrough curve for the lead column (Figure

S1). For each PFAS, PSDM results were used to determine the bed volumes of water that could be treated until 20% breakthrough was reached.

RESULTS AND DISCUSSION

PFAS Characterization of GAC Influent. The branched and linear PFAS quantified in the GAC influent included C4-C9 PFCAs, C4-C8 PFSAs, 4:2 FTS, 6:2 FTS, and 8:2 FTS, FPeSA, FHxSA, FOSA, and N-TAmP FHxSA (Table 2). The most prevalent PFAS in the average influent were PFOS (summed Br and L: 2,700 ng/L) and FHxSA (summer Br and L: 2,800 ng/L), followed by PFHxS (summed Br and L: 2,100 ng/L), 6:2 FTS (L only: 1,000 ng/L), PFOA (summed Br and L: 900 ng/L), and PFHxA (L only: 740 ng/L). To the best of our knowledge, this is only the second report of FHxSA in AFFF-impacted groundwater[59] and the first to report Br and L isomers (Table 2). The only other report of FHxSA is for Canadian surface waters.[46] A recently reported PFAS,[20] N-TAmP-FHxSA, was also present initially in the influent, but was not detected after the 4 week shutdown and is not discussed further.

Influent PFAS composition along with Br:L isomer ratios was used to infer the AFFF(s) used at this site. PFAS composition of AFFFs varies significantly among manufacturers.[18, 60] The PFASs in 3M AFFFs are comprised of a significant proportion of branched and linear PFASs and are comprised mainly of PFSAs, namely PFOS. In contrast, fluorotelomer-based AFFF do not contain PFSAs but contain partially biodegradable polyfluorinated compounds that biodegrade[61-63] and oxidize[64, 65] to only linear PFCAs. Understanding the AFFF source provides insight that can be used for site characterization, interpret TOP assay data, and for forensics purposes.

The influent contained Br and L isomers of PFCAs, PFSAs, and FASAs, which indicates the use of 3M AFFF at this site.[66, 67] The Br:L isomer ratios for 3M-derived PFAS, except for PFHxS (12:88), ranged from 25:75 (FHxSA) up to 39:61 (PFOS; Figure 1a), which is similar to the 30:70 ratio reported for PFOS.[5, 7, 68] Branched isomers of PFOS and PFOA exhibit lower partition coefficients between soil and water (K_d) or soil organic matter and water (K_{oc}),[69, 70] as well as shorter chromatographic retention times (Table 2) than L isomers, so differential transport is expected for L and Br isomers. In the absence of biotransformation of precursors, enrichment of Br-PFOS in the GAC influent, which was collected 150 m downgradient from a source zone, can be explained by greater retardation of L-PFOS. Similar PFCA Br:L ratios would be expected if the PFCAs were derived only from ECF chemistry. However, the Br:L isomers ratios for PFCAs including PFPeA, PFHpA, and PFOA (Figure 1b) are 9:91 (Table 2), which indicates enrichment of L over Br PFCA isomers. Furthermore, the influent ratio of PFOA to PFOS is 1:3 (Table 2), which indicates more PFOA is present than expected based on the ratios of PFOA to PFOS (1:100) in 3M AFFFs dating back to 1989.[18] Thus, the overall greater proportion of PFOA relative to PFOS, combined with the enrichment of L over Br isomers for PFCAs, indicates transformation of linear precursors associated with fluorotelomer-based AFFFs to linear PFCAs.

The presence of FTSs (Table 2) is direct evidence of the use of fluorotelomer-based AFFF at this site. Both FTSs and the fluorotelomer thioether amido sulfonate (FtTAoS) precursors found in Ansul AFFF are comprised of only linear components.[61, 71] Because FtTAoS was not detected in the influent, it is likely that FtTAoS was biotransformed to FTSs as well as to PFCAs.[61, 71] Biotransformation of FtTAoS can only result in linear FTSs and PFCAs. McGuire et al. also attributed increases in PFHxS relative to PFOS to precursor transformation but did not report an analysis of isomer ratios.[59]

TOP Assay of GAC Influent. The TOP assay was applied to estimate the presence of unknown precursors not captured as individual PFAS in the GAC influent. In addition, the TOP assay was conducted for selected effluent samples from the lead vessel to estimate breakthrough of unknown precursors, and these results will be presented in a separate section later in the paper. During the TOP assay, individual known precursors (FASAs, FTSs, and N-TAmP-FHxSA;Table S2) and unknown precursors are oxidized to PFCAs. The TOP assay does not provide information on individual precursors nor can it account for any precursors that are not oxidizable or that oxidize to substances other than PFCAs.

Precursors in the lead vessel influent were oxidized into a range of PFCAs including PFBA (10%), PFPeA (11%), PFHxA (73%), PFHpA (0.8%), and PFOA (5%) (Table 3). The predominant production of PFHxA (73%) generated by the TOP assay is consistent with the oxidation of the C6-based precursors[52, 72] present in the influent, including 6:2 FTS, FHxSA, and N-TamP-FHxSA (Table 2). A more precise delineation of the chain length of any additional precursors is not possible since the original chain length of precursors is not always preserved under TOP assay conditions. For example, 6:2 FTS oxidizes to PFHpA, PFHxA, PFPeA, and PFBA.[16, 52, 64, 65, 73, 74] As expected, the PFSA concentrations before and after the TOP assay were not statistically different since the values before and after oxidation overlapped given the propagated standard error (Table S2, Equation S2). Oxidation did not significantly change the Br:L isomer ratios, which indicates that precursors had similar isomer ratios to that of the PFCAs, which were predominantly linear in nature (Table 2). Changes in isomer ratios upon oxidation are rarely reported, but can offer information on the Br:L character of oxidizable precursors.[52]

For mass balance purposes, a single influent sample was analyzed in replicate (n=4) by LC-MS/MS for individual PFASs and by the TOP assay (n=4). Post-oxidation, the influent PFCAs and PFSAs gave a total mass of 36.4 ± 1 nmol, which is greater than the total mass of PFAS pre-oxidation (27.7 ± 1 mmol), which was computed as the sum of PFCAs, PFSAs, FASAs, N-TAmP-FHxSA (Table S2). Thus, 76% of the total PFAS in the influent, as determined by the TOP assay, is accounted for by individual PFAS on a molar basis, and the remaining 24% (9.6 ± 2.1 mmol) consists of unknown precursors (Table 3). The influent was screened again for approximately 450 individual suspect PFAS by LC-HRMS;[20] however, only a number of low abundance precursors were detected. Identifying additional precursors not on the suspect list by non-target LC-HRMS was beyond the scope of the study. Equations and calculations for TOP assay can be found in the SI and were also applied to determine the concentration of precursors in lead vessel effluent at various bed volumes (Table 3).

PFAS Breakthrough. Breakthrough curves for individual PFASs were constructed from both lead and lag vessel effluent data and described with the PSDM to determine the bed volumes that corresponded to a C/C_0 =0.2. The 0.2 breakthrough value was selected to avoid extrapolation since not all PFAS reached complete breakthrough by the end of the study. Also, GAC changeout in remediation settings will likely occur once relatively low levels of breakthrough are reached for a criteria PFAS. Lag vessel data are presented (Figures 2a, 2b), and lead vessel data are shown for completeness in the SI (Figure S2).

Breakthrough curves were obtained for C4-C8 PFCAs (Figure 2a and S2a), C5-8 PFSAs, FHxSA, and 6:2 FTS (Figure 2b and S2b). For PFCAs and PFSAs, adsorbability increased with increasing length of the perfluoroalkyl chain, as highlighted by K* values (Table 2) and order of PFAS breakthrough (Figure 2). The effect of perfluoroalkyl chain length on the adsorbability of PFCA and PFSA has been reported for GAC and powdered activated carbon (PAC) systems that treat drinking water[24, 75] and has also been reflected in K_d values determined in batch systems with AFFF-impacted groundwater.[40] It is interesting to note that K* values determined here for a reactivated GAC and a groundwater matrix with a TOC concentration of 2 mg/L were similar to those determined by Liu et al.[45] for different GACs and a different groundwater with a TOC concentration of 2.7 mg/L. Specifically, when K* and K_d values are expressed in units of L/kg, log K* values in our study were 4.60 and 4.93 for PFOA and PFOS, respectively, while log Kd values in Liu et al.[45] ranged from 4.59 to 4.80 for PFOA and from 4.66 to 4.89 for PFOS for 4 different GACs. Similar agreement was observed for other PFAS, for which breakthrough curves were determined in both studies. For a given perfluoroalkyl chain length, PFCAs broke through earlier than PFSAs (e.g., C6: PFHxA < PFPeS; C7: PFHpA < PFHxS; C8:PFOA < PFHpS), consistent with other GAC and PAC adsorption studies.[76] [45, 75] The effect of head group was further evaluated since four L-PFAS each had perfluoroalkyl chains with six fluorinated carbons, including L-PFHpA, L-PFHxS, L-6:2 FTS, and L-FHxSA; breakthrough occurred in the order:$COO^- < -SO_3^- < -CH_2CH_2SO_3^-$ (FTS)$< -SO_2NH^-$(FASA). Xiao et al.[40] reported greater K_d values in batch experiments for the following head groups: $-COO^- < -SO_3^- < -SO_2NH^-$; however, no data for $-CH_2CH_2SO_3^-$ were reported.

The isomer ratios for PFOS, PFOA, and all other Br and L PFAS shifted over time with early lag vessel effluent samples (11,000 bed volumes) enriched in Br isomers over the L isomer (Figure 1c and d). To the best of our knowledge, there are only two other reports that characterize the differences in branched and linear isomer breakthrough on GAC.[76, 77] Earlier breakthrough of Br isomers relative to the L isomers (Figure S2) is also consistent with lower K_{oc} and K_d values for the Br isomers of PFOS and PFOA than for their L isomers.[69, 70] The Br isomers also gave lower fitted K* values than did the L isomers (Table 2).

Breakthrough of PFBA (3,900 bed volumes at $C/C_0=0.2$) occurred significantly before PFOA (8,500 bed volumes) and PFOS (14,900 bed volumes). In a comparison between this study and Hopkins et al., which examined virgin reagglomerated coal-based GAC in coagulated surface water, and had the same TOC concentration (2 mg/L), PFOA and PFOS breakthrough reached 20% after treating 9,000 and 13,500 bed volumes, respectively.[78] Concentrations of PFBA in lag vessel effluent exceeded influent concentrations (Figure 2a) were also reported by others including Liu et al.[45] and Appleman et al.[24] They hypothesized PFBA and other short chain PFAS are displaced by longer-chain PFAS[24] or other co-contaminants,[24, 45] such as hydrocarbon surfactants.[11] In this system, the influent is comprised of a mixture of solvents, fuels, and hydrocarbon surfactant[11] co-contaminants that may compete with shorter chain PFAS. While only PFOA and PFOS have Health Advisory Limits (HALs),[23] other states have health based advisory level for other PFAS including PFBA.[79] To target efficient removal of PFBA, frequent GAC change-out would be required, which is likely cost prohibitive for long-term use.[33, 80]

Breakthrough and Chromatographic Retention Time. The number of log bed volumes required to reach a $C/C_0=0.2$ on the GAC system correlated (r^{2}-value of 0.6094; r^2 value of 0.7268 without PFPeS (an outlier due to low concentrations)) with chromatographic retention times of the individual Br- and L-PFAS on the C18 analytical column (Figure 3, Table 2). Similar relative orders of PFAS breakthrough on GAC and the C18 analytical column suggest similar mechanisms of retention. The C18 analytical column used in this study was endcapped, thus minimizing the potential for specific retention mechanisms (e.g., polar interactions). As a result, non-specific retention mechanisms (e.g., van der Waals interaction) were expected to be dominant between PFASs and both the C18 analytical column and GAC. The agreement between analytical retention time and order of breakthrough on this pilot-scale GAC system with AFFF-contaminated groundwater confirms the findings of Xiao et al.,[40] who found a r^2 value of 0.7082 for the correlation between batch K_d and chromatographic retention times. Strong correlations between simulations using K_d (as in Xiao et al.)[40] and the pilot scale in this study indicates that the relative breakthrough of other PFAS can be predicted from chromatographic retention times.

For example, FHxSA is present in AFFF-groundwater and has a chromatographic retention time of 13.6 min, which is between PFHxS (11.2 min) and PFOS (15.5 min). Thus, based on chromatographic retention time, breakthrough of FHxSA is expected after PFHxS but before PFOS, which is the case (Figure 2b and Figure 3). A single analysis of influent groundwater for a broad array of PFASs can provide the characteristic chromatographic retention time on a reversed-phase (e.g., C18) analytical column, from which the order of breakthrough of individual PFASs, including precursors, can be established. Once the influent is fully characterized, it is not necessary to continually monitor precursor PFAS, thus reducing analytical costs.

Breakthrough and TOP Assay. Select samples of lead vessel effluent were analyzed by the TOP assay and resulted in net PFCA increases, but only for L-PFCAs (Table 3). No lag vessel effluent samples were analyzed by the TOP assay. Irrespective of bed volume, L-PFHxA was the dominant PFCA produced, which was consistent with the concentration and breakthrough of linear C6-based precursors (6:2 FTS, FHxSA; Figure S1). Summed PFCA concentrations obtained by the TOP assay were plotted for five bed volumes (Table 3) to obtain a breakthrough curve (Figure S1b). The TOP assay breakthrough curve is similar to those for 6:2 FTS and FHxSA (Figure S1b) which is consistent with the abundance of the two oxidizable precursors. For the same reason, breakthrough of oxidizable precursors occurred before PFOS and PFOA. Therefore as an alternative to analyzing a broader array of individual precursors, the TOP assay is useful for quantifying oxidizable precursors in GAC influent and can be used to track the breakthrough of oxidizable precursors into effluent. The degree to which oxidizable precursors (known and unknown) influence the sorption of PFOS and PFOA onto GAC is not yet understood yet could affect operational costs.

CONCLUSIONS

Nearly half of the observed PFAS in the GAC influent had shorter perfluoroalkyl chain lengths than PFOS and PFOA (Table 2) and were not as effectively retained by GAC compared to PFOS and PFOA. To reduce the frequency of GAC change-out, longer empty bed contact times are needed to effectively retain shorter-chain PFAS. Although short chain PFAS are known to break through before PFOS and PFOA, it is important to include PFAS such as short-chain PFCAs (e.g., PFBA, PFPeA) PFSAs (e.g., PFBS, PFPeS), FASAs (FHxSA), and FTSs (e.g., 4:2 FTS) into PFAS monitoring programs to account for the potential discharge of shorter-chain PFAS back into the environment. Analytical standards for these short-chain PFAS, including 6:2 FTS and FHxSA, are commercially available, and should be included in the groundwater monitoring programs because they are abundant in groundwater at AFFF-impacted sites. If not effectively retained by GAC, short-chain precursors such as FTSs and FHxSA upon effluent discharge to the environment may biotransform to persistent products including PFCAs and PFSAs, respectively.[63, 81, 82]

The use of branched to linear (Br:L) isomer ratios provided diagnostic evidence of precursor transformation to predominantly L-PFCAs. As expected,[76, 77] branched isomers broke through earlier than their respective L isomer, which indicates stronger interactions between the L isomer and GAC. More importantly, the presence of branched isomers (e.g. PFPeA, PFHpA, PFOA, PFHpS, FHxSA, FOSA, N-TAmP-FHxSA) indicate the need to accurately track and account for Br and L isomers of all ECF-based PFAS when reporting concentrations.

While LC-MS/MS can quantify some precursors and a larger number of suspect PFAS can be determined by targeted and untargeted LC-HRMS, LC-HRMS is expensive and not yet commercially available. Thus, the TOP assay adds value to the understanding of total PFAS loading to a GAC system by signaling the presence of precursors that may compete for adsorption sites on GAC. The presence of precursors, particularly short-chain, may result in a treatment system that is not designed for their effective removal. The TOP assay provides some information on the chain length of precursors and the breakthrough of precursors, which preceded that of PFOS and PFOA. Untreated precursors are likely to end up in treated GAC effluent if changeout is only triggered by PFOS and/or PFOA breakthrough reaching the HAL (70 ng/L).

The breakthrough of PFAS on the pilot-scale GAC system correlated with chromatographic retention time. Once the chromatographic retention time of a new PFAS is known, the breakthrough behavior of that PFAS can be predicted relative to the well-known and conventionally measured PFCAs and PFSAs. Thus, the potential breakthrough behavior of a broad array of PFAS can be predicted without having to measure the concentration of every PFAS in all effluent samples. This is particularly important since commercial analyses for precursors are not yet available, but are likely to become available with time.

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Table 1. Design parameters for GAC pilot-scale system.

Design Parameter	**Value**
GAC, type	DSR-A 8x40 Bed density (ρ_{bed}) = 0.54 g/cm^3 BET surface area: 750 m^2/g Micropore volume: 0.310 cm^3/g Macropore plus mesopore volume: 0.242 cm^3/g
Number of GAC vessels	2 in series
GAC quantity per vessel	91 kg
Volume per vessel	200 L
Hydraulic loading rate	1.87 m/h
Empty bed contact time	13 min (lead) 26 min (lead + lag)

Table 2. Average Br and L PFAS influent concentrations (ng/L) ± standard error, analytical retention time (min), PSDM modeling parameters Freundlich capacity parameter (K*), tortuosity (τ), and lag vessel breakthrough bed volume at $C/C_0 = 0.2$.

		Influent Concentration (ng/L)		Retention Time (min)		K* (L/g),[1] τ		Bed Volume at C/C_0=0.2
PFAS	# C_F	Branched	Linear	Branched	Linear	Branched	Linear	
PFBA	3	<LOD	100 ± 22	NA	6.8	NA	12, 1.0	3900
PFPeA	4	19 ± 2.5	350 ± 47	7.5	7.9	NA	16, 1.5	3500
PFHxA	5	<LOQ	740 ± 70	8.9	9.4	NA	17, 1.0	5500
PFHpA	6	15 ± 2.0	150 ± 20	10.8	11.3	NA	27, 2.5	4100
PFOA	7	81 ± 7.2	820 ± 73	12.8	13.3	18, 1.0*	40, 2.0	6,200/8,500
PFNA	8	<LOD	18 ± 5.7	14.8	15.6	NA	NA	ND
PFBS	4	<LOD	17 ± 3.0	7.6	8.0	NA	NA	ND
PFPeS	5	<LOD	30 ± 9.0	9.2	9.4	NA	35, 1.0	10,500
PFHxS	6	190 ± 29	1400 ± 210	10.8	11.2	30, 1.0	70, 3.5	9,000
PFHpS	7	29 ± 5.5	62 ± 11.9	12.7	13.3	NA	NA	ND
PFOS	8	1200 ± 110	1900 ± 170	14.8	15.5	55, 1.5	80, 1.5	12,900/14,900
4:2 FTS	4	NA	13 ± 3.0	NA	9.2	NA	NA	ND
6:2 FTS	6	NA	1000 ± 76	NA	13.3	NA	45, 1.3	10,800
8:2 FTS	8	NA	170 ± 35	NA	17.9	NA	NA	ND
FPeSA	5	<LOQ	125 ± 5.8	10.8	11.6	NA	NA	ND
FHxSA	6	700 ± 48	2100 ± 140	13.1	13.6	40, 1.0	60, 2.0	11,600/13,000

FOSA	8	100 ± 9.4	200 ± 19	17.7	18.6	NA	NA	ND
N-TAmP FHxSA	6	51 ± 21	97 ± 40	13.5	14.1	NA	NA	ND

<LOD = not detected; <LOQ = less than the limit of quantification, 10 ng/L for all analytes except FHxSA and FOSA which have an LOQ of 50 ng/L; NA = not applicable because Br-isomers are not detected because they are not present in fluorotelomer-based AFFF, ND = not determined due to insufficient breakthrough; *Surface-to-pore diffusion was needed for modeling, so SPDFR was 1 rather than the 10^{-30} value used for all other analytes. [1]K values for the lead and lag vessels were similar and are reported as a single value.

Table 3. Net production of PFCAs by TOP assay (nmol) ± propagated relative standard error and the total mass of unknown precursors in lead vessel effluent samples following treatment of five selected lead vessel bed volumes

		Bed volumes (nmol)[1]				
	Influent[2]	**3192**	**5759**	**9192**	**10992**	**16280**
PFBA	2.0 ± 0.34	<LOQ	0.27 ± 0.046	0.36 ± 0.060	0.55 ± 0.093	1.2 ± 0.21
PFPeA	2.2 ± 0.63	0.19 ±0.05	0.31 ± 0.0019	0.63 ± 0.18	0.0064 ± 0.0019	0.41 ± 0.12
PFHxA	15 ± 1.4	0.55 ± 0.052	2.3 ± 0.22	2.7 ± 0.26	2.6 ± 0.24	5.3 ± 0.50
PFHpA	0.22 ± 0.03	<LOQ	0.065 ± 0.012	0.086 ± 0.015	<LOQ	<LOQ
PFOA	0.7 ± 0.5	<LOQ	0.52 ± 0.048	0.58 ± 0.53	<LOQ	<LOQ
Total PFCAs	20.10 ± 5.3	0.74 ± 0.12	3.5 ± 1.0	4.3 ± 1.2	3.2 ± 0.84	6.9 ± 1.6
Unknown precursors	9.6 ± 2.1	0.41 ± 0.12	3.1 ± 1.0	3.4 ± 1.1	1.4 ± 0.52	2.2 ±1.1

[1] The propagated relative standard error from the influent was applied to the single samples at each of the five bed volumes

[2] Propagated relative standard error based on measurement of n=5 influent replicates

Figure 1. Br and L isomers for a) PFOS and b) PFOA in influent and c) PFOS and d) PFOA in lead vessel effluent at 11,000 bed volumes.

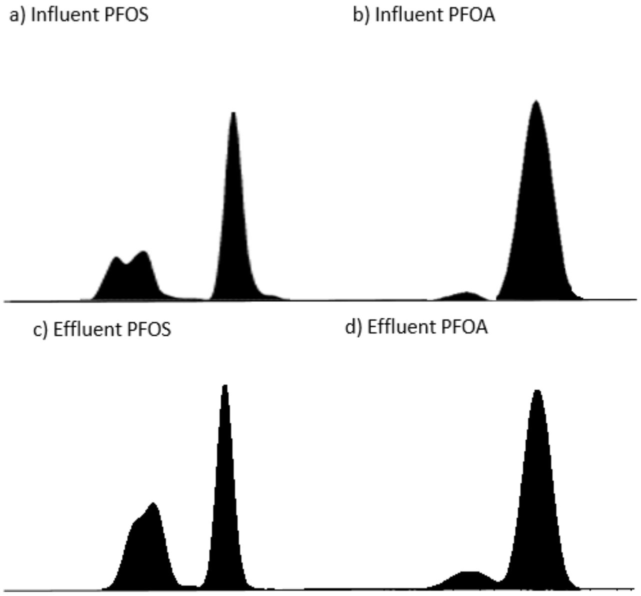
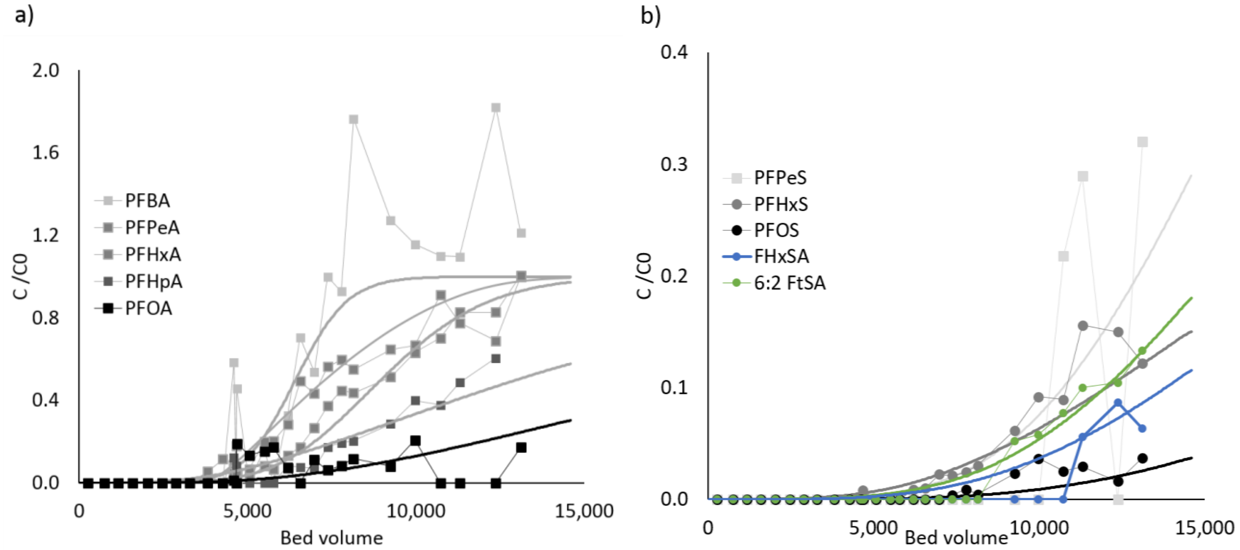
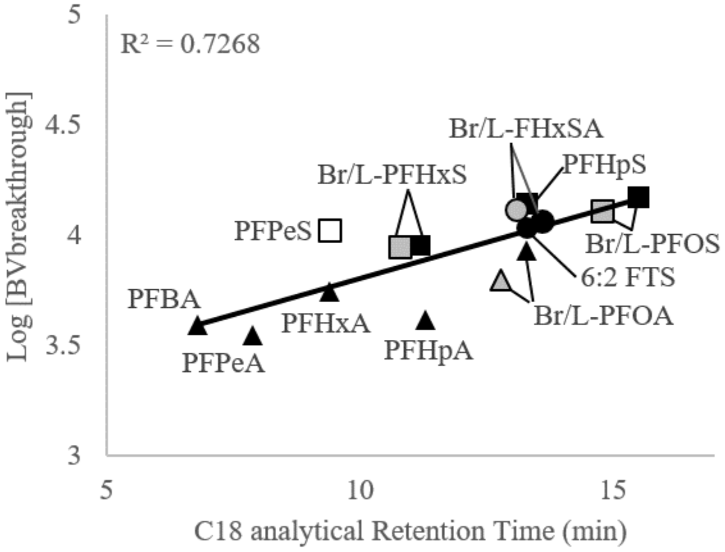


Figure 2. Breakthrough curves with model fits for a) PFCAs and b) PFSAs, FHxSA, and 6:2 FTS in lag vessel effluent.[a]



[a] Due to low concentrations, breakthrough curves for PFNA, PFBS, PFHpS, 4:2 FTSA, 8:2 FTSA, FPeSA, and FOSA are not plotted.

Figure 3. Correlation of log bed volume at 20% breakthrough (C/C_0=0.2) in lag vessel with chromatographic retention time using a C18 analytical column. Square symbols represent PFSAs, circle symbols represent polyfluoroalkyl substances FHxSA and 6:2 FTS, and triangle symbols represent PFCAs. Br PFAS are depicted by grey symbols whereas L PFAS are depicted by black symbols. PFPeS was an outlier and was excluded from the shown R^2 value. Only data for PFAS with concentrations greater than LOQ are plotted.



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