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Modeling PFAS Removal Using Granular Activated Carbon for Full-Scale System Design

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are increasingly of interest to drinking water utilities due to state regulations, the release of federal and state health advisories, and public concern. Pilot-scale data were fitted for 16 PFAS species and five commercial-activated carbons using an open-source pore and surface diffusion model that includes an automated parameter-fitting tool. The estimated model parameters are presented, and an uncertainty analysis was evaluated considering the expected temporal variability of influent concentrations. Expected treatment performance differed between two seasons in the pilot phase for the same carbon, which was not captured by modeled uncertainty. However, modeling results can support a utility's decision to choose activated carbon, and make design and operational decisions that can address changing water production rates and treatment goals. For the utility that undertook this pilot study and their desired treatment goals, granular activated carbon (GAC) was found to be an effective treatment technology for PFAS removal.

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Disclaimer

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Supplemental Materials

Tables S1–S5, Figs. S1–S7, and additional text are available online in the ASCE Library (www.ascelibrary.org).

Keywords

Per- and polyfluoroalkyl substances (PFAS); Granular activated carbon; Granular activated carbon (GAC); Treatment; Modeling; Carbon fouling

Introduction

The presence of per-and polyfluoroalkyl substances (PFAS) in source waters has become a concern for drinking water utilities and their communities. Waterbodies can be contaminated by PFAS from numerous sources (e.g., manufacturing, industrial users, land-fills, firefighting applications—specifically in airports or training facilities) potentially impacting both the quantity and speciation of PFAS in waterbodies used for drinking water. To date, several states have set health advisories or regulatory levels for various PFAS, where levels associated with perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are among the most common. Although there are no federal regulations for PFAS, the United States Environmental Protection Agency (USEPA) has released health advisories (USEPA 2016) and a proposed decision to regulate (USEPA 2020) PFOA and PFOS in drinking water. The USEPA also released draft toxicity assessments in 2018 for perfluorobutane sulfonate (PFBS) and hexafluoropropylene oxide, dimer acid (HFPO-DA, Gen-X) (USEPA 2018). Hopkins et al. (2018) reported concentrations of various PFAS in a water source used by utilities in North Carolina, which included the Cape Fear River that was the source of water for this study. Given this increased attention to PFAS in drinking water sources, utilities need information and tools to assess treatment options.

Several PFAS treatment studies have been published, primarily focusing on bench-scale research for PFOA and PFOS (USEPA 2016; Dickenson and Higgins 2016; Kucharzyk et al. 2017; Sun et al. 2016; Crone et al. 2019; USEPA 2019; Wang et al. 2016; Aly et al. 2018; Schaefer et al. 2019). A recent study on removal of PFAS using point-of-use/ point-of-entry devices that used rapid small-scale column tests (RSSCTs) was published to help home-owners understand the available options for treating contaminated well water (Patterson et al. 2019). Although generally lacking data on shorter-chain PFAS, these studies indicate granular activated carbon (GAC) may be an effective technology for PFAS removal for many water qualities and treatment goals.

To date, GAC treatment has been studied more often and under a wider range of test conditions than other PFAS removal technologies such as high-pressure membrane systems and anion exchange treatment (Crone et al. 2019). However, given this, there continues to be an information gap about how to best implement GAC nation-wide. Utilities would need to consider GAC effectiveness related to various mixtures of PFAS, wide differences in background water chemistry, other site-specific factors, and any applicable regulatory levels or treatment goals.

To help address some of these information gaps, modeling tools can be used to explore treatment effectiveness under a variety of conditions. Historically, multiple approaches have been used for GAC modeling (Sontheimer et al. 1988; Summers and Roberts 1988a, b; Knappe et al. 1999; Munz et al. 1990; Crittenden et al. 2012). Generally, simplified

approaches consider adsorption capacity while ignoring the effects of diffusion, such as simplified single-solute mass balances (Sontheimer et al. 1988). Modeling approaches can become more complicated by adding factors such as dispersion, external mass transfer, surface and pore internal diffusion, multicomponent adsorption, and preloading of background organics (Sontheimer et al. 1988; Summers and Roberts 1988a; Knappe et al. 1999; Munz et al. 1990; Carter et al. 1992; Jarvie et al. 2005; Summers et al. 1989). Adsorption capacity parameter values are required for modeling within all these approaches. Adsorption capacity for GAC is typically determined in single-solute isotherm studies and represented by the Freundlich adsorption equation (Sontheimer et al. 1988; Mittal et al. 2007). However, single-solute isotherms and their Freundlich values are not currently available for many PFAS and GACs (Crone et al. 2019; Wang et al. 2016). Recent efforts explore carbon and PFAS characteristics to help understand adsorption by GAC and its effectiveness (Kempisty 2014; Xiao et al. 2017; Park et al. 2020). These studies are likely beyond the scope of most water utilities due to prohibitive cost, limited personnel, and duration of the experiments. Additionally, if factors associated with natural organic matter (NOM) fouling are to be considered, then the number of experiments will also grow.

Knappe et al. (1999) investigated atrazine removal by GAC and highlighted the various uncertainties in model parameters and how they might be impacted by fouled GAC. The variability in both Freundlich isotherm K and $1/n$ [Eq. (1)] for atrazine were reported based on preloading (i.e., fouling) of the GAC. Further, Knappe et al. (1999) and Speth (1991) discuss the impact of different mass transfer coefficients related to fouling, noting that while having a smaller impact than K and $1/n$, both d_s (surface diffusion coefficient) and k_f (film transfer coefficient) were expected to decrease over time due to fouling. This was also seen to be a function of bed depth (Summers et al. 1989), although generally NOM tends to evenly foul throughout a column due to its slower adsorption kinetics (Zimmer et al. 1987) and was assumed to foul evenly in the model (Jarvie et al. 2005). Experiments designed to predict unfouled K and $1/n$ for PFASs are needed to reduce the uncertainty related to the impact of fouling or allow a more thorough investigation into those effects and are used as inputs to the modeling effort discussed herein. Although some values for K and $1/n$ are available (reviewed in Crone et al. 2019), there is significant variability, and it is difficult to draw conclusions on a true parameter set for each compound and GAC.

Although there are many obstacles to overcome, modeling tools can be used to analyze or predict treatment performance. In an ideal modeling situation, the relevant model inputs would be known for all compounds to be modeled. However, as previously stated, a great deal of work is required to generate these parameters, which include single-solute isotherms, external mass-transfer coefficients, internal diffusion coefficients (surface and pore diffusion), adsorption parameters for background organics as a whole, and fouling factors for both adsorption capacity and kinetics. The effort needed to generate this list of parameters is likely more onerous than simply operating a pilot column study. Also, further temporal changes in water quality, and other parameters such as temperature, can make it difficult for predicting long-term, full-scale GAC column operations via modeling. Although this suggests that advanced modeling is not worth the effort, pilot studies also suffer from some of the same uncertainties from temporal changes in water quality. A combination approach of both piloting and modeling may give more confidence to the pilot-scale results

when trying to predict treatment performance at conditions not tested at the pilot scale (other bed sizes and flow rates, potential changes in influent concentrations, and so forth). This approach would help with discerning optimal operations such as bed staggering and replacement frequency. Although all uncertainties cannot be eliminated, it would be helpful for a utility to have an idea of the magnitude of possible impacts.

Data for 16 different PFAS compounds were modeled from a two-phase pilot study conducted using Cape Fear River water with five different activated GACs (seven total columns). The specific objectives of this article are to (1) demonstrate an automated model fitting procedure for pilot data that can be used by any utility, (2) demonstrate the use of these estimated parameters to predict pilot column performance against a multi-PFAS treatment objective, and (3) evaluate uncertainties. Automation of data analysis and parameter prediction from site-specific pilot or RSSCT data can simplify model use and provide utilities valuable information for system design and operation. In addressing system design and operation, the treatment objective is critical, and the full-scale predictions generated herein were based on a system-specific design treatment objective as defined by the water utility. The general procedure, however, would be applicable to other systems or treatment objectives. To the authors' knowledge, this work is the first comprehensive pilot-to full-scale analysis related to PFAS compounds.

Methods

This article discusses the application of pore and surface diffusion model (PSDM) to predict pilot- and full-scale PFAS removal results. Specifics regarding the pilot phase of this study are presented in Supplemental Materials. In brief, a two-phase pilot study was conducted at a water utility, which analyzed for nine PFAS compounds in Phase I and 16 PFAS in Phase II (see Table 1) and included five different GACs (see header rows of Table 2). All pilot columns reported herein were operated at a 10-min empty bed contact time (EBCT). The parameters that were determined in the prediction phase of the modeling were then used to simulate full-scale performance under different scenarios such as different influent concentrations and flow rates. Because the intent of the project was to evaluate the chosen design parameters under potential future scenarios such as an increase of flow from 19 to 44 million gallons per day (MGD), the modeled EBCTs were adjusted accordingly to match the desired EBCT (20 min) at 44 MGD, as stipulated by the utility's design plans.

Table 1 shows the included PFAS, their acronyms, measured compounds, and summary concentrations in the influent to the pilot columns during the entire piloting period. Only compounds that occur in over half of the influent samples at concentrations above the minimum reporting limit were included in this study. Total organic carbon (TOC) concentration averages were 2.6 ± 0.3 mg L⁻¹ for "raw" water and 2.2 ± 0.3 mg L⁻¹ for postbiologically activated carbon (BAC) water during the study [$N = 9$ (Phase I) or 17 (Phase II)]; for this study the term raw water was used to indicate water that was supplied to BAC beds. Most PFAS compounds had mean concentrations of 3–100 ng L⁻¹, while perfluoro-2-methoxyacetic acid (PFMOAA) was estimated to have an average concentration exceeding 1 μ g L⁻¹. Compounds marked with "estimated" concentrations were reported as

such from the analytical labs providing the data due to the lack of standard methods for those compounds during the pilot period.

Adsorption Modeling

The PSDM tool within EPA's "Water Treatment Models" GitHub site (USEPA 2021) was used in this study. This tool uses the same PSDM with fouling model utilized in AdDesignS (Mertz et al. 1999; Jarvie et al. 2005) and was used to simulate PFAS adsorption, but it was developed in Python version 3.8.

Parameter Estimation

The general approach for parameter estimation used within the Python code was as follows. Each PFAS/GAC combination was fit individually. The first step within the parameter estimator is to calculate a "fouled capacity" [q ; see Eq. (1) and Table S1] by calculating the area between influent and effluent pilot data prior to complete breakthrough. Breakthrough was established as either where measured effluent intersected influent data or where the intersection would occur (extrapolated) for the average influent concentration, based on a linear estimate for any partial breakthrough data. Breakthrough was also manually established for some compounds where influent and effluent concentrations shared the same trends and differed by less than 20%, which was treated as an implied breakthrough. This was considered the fouled capacity because it was calculated based on the actual water not an organic-free test water. From this fouled capacity, an estimate for the Freundlich constant was calculated from the Freundlich adsorption isotherm as

$$q = \frac{x}{m} = Kc^{1/n} \quad (1)$$

where, q ($\mu\text{g g}^{-1}$) and x = adsorbed mass of chemical (μg); m = mass of the adsorbate (g); c = average concentration of the adsorbing compound in liquid ($\mu\text{g L}^{-1}$); and $1/n$ (unitless) and $K [(\mu\text{g g}^{-1})(\text{L } \mu\text{g}^{-1})(1/n)^{-1}]$ = compound-specific Freundlich constants. For the initial estimate, a $1/n$ value of 0.45 was used based on previous experience and the assumption that PFAS would have some affinity for GAC, and the average prebreakthrough influent concentration was used for c .

Mass-transfer parameters used by PSDM were correlated based on previously reported studies and incorporated into the current available code. The pore diffusion coefficient (d_p) was calculated based on the correlation for fluid diffusion coefficient (Hayduk and Laudie 1974) and the film transfer coefficient (k_f) was calculated using the simplified Gnielinski's correlation (Roberts et al. 1985). The surface diffusion coefficient (d_s) was calculated using the correlation described in Mertz et al. (1999) and Sontheimer et al. (1988).

Optimization Approach

A brute-force optimization approach was used to find the set of parameters that minimized sum-of-squared error (SSQ) between the effluent and modeled data [using PSDM function *analyze_all()*] to determine the unfouled Freundlich K and $1/n$. The brute-force search space was 1–3.5 times (K_{mult} ; or K -multiplier, increment 0.1) the unfouled K and 0.3–1.0 for $1/n$ (increment 0.01). This provides optimization for two parameters: Freundlich constant

(K) and adsorption isotherm exponent ($1/n$). The optimal K_{mult} multiplied by unfouled K established the unfouled or organic-free value of K . This range of $1/n$'s was selected based on values presented in Wang et al. (2016) and previous PSDM experience. The range of K_{mult} 's was selected based on expected impact of fouling. The Rhine River was selected as the fouling water type (Jarvie et al. 2005) because the source of this pilot was an industrialized river with similar TOC levels. It is recognized that this is a source of potential error; however, to address this water specifically would require a significant experimental effort. Since a contaminant-specific category for PFAS was not available in the AdDesignS software, each PFAS was modeled individually with the PFAS-specific fouling factors listed in Table 1 [derived using the method outlined in Magnuson and Speth (2005); quantitative structure-property relationships (QSPR); a and b are parameter identifiers]. The input values to derive the QSPR values are presented in the Supplemental Materials (Table S4; section "Estimation of QSPR Correlation Factors for Capacity Reduction Equation"). For fouled cases, the value of d_s reduced the correlated value by a factor of 10^{10} rather than set to 10^{-30} (original PSDM behavior) due to numerical convergence issues in the solver. To better capture the breakthrough trend, especially for compounds with only a few prebreakthrough effluent points, the SSQ was calculated for every day within the pilot—where daily values were linearly interpolated for sampled effluent data.

The tool uses orthogonal collocation to solve partial differential equations in PSDM (for a full description, see Crittenden et al. 1986). For this work, eight (8) radial and eleven (11) axial collocation points were used. The SciPy function *integrate.solve_ivp* was used to solve the differential equations related to column adsorption (Jones et al. 2001).

Full-Scale Modeling

The best-fit parameters for the six compounds (PFHpA, PFOA, PFNA, PFHxS, PFOS, and GenX) were then used to model full-scale GAC beds based on the utility's preferred bed design and a treatment objective that was being used by the utility for GAC assessment. The simulated full-scale system was supplied with water having the average concentrations, or multiples of average, for each compound. The hypothetical system considered by the utility contained eight beds that each had surface areas of 76 m^2 (820 ft^2) and a media depth of 3.8 m (12.5 ft), which are operated in parallel (to simulate a proposed system design, staged-parallel operations discussed in Denning and Dvorak 2008; Corwin and Summers 2012). No other configurations, such as series or lead/lag operation, were considered. The reported apparent densities were used to estimate GAC mass for each bed, which ranged from approximately 113,398 kg (250,000 lbs) (Hydrodarco 4000) to 167,829 kg (370,000 lbs) (Calgon F300). The system was modeled at the current system max-day demand, $0.83 \text{ m}^3/\text{s}$ ($0.10 \text{ m}^3/\text{s}$ per bed) [19 MGD (2.375 MGD per bed)], and a future expected max-day demand of $1.9 \text{ m}^3/\text{s}$ ($0.24 \text{ m}^3/\text{s}$ per bed) [44 MGD (5.5 MGD per bed)]. Both flow rates were tested with water having influent concentrations of pilot period average, twice average, and 75% of the average for each compound. GACs were assessed by comparing the calculated bed replacement interval—expected two beds per cycle replacement—with a treatment goal of 70 ng L^{-1} total of the six PFAS chemicals. This treatment goal was not a regulatory value but merely a standard target, defined by the water utility, against which to assess configurations. The system was designed to yield a 20-min EBCT for the max-day

production of 44 MGD. Fouling parameters for Rhine River water were used due to its analogous industrially impacted water quality. Total PFAS results were modeled using sums of the individual PFAS model runs. For more information about the scale-up of pilot data to large-scale models, see Crittenden et al. (2012) and Sontheimer et al. (1988).

Results and Discussion

Fitting of Parameters

In this work, Freundlich isotherm parameters for unfouled or organic-free water were estimated from pilot data collected from columns, each loaded with fresh GAC that became fouled and experienced competitive adsorption throughout the study (see Table 2). Fig. 1 contains an example of a model fit Fig. 1(a), the associated SSQ maps Fig. 1(b), and an example of a parameter uncertainty analysis Fig. 1(c). The “x” in Fig. 1(b) indicates the selected minimum, which was selected to correspond to the minimum that fell within a general area of decreasing SSQ, where a minimum that was not surrounded by other similar (within 15%) SSQ values was rejected as an outlier. Most of the SSQ maps looked like 1b, where a clear minimum was evident and subsequently selected. Values that correspond to either extreme of the search range (0.3 or 1.0) may have experienced further improvement in fit but were not considered—discussed subsequently. For Fig. 1(c), uncertainties of $\pm 10\%$ error in K and $\pm 10\%$ error in $1/n$ were selected to provide a general indication of how these values impact modeled predictions for the signal PFAS and carbon.

The selection of an optimal GAC is a function of a utility’s influent water quality, specific conditions, intended application, and design objectives. While some GACs performed less well than others (as observed in Table 2), that does not necessarily mean that they would perform similarly in all cases. Some GACs may perform better against certain PFAS compounds, so the unique PFAS mixture, treatment objective, and other system-specific considerations may change the relative performance of GACs compared to this study. Additionally, previous studies have highlighted that the impact of NOM varies depending on the type of GAC (Knappe et al. 1999; Zimmer et al. 1987; Summers et al. 1989), which was not directly investigated here. The modeling approach and data-fitting functionality used in this study would be of value for utilities with site-specific data or those conducting pilot/RSSCT studies. The values presented in Table 2 could provide estimates for other industrialized river sources, but care should be used when extrapolating it to other systems, because the parameters are implicitly related to the source water concentrations of all PFAS and non-PFAS compounds that were present during the pilot periods.

We found that the automated fitting of effluent data provided a more rigorous, consistent, and faster approach compared to manual fitting of the breakthrough profiles. The addition of a goodness-of-fit metric, SSQ, also provided a measure of how sensitive the model was to different parameters. This study limited the search space for values of $1/n$ to between 0.3 and 1.0. Minima for some PFAS-GAC combinations were found at either extreme, suggesting that further improvement could be achieved. Many of the PFAS-GAC combinations were found to have $1/n$ values within the tested range, and the calculated unfouled K values were likely close to the best value even if the true $1/n$ value is slightly outside the tested range. The method allows for any range of $1/n$ to be supplied, so a user could expand the search

space if desired. Previous studies (reviewed in Crone et al. 2019) have reported $1/n$ values outside 0.3–1.0 and future dedicated PFAS-GAC isotherm research may shed more light into more appropriate ranges for values of $1/n$ for different PFAS. Corwin and Summers (2011) proposed a simplified Freundlich K (as K^*) by using a linearized isotherm ($1/n = 1$) based on 50% breakthrough. This is similar to the integration method used herein to establish the initial fouled- K , but further refinement of K and $1/n$ would be needed to explore other $1/n$ values. This approach explores a range of both K and $1/n$ to determine best fit.

Overall, comparing parameter values presented in Table 2 with previously reported Freundlich isotherm parameters is challenging. Most previous studies have been conducted in concentration ranges far exceeding those experienced during the pilot phase—(mg or μg) L^{-1} in those experiments versus ng L^{-1} here. Experimentally determined parameters suggest considerably higher expected capacities. This is not surprising because (1) the values calculated here include all competitive behaviors with other constituents, which would be expected to lower capacities; and (2) the PFAS concentrations were much lower, and low concentration isotherm behavior for these compounds may be different from those experimentally tested. The fact that these parameters do inherently include the impact of the other chemicals in the source water does limit their applicability to other systems but highlights the potential for the approach. The alternative to using implicitly impacted Freundlich parameters—presented herein—is to explicitly model all chemical species competitively, which can quickly become a significant challenge as even just considering all PFAS studied here would require sixteen PFAS species to be modeled and still omit any other adsorbable species that were present in the source water that were not considered here. This would also require sampling data for any other adsorbable species in the source and associated isotherm parameters.

The aforementioned approach also assumed that the loss of capacity associated with NOM fouling was related to a reduction in Freundlich K over time (Jarvie et al. 2005; Crittenden et al. 2012). Freundlich K 's are determined by single-solute batch equilibrium (or as close to it as possible) studies. This approach, however, perhaps counter intuitively accounts for a time variable capacity via adjustments to the K parameter. An alternative approach was discussed in the Supplemental Materials, where K was determined from pilot data with an assumed $1/n$, and d_s was adjusted to account for NOM fouling. In actuality, multiple parameters may all be impacted by fouling, including $1/n$ (Knappe et al. 1999) that was not considered here. The capability to perform the analyses presented here is already available in the “Water Treatment Models” repository, but additional, more complex approaches could be developed. This work was intended to highlight a general approach to estimate reasonable parameter values to extrapolate to a full-scale analysis. Additional parameters could have been added to the search space, at the expense of extending the solution times. However, determining the best solution will become very complex if multiple parameter sets yielded similar results. Future work can reassess the results presented here against these more rigorous isotherm derived parameter values and help shed light into (1) how multicomponent competitive behavior impacts modeled results, (2) how accurately was fouling considered here and what can be improved, and (3) uncertainty associated with mass-transfer coefficient parameters and if improvements related to PFAS-specific parameters are needed. The implementation of ideal adsorbed solution theory (IAST) in AdDesignS (upon which this

work is based) can model competitive behavior between species (previously limited to fewer than six compounds) or include a fouling mechanism but not both. The Python version used here can include both, however, limited validation data is available, and this capability was therefore not used.

Interpreting Pilot-Scale Modeling

Because PFAS-specific capacity and kinetic model parameters have not yet been fully developed for PFAS compounds from bench-scale experimental studies, the aforementioned pilot-scale approach can provide a valuable estimate. Pilot data captures site-specific behavior, which then can be used to explore a broader range of potential scenarios during system design or retrofitting exercises. Extending modeling to a staged-parallel contactor operation provides even more information by providing more applicable operational estimates for GAC replacement intervals than by just relying on single-bed models. Models can be applied in a variety of ways to help water utilities to understand the expected performance of GAC for PFAS removal for their system while considering applicable treatment objectives or regulations. Modeled results can help predict bed replacement intervals, which can help establish whether GAC will be a viable technology for PFAS removal for that system under current or future conditions.

Pilot studies are valuable because they typically use real system water, full-size media (i.e., unground, unmodified), and column depth and loading rate that result in test durations more comparable to full-scale systems compared to RSSCTs. These advantages are not without some challenges. An ideal data set for the aforementioned modeling approach would capture a complete breakthrough profile with enough data points to clearly highlight the effluent concentrations from initial to complete breakthrough. For some PFAS-GAC combinations, the Phase I and Phase II profiles were good [example, Fig. 1(a)] such that more time resolution (i.e., more samples) would likely only increase the certainty in the resulting fit.

Visual inspections of the resulting model fits demonstrated that best-fit parameters led to modeled effluent breakthroughs that fell within the sampled effluent data [Figs. S1(a–g)]. Compounds with six to eight carbons tended to agree well with breakthrough curves, where the overall breakthrough was long enough to result in more than four nonzero effluent samples prior to complete breakthrough. Compounds with fewer than six carbons tended to breakthrough quickly, resulting in only one or two nonzero samples before breakthrough, while those with more than eight may have only had one or two nonzero samples near the end and had not resulted in complete breakthrough. More frequent sampling and a longer pilot period could help address the challenges mentioned here.

The influent concentrations for the majority of PFAS compounds decreased from Phase I to Phase II. Both pilots seem to reach a cumulative breakthrough at about the same time, but individual compounds tended to break through more slowly (flatter slope) suggesting a less favorable adsorption during Phase II (Fig. 2). Although the calculated capacities did not change significantly, the loading rate—mass per time—dropped resulting in delayed initial breakthrough. This can impact overall model fit because it changed which portions of the fouling algorithm could impact overall breakthrough. For the Rhine River water fouling parameters, the loss of effective capacity—reduction in K over time—occurs rapidly (first

5 weeks), but then remains essentially flat for any subsequent time, whereas the increase in tortuosity occurs only after 70 days (10 weeks). If the lower mass loading rate due to decreased influent concentrations results in a broader breakthrough profile, the modeled effluent profile associated with later time points will be more influenced by one or both fouling components because they are directly related to time and not mass loading rate. This also assumes that the general capacity reduction of GAC is only related to time, and not throughput. Considering PFHpA, for column C3 (Phase I) the complete breakthrough occurs at day 96, while for column C5 (Phase II) breakthrough occurs on day 154. The calculated capacity, q , based on column C5 was higher for PFHpA than that of column C3, but the additional 60 days of breakthrough for column C5 was likely more influenced by these time-based fouling characteristics than for column C3. Complete breakthrough occurred approximately 40 days later for column C5 relative to column C3 for compounds that were reported in both phases. This generally resulted in an increase in $1/n$ values to 1.0 for many compounds with later breakthrough times, indicating a generally less favorable predicted adsorption and the linearization effect of NOM observed by others (Corwin and Summers 2011; Knappe et al. 1998, 1999). A further examination of how fouling is treated in the PSDM algorithm may be necessary to determine its impact on how capacity reduction is treated in the model. More data on adsorption of PFAS associated with unfouled or organic-free water would assist in establishing the impact of how fouling is modeled. The presented approach has focused on an aggregated behavior, specifically with “effective” adsorption capacities for each carbon. These effective capacities reflect the ability of that carbon to adsorb individual PFAS under the influent concentration conditions at the time of the study. An exhaustive exploration of the differences in these effective capacities (K and $1/n$ combinations) was beyond the scope of this work, but these differences do highlight the complexity related to interpreting and using natural water in pilot studies.

Results from an alternative modeling approach are presented in the Supplemental Materials, in which only the surface diffusion value (d_s) was varied to account for fouling and all other parameters are assumed or derived directly from the pilot data. Although the approach to fit d_s yielded similar results for expected replacement intervals, it was felt to limit the ability to extrapolate results onto other scenarios. Since the values for K were inherently fouled, they were more directly linked to the initial influent composition of the water and may limit the ability to test drastically different influent conditions. However, this approach is faster to manually conduct since it only requires fitting d_s value after precalculating a value for K from pilot results (as discussed in “Methods”).

Fig. 2 highlights the potential of the approach for evaluating a treatment goal since it depicts the sum of six individual PFAS. The modeled effluent lines are the summation of six individual model runs and the cumulative breakthrough profile generally agreed with the cumulative sampled effluent concentrations. This suggests that the approach applied to assessing full-scale behavior against a treatment objective can yield acceptable results for these performance models.

General Errors and Uncertainties

Extrapolation from a single model to the large-scale system compounds uncertainty in two ways: the totalized PFAS value carries the uncertainty of each singular model; and the blended staged-parallel effluent value used to establish replacement intervals for a treatment objective further amplifies this uncertainty based on how many beds are considered. In the hypothetical system arrangement discussed herein, the oldest four beds (half the system) will likely have exhausted much or all their removal capacity with respect to many PFAS, with two beds (quarter of the system) offering partial removal, and the two freshest beds offering most of the system's PFAS removal. However, the uncertainty in bed replacement interval will be dominated by this initial breakthrough for the compounds in a treatment objective that breakthrough earliest—in this system PFHpA, PFOA, and GenX.

The value of model results is related to sources of error or uncertainty in input data and associated model parameters. For this work, three types of uncertainty could have impacted results: (1) uncertainty in model parameters, (2) uncertainties with experimental results, and (3) unsampled periods impact on ability to model or fit results. For this work, all these sources of uncertainty or error were treated as nonexistent for calculating parameters from pilot data and extrapolating to full-scale systems.

To reduce the complexity of model fitting, it was assumed that the correlation values for mass-transfer coefficients had no uncertainty (i.e., produced correct values). Fig. 1(c) depicts the impact of uncertainty in the two model parameters used to adjust goodness-of-fit in this effort. Future work could include automated searches into other model parameters or carry uncertainty through to full-scale analysis. It is also important to restate that any error is compounded when calculating full-scale results based on modeled results, where error in individual effluent profiles may be additive when considering multiple compounds, and those errors are compounded when considering staged-parallel contactor design to determine bed replacement intervals.

Uncertainty in unsampled periods is a challenge for any data-driven approach. This work assumed a linear relationship between concentrations of two sampled points and was modeled as such. This can impact both influent and effluent concentrations; however, changes in influent concentrations that were not accurately captured would be expected to propagate an incorrect concentration profile through a column and relates to predicted adsorptive capacity. If enough data exist to provide a good estimate of influent average concentrations, these could be used to provide a secondary set of parameters to consider (not done here). Missing points in effluent data may have less of an impact because the fitting routine will compare all points to the generally smooth modeled profile.

Uncertainty in laboratory results was not directly assessed but could relate to model uncertainty in two ways. Values reported as nondetect or below the limit of quantification (LOQ) were set to zero for the analysis. If this was associated with the influent, then the calculated capacity would be lower than reality. For this study, PFDA, PFNA, and PFBS all had influent concentrations that had some nondetects reported and other samples near the LOQ. When this is associated with the effluent, the capacity could be lower, or the shape of the breakthrough curve could be different. Given that most of the modeled results were

able to match the measured curves, it was assumed that the use of zero for nondetects was acceptable in this case. Users could supply input data that treated non-detects differently (e.g., 50% LOQ) to assess the effect of this uncertainty, but this was outside the scope of the current effort. The acceptable error in analytical calibration impacts laboratory uncertainty, which could translate to a potential shift in input concentration values. For this reason, it was assumed that effluent concentrations, which were within 20% of influent concentration and showed similar trends near the end of the pilots, were an implied breakthrough. These errors impact the predicted mass loading and can result in errors in the modeled parameters; however, these errors may cancel each other since each set of samples may experience different calibration tolerances if they are not analyzed within the same batch.

Temporal Factors that Cannot Be Modeled

Utilities treating surface water, especially an industrially impacted river water as was the case here, may experience treatment performance changes with time due to changes in water quality. This could be a seasonal issue with changing temperatures or background water quality, or it can be a change in the influent concentrations of the contaminants of concern itself. This was observed in this study, as mentioned previously. The difference between the time to reach the treatment goal for a single bed observed in Fig. 2 suggests that a change in background water chemistry or temperature can have an impact. Fig. 3 shows the effect of using the same parameter set on different influent conditions. Fig. S3 shows the effect of using different parameter sets for the same influent compared to pilot results and applies uncertainty.

Because the time to replacement is an additive type of analysis, a minor change in fitted K and $1/n$ could have an impact. For parameters derived for F400 in columns C3 and C5, for the sum of the six PFAS when an uncertainty of $\pm 10\%$ in K and $1/n$ (see Table S3; Fig. S3) were applied, the range of predicted bed replacement intervals begin to overlap and were 172–327 days for column C3 and 267–524 days for column C5 at current capacity and concentrations. Fig. S3 shows that there is some overlap when both K and $1/n$ had 10% uncertainty (lighter shaded regions), but minimal overlap when only uncertainty of 10% in K (darker regions) is considered. Although the error evaluation starts to overlap the alternate breakthrough profile in some cases, suggesting that the results may not be as far apart as initially perceived, the change in K and $1/n$ for this overlapping prediction results in a poor fit in Fig. 1(c) for the original parameter estimation for a single PFAS and carbon. This suggests that seasonal or long-term changes in background water quality impacted the effective K and $1/n$ for PFAS related to a given carbon.

Modeling Scenarios Important to Design and Operation

The calculated values of K and $1/n$ in Table 2 were used to model a full-scale system containing each GAC. The projected single-bed breakthrough profiles for the six PFAS compounds were modeled (example Fig. 4), which were then used to calculate a blended effluent concentration. Fig. S4 shows the simulated staged-parallel effluent based on Calgon F400 (parameters from column C1) at two total system flows and at three different influent concentrations. The concentrations for each bed were determined by shifting the time of each bed by effective start dates [i.e., 0 days, $1 \times$ replacement interval (RI), $2 \times$ RI, $3 \times$

RI] and averaging concentrations. Intervals between bed replacements are longer for the 19-MGD system throughput and when influent concentrations were lower. Table 3 contains the projected replacement intervals, in days, for the different GACs and modeled influent concentrations. A replacement interval discussed herein corresponds to the time between replacing two beds, not the cumulative time for all beds, where an individual bed will be replaced every fourth cycle. For the 19-MGD treatment capacity, many of the GACs were predicted to require bed replacements every 180–400 days when treating water with the average PFAS concentrations of the pilots. When considering the 44-MGD treatment capacity, this was reduced to 80–180 days at the average concentrations. Reducing the influent concentrations by 25% increased the predicted times between bed replacements to over two years for 19 MGD but was closer to one year for many GACs when the flowrate was 44 MGD. This is in part because a 25% reduction in average influent concentrations only slightly exceeds the 70 ng L⁻¹ threshold. If the influent concentration doubles, the expected bed replacement interval was only approximately one month for 44 MGD for most GACs, and approximately three months for many of the GACs at current production.

The values in Table 3 are meant to capture general trends in likely bed replacement intervals for a given system design and would not eliminate the need for effluent sampling. Actual systems would be expected to experience variable water qualities that were not considered during this step of the effort, which would change how breakthrough occurs. The values in Table 3 should also not be extended to other systems. They resulted from the interrelationship between the GAC, influent PFAS concentrations, source water type, and system design—GAC contactor size and number of contactors—system flowrate and the potential treatment objective. Changing any one of these characteristics will result in different predicted bed replacement cycles.

The approach discussed here provided estimates for model parameters based on pilot results, not bench studies. This approach could provide utilities that plan to conduct pilot studies with valuable tools to extrapolate those results to explore different scenarios of concern for full-scale design without the need for exhaustive pilot studies. A more rigorous approach to parameter determination to be used in competitive adsorption models would be to use isotherms developed from bottle tests. Although important to determine for future advancements of GAC modeling, an isotherm approach is more complicated, which also increases the required time, resources, and analyses. For example, to generate Table 2 with an isotherm approach would have required 400 bottle tests for a single set of single-solute tests (5 GACs, 16 compounds, and 5 concentrations, possibly more, to generate an isotherm curve), and for each duplication experiment (not including required controls) with an equal number of analytical tests. Additional studies could also be conducted with natural water, mixtures, or other mixtures of interest; however, modeling would still be needed to extract the single-solute parameters. Also, isotherm studies can provide a high level of certainty in the isotherm parameters, but more investigations may still be required to determine how that media may perform at full scale. The use of pilot (or RSSCT, or full scale) data as a basis for modeling provides less certainty about the true isotherm parameters but does capture all the other factors that impact the breakthrough for that system. Although having pure isotherms for PFAS on GAC will be valuable, the other adsorbable compounds, not discussed herein, are impacting the effective capacity of the GAC. These other chemicals

found in many industrialized rivers occur at much higher concentrations than PFAS and would need to be modeled concurrently with PFAS to get a true estimate of PFAS removal and may help explain why many laboratory-based capacities are higher than those reported here. The implicitly captured background effects related to estimating parameters from pilot data make transferring those parameters to other sites harder, but having to explicitly model all background constituents may also become intractable. Future work could include the development of parameters from isotherm studies and comparison with the approach discussed here. This could lead to improvements in the treatment of fouling in PSDM modeling and more certainty in the application of these models for more sites. Such an effort could help a utility in their evaluation of possible source mitigation efforts or the selection of an alternate source of their drinking water if that is possible.

Fig. S2 compares the predicted replacement intervals for columns C3 and C5 over a range of flowrates and influent concentrations. Based on the results in Table 3 and Fig. S2, GAC adsorption was deemed to be a satisfactory treatment technology. The utility's desired minimum bed replacement interval was 90 days, which would be achievable for all scenarios except for the higher throughput (44 MGD) and the higher influent concentrations (200% of the average).

Another key parameter is the treatment goal. The treatment goal of 70 ng L^{-1} for these six PFAS compounds was not intended to reflect a regulatory limit, but rather a standardized metric for assessing designs and to demonstrate the approach of extrapolating pilot data to a full-scale system. This approach could be applied to other treatment goals based on different PFAS compounds and concentrations. This work did not consider treatment goals based on individual PFAS removal efficiencies; however, the general approach could be extended to include both individual and cumulative PFAS concentrations to assess potential designs. Utilities interested in treating to zero effluent PFAS could use this approach to model their system, but no such effort was undertaken for this work. Finally, by replacing the GAC on a more frequent basis than that listed in Table 3, as expected, the utility will achieve greater removal efficiencies both for individual and group PFAS. Based on this evaluation, the utility is anticipating a replacement interval of approximately one year at current production levels and average concentrations.

An alternative visualization (Fig. S5) was created to compare each GAC at the 19-MGD flow rate with pilot-average influent concentrations. Differences in predicted bed replacement intervals among GACs for this water can be observed. Undulations in the lines correspond to individual PFAS breaking through. For the system design considered herein, PFHpA, GenX, and PFOA were the major contributors to predicted bed replacement intervals, with their combined concentration equal to 66.6 ng L^{-1} in the example (71% of the total influent PFAS considered for the treatment goal). In a blended effluent, as the freshest beds begin to break through for these compounds, the system will need to replace the oldest beds. Although PFOS had an average concentration of 16 ng L^{-1} , its initial breakthrough from all GACs did not occur until later in simulated beds, which reduced its impact on the overall treatment objective. If the utility was considering a lead-lag bed operation, ultimately PFOS may have a greater role; however, because this utility plans on utilizing a staged-parallel blended system, this was not a concern. This type of analysis can help

utilities to understand driving forces behind bed replacement given their design objective and influent mixture. Compounds that occur in higher relative concentrations and have lower GAC capacities drive bed replacement, but overall treatment objectives, or goals, may shift the importance of these if some compounds have different desired effluent concentrations.

Summary and Conclusions

This work fit PFAS adsorption profiles from two separate pilot studies over two seasons at a water utility using a PSDM model that considered fouling due to NOM. Up to sixteen PFAS compounds were fit for multiple different GACs. The automated parameter-fitting protocol, unique to this study, provided a mathematically based repeatable analysis for all GACs, eliminating the potential inconsistent results associated with “eyeball” fits. The fitted parameters were then used to predict full-scale performance for numerous other conditions such as variable influent concentrations, flow rates, and treatment objectives.

All the PFAS in this study were found to have some removal capacity with GAC treatment. However, the individual PFAS had widely ranging adsorption characteristics that also varied temporally as demonstrated by the difference in treatment performance between the two pilot phases conducted at different times of the year. This caused concern about how the full-scale systems should be designed and operated, and even whether GAC should be considered an applicable treatment. Therefore, it was critical to extrapolate the pilot results into untested scenarios for a wide range of conditions. This effort highlighted the potential for GAC models to predict treatment based on complex treatment objectives, such as the six PFAS combined effluent concentration goal provided by the drinking water utility. As expected, the modeling effort was not able to fully describe why there were seasonal differences in treatment, other than to attribute it to changes in background constituents that could never be discerned due to lack of knowledge of cocontaminants at levels that would impact the breakthrough of PFAS at these low concentrations. However, the approach was still shown to be helpful in predicting system performance for any combination of treatment designs or objectives. Regarding the needs of this water utility, the results of the analysis reported herein showed that GAC was an effective option for treatment at this location based on the influent concentration and general water quality, operating requirements, and chosen treatment goals. Other conditions, especially those for lower treatment goals for weaker adsorbing PFAS, may result in different conclusions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Data Availability Statement

Data reported in this work can be found at <https://catalog.data.gov/dataset/epa-sciencehub>. Modeling tools used in this work are available at https://github.com/USEPA/Water_Treatment_Models.

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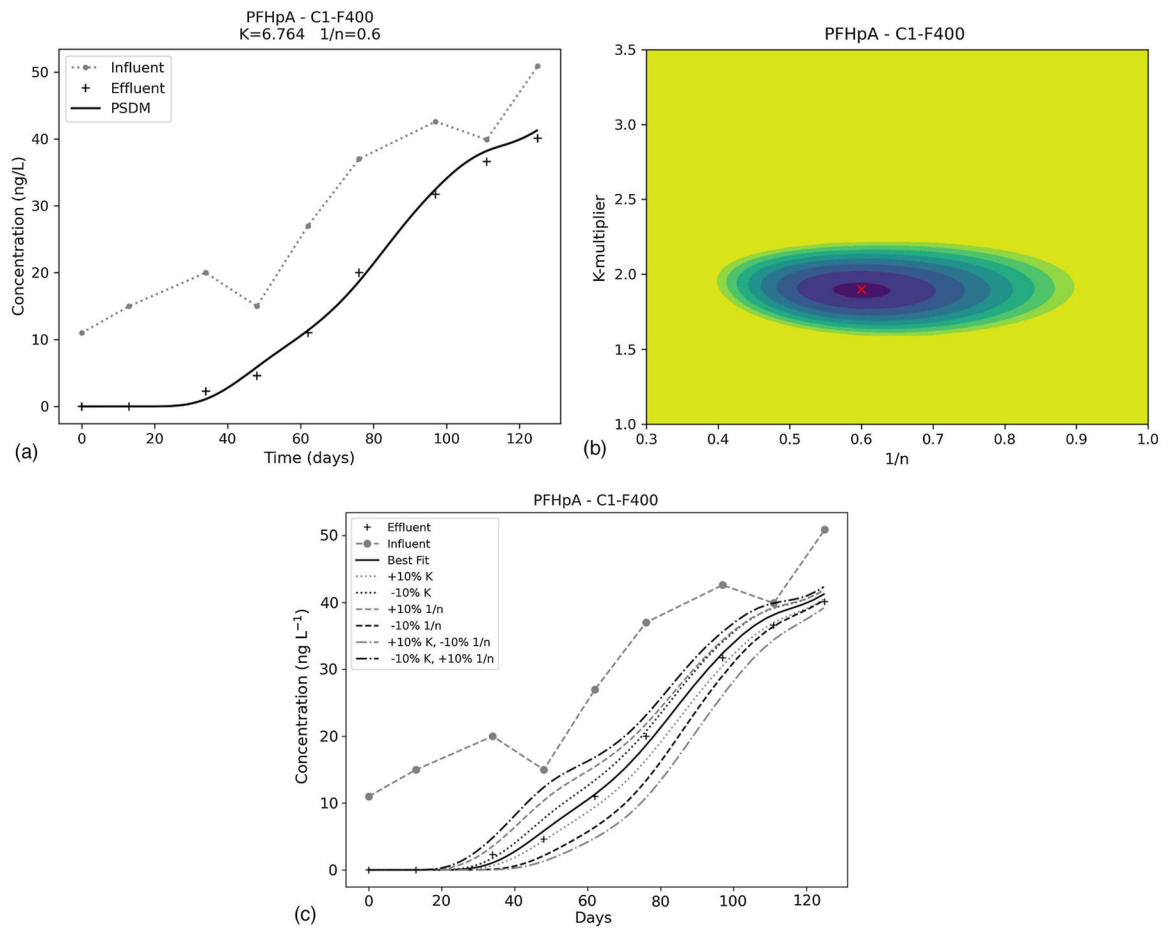


Fig. 1. Example fit for best-fit parameters: (a) model fit with influent and effluent data; (b) SSQ plotted for $1/n$ versus K -multiplier (x indicates minimum); and (c) plot of parameter uncertainty plotted of best-fit model parameter set.

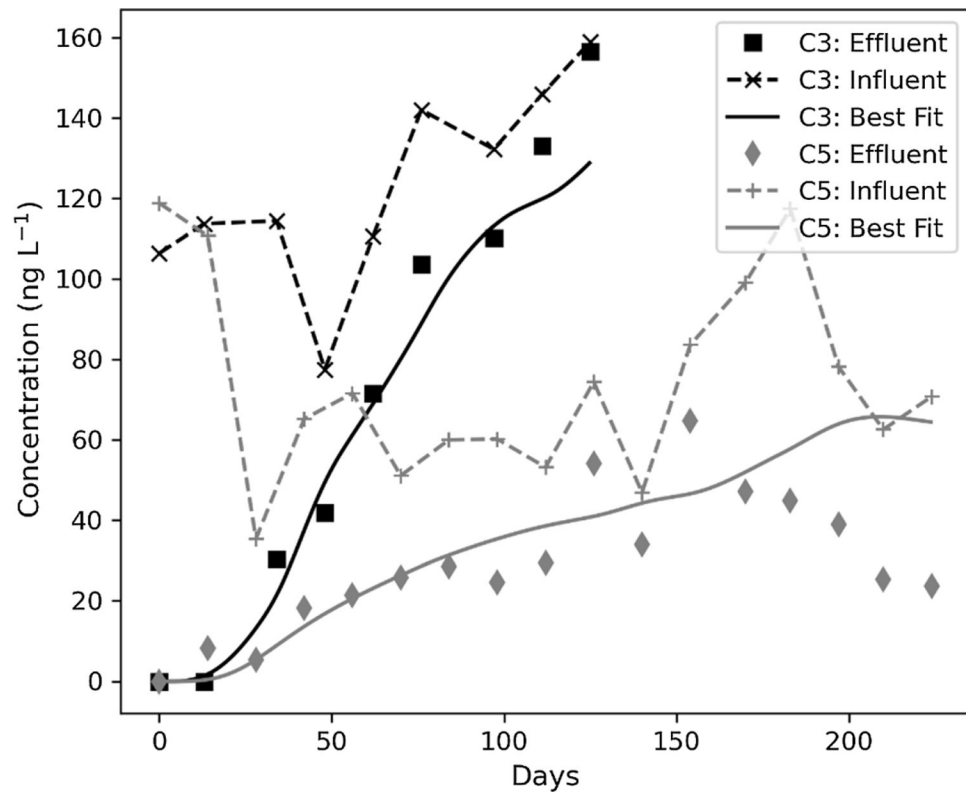


Fig. 2. Total of summed-six-PFAS concentration comparison for F400 between Phase I and II.

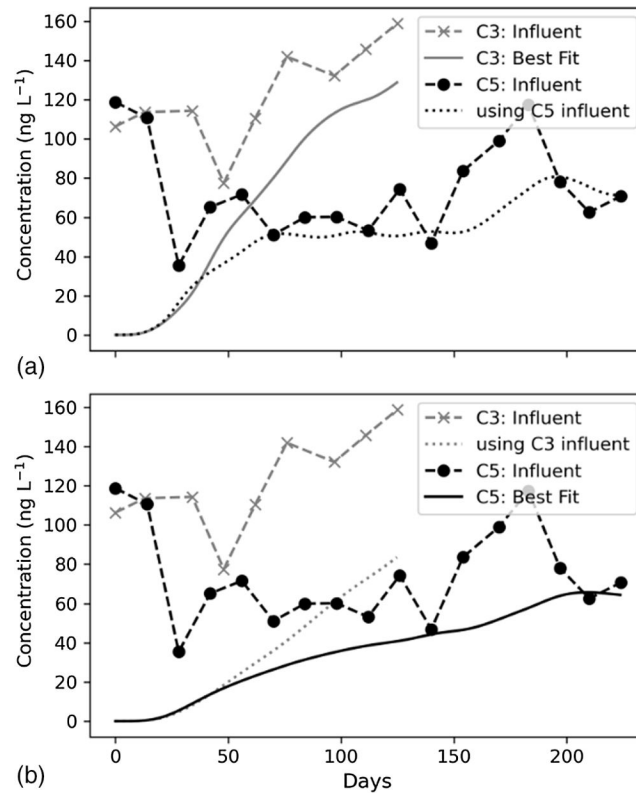


Fig. 3. Comparison of Calgon F400 parameters developed in (a) Phase I (C3); and (b) Phase II (C5) for summed-six-PFAS.

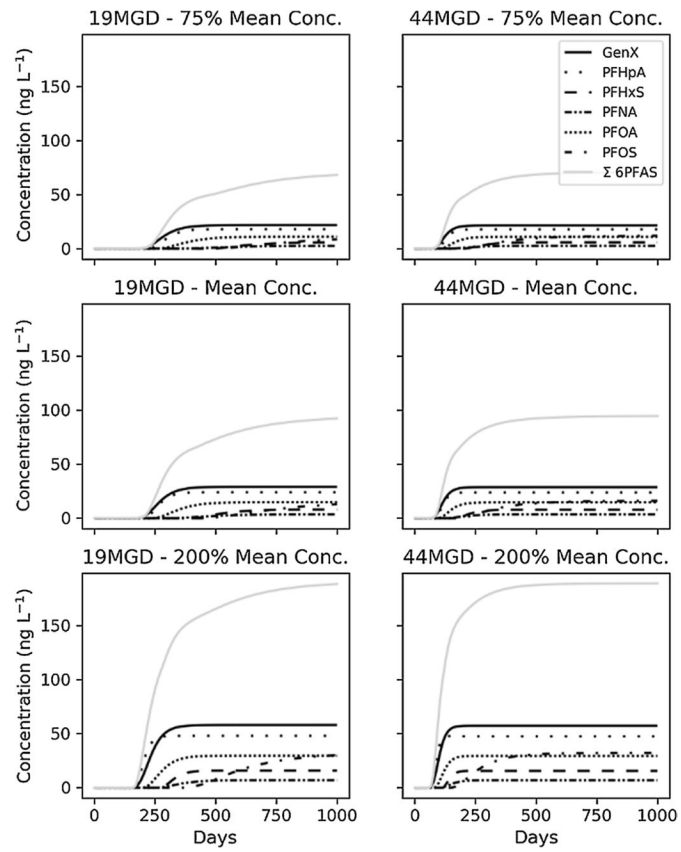


Fig. 4. Example for multicomponent projection example for single-bed operation for different operational cases (Column 1: Calgon F400).

Table 1.

Table of compounds

Compound (acronym)	CAS No.	Influent concentration (ppt)		Influent concentration (ppt) mean \pm standard deviation	QSPR fouling parameters	
		Min-Max			a	b
Perfluorobutanoic acid (PFBA)	375-22-4	5.6-30.9		14.3 \pm 5.8	0.82	0.12
Perfluoropentanoic acid (PFPeA)	2706-90-3	7.6-102.0		34.3 \pm 20.4	0.67	0.19
Perfluorohexanoic acid (PFHxA) ^a	307-24-4	7.9-80.5		34.8 \pm 16.4	0.55	0.28
Perfluoroheptanoic acid (PFHpA)^a	375-85-9	5.1-47.8		23.6 \pm 10.6	0.44	0.36
Perfluorooctanoic acid (PFOA)^a	335-67-1	5.1-25.0		14.6 \pm 4.5	0.34	0.44
Perfluorononanoic acid (PFNA)^a	375-95-1	ND-6.5		3.4 \pm 1.4	0.24	0.53
Perfluorodecanoic acid (PFDA) ^a	335-76-2	ND-5.9		2.4 \pm 1.6	0.17	0.61
Perfluorobutanesulfonic acid (PFBS) ^a	375-73-5	2.2-7.35		4.9 \pm 1.5	0.68	0.24
Perfluorohexanesulfonic acid (PFHxS)^a	355-46-4	3.5-11.1		7.7 \pm 2.3	0.44	0.48
Perfluorooctanesulfonic acid (PFOS)^a	1763-23-1	9.7-25.0		16.0 \pm 4.4	0.25	0.66
Perfluoro-2-methoxyacetic acid (PFMOAA) ^a	674-13-5	0.33-2,900		890 \pm 930	0.88	0.055
Perfluoro(3,5-dioxahexanoic acid (PFO2HxA) ^a	39492-88-1	19.6-240		102 \pm 57	0.63	0.17
Perfluoro(3,5,7-trioxaoctanoic acid (PFO3OA) ^a	39492-89-2	11.7-214		76.3 \pm 64.3	0.43	0.27
Perfluoro-2-proxypropanoic acid (PFPrOPrA/GenX)^a	13252-13-6	7.1-57.1		28.4 \pm 15.2	0.50	0.37
Perfluoro(3,5,7,9-tetraoxadecanoic acid (PFO4DA) ^b	39492-90-5	4.92-91.6		32.9 \pm 25.8	0.25	0.37
Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro- (Nafion BP2) ^b	749836-20-2	6.75-76.0		23.9 \pm 15.6	0.29	0.63

Note: ND = nondetect. Bold indicates the six compounds used in establishing the design treatment goal (total < 70 ppt).

^a Compounds were measured for every sampling period during both phases of pilot testing.

^b Indicates estimated analytical values for compounds.

Table 2.

Best-fit parameter estimates for organic free Freundlich $K [(\mu\text{g/g})(\text{L}/\mu\text{g})^{1/n}]$ and $1/n$

Phase	Phase I raw inlet water			Phase I postbiological filtration			Phase II postbiological filtration							
	C1 Calgon F400	C2 Calgon F300	C3 Calgon F400	C4 Calgon F400	C4 Evoqua 1230AWC	C5 Calgon F400	C6 Hydroarco 4000	C7 Norit GAC400	K	1/n	K	1/n	K	1/n
Compound	K	1/n	K	1/n	K	1/n	K	1/n	K	1/n	K	1/n	K	1/n
PFBA	—	—	—	—	—	—	10.6	0.70	15.1	1.0	6.91	0.65	—	—
PFPeA	—	—	—	—	—	—	51.3	1.0	30.5	1.0	13.2	0.70	—	—
PFHxA	6.61	0.57	3.22	0.41	2.14	0.30	56.0	1.0	25.1	0.84	10.7	0.63	—	—
PFHpA	6.76	0.60	5.24	0.58	1.76	0.30	66.5	1.0	65.0	1.0	57.4	1.0	—	—
PFOA	9.08	0.67	6.08	0.61	8.95	0.71	62.3	1.0	77.7	1.0	67.2	1.0	—	—
PFNA	3.77	0.56	0.83	0.31	9.43	0.70	3.87 ^a	0.30	19.1	0.61	1.85	0.30	—	—
PFDA	15.1	0.82	3.85	0.62	3.90	0.51	4.56	0.54	2.05	0.30	1.26 ^b	0.30	—	—
PFBS	7.80	0.64	1.36	0.35	9.17	0.71	33.1	1.0	1.35	0.30	1.24	0.30	—	—
PFHxS	1.70	0.31	4.03	0.51	21.6	0.85	24.3	0.88	2.45	0.30	7.86	0.56	—	—
PFOs	15.0	0.65	4.04	0.40	79.3	1.0	4.54	0.40	70.4	0.72	57.9	0.78	—	—
PFMOAA ^c	—	—	—	—	—	—	57.6	1.0	35.3	1.0	36.9	0.89	—	—
PFO2HxA ^c	—	—	—	—	—	—	61.3	1.0	84.5	1.0	25.6	0.79	—	—
PFO3OA ^c	—	—	—	—	—	—	9.25	0.42	31.6	0.62	13.2	0.56	—	—
GenX	14.6	0.79	2.42	0.30	26.0	1.0	44.6	1.0	24.1	1.0	43.6	1.0	—	—
PFO4DA ^c	—	—	—	—	—	—	142	1.0	27.8	0.36	92.4	0.95	—	—
Nafion BP2 ^c	—	—	—	—	—	—	7.47	0.58	9.84	0.56	10.9	0.65	—	—

Note: (—) represents no data for these compounds collected during Phase I to perform capacity calculation. Bold indicates the six compounds used in establishing the design treatment goal (total < 70 ppt).

^aNo breakthrough occurred during pilot study, capacity is expected to be greater than value calculated from data.

^bLimited breakthrough data.

^cIndicates estimated analytical values for compounds.

Table 3.

Predicted bed regeneration intervals in days: configuration of eight beds with two beds per cycle

Type of GAC	19 MGD				44 MGD				
	Average concentration	75% of average concentration	200% of average concentration	Average concentration	75% of average concentration	200% of average concentration	Average concentration	75% of average concentration	200% of average concentration
C1-Calgon F400	260	824	94	115	441	41			
C2-Calgon F300	242	719	79	106	389	34			
C3-Calgon F400	231	925	80	102	541	34			
C4-Evoqua 1230AWC	183	686	61	81	359	27			
C5-Calgon F400	423	1,243	176	191	837	76			
C6-Hydrodarco4000	345	>1,460	113	154	1,060	48			
C7-Norit GAC400	382	1,230	157	172	794	69			