EMERGING CONTAMINANT ARTICLE
TOPICAL COLLECTION ON PFAS ANALYTICS AND TREATMENT

Per- and polyfluoroalkyl substance removal in carbon-based advanced treatment for potable reuse

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Abstract
The persistence of perfluoroalkyl acids (PFAAs) in wastewater effluent highlights the need for active monitoring and targeted removal of these compounds in potable reuse applications. The City of Altamonte Springs' permanent potable reuse demonstration facility, pureALTA, employs a carbon-based advanced treatment process using multiple treatment barriers to provide potable water that meets state and federal regulatory requirements and health guidelines for unregulated contaminants. The combination of ozonation, biological activated carbon filtration (BAC), ultrafiltration (UF), granular activated carbon adsorption (GAC), and UV advanced oxidation process (UV AOP) showed complete removal of long-chain PFAAs (perfluoroalkyl sulfonic acids with ≥6 carbons and perfluoroalkyl carboxylic acids with ≥7 carbons) with federal health guidelines, such as perfluorooctanoic acid and perfluorooctane sulfonate in the advanced treated water while maintaining total organic carbon (TOC) levels below 3 mg/L, the regulatory limit in Florida for indirect potable reuse. Ozone, BAC, and UF showed increases in PFAAs to varying levels based on the transformation of precursors. GAC was the critical process for both TOC and PFAA removal; as anticipated GAC media's age defined the extent of removal of short-chain PFAAs such as perfluoropentanoic acid and perfluorohexanoic acid. Because of regulatory limits on TOC in Florida potable reuse projects and the absence of regulations on short-chain PFAAs, TOC continues to dictate GAC media change-out frequency and operating cost. However, the performance control strategy for GAC at pureALTA may change if stringent limits are set for short-chain PFAAs in the future. As of May 2021, pureALTA has been in operation for more than 4 years and continues to operate, providing an opportunity for continued research and community engagement.

KEYWORDS
biological activated carbon, granular activated carbon, ozone, per- and polyfluoroalkyl substances, potable reuse, total organic carbon

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INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are manmade compounds that often make their way into natural bodies of water and wastewater given their presence in everyday products such as food-packaging materials, cleaning products, firefighting foam, and cosmetics (ATSDR, 2017). The persistence of these compounds in drinking water and treated wastewater effluent and associated health effects have led federal and state regulatory agencies to establish regulatory limits and guidance to protect the public and the environment from adverse effects.

In 2016, the U.S. Environmental Protection Agency (EPA) released health advisory levels (HALs) for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) set at 70 nanograms per liter (ng/L) either individually for each long-chain compound or combined concentration. Meanwhile, several states have developed enforceable maximum contaminant levels (MCLs) for prevalent PFAS that are even lower than the EPA advisories. For instance, the State of Michigan, in 2019, established MCLs for PFOA and PFOS at 8 and 16 ng/L, respectively, among five other PFAS (EGLE, 2020).

Typical water and wastewater treatment processes, such as biological treatment and chlorine disinfection, are relatively ineffective in removing PFAS (Appleman et al., 2014). Advanced treatment processes used for potable reuse often include micro- or ultrafiltration (MF/UF), reverse osmosis (RO), and UV advanced oxidation process (UV AOP), which achieves high-quality purified water.

Among these, RO provides excellent removal of PFAS (Glover et al., 2018; Patterson et al., 2019); even nanofiltration has been shown to be highly effective (Steinle-Darling et al., 2010). The feasibility of implementing an RO-based treatment solution depends heavily on site-specific conditions for brine disposal, and its implementation may be associated with relatively high construction and operating costs. A viable alternative to RO-based systems is a carbon-based advanced treatment (CBAT) approach that employs multiple other treatment barriers such as ozonation, biodegradation, and adsorption coupled with robust disinfection with UV and chlorine, for example. In these carbon-based systems, adsorption to granular activated carbon (GAC), in particular, provides significant removal of PFAS, total organic carbon (TOC), and other trace organics (Appleman et al., 2013; Crone et al., 2019; Glover et al., 2018; Salveson et al., 2018). Multiple studies have proven GAC's efficacy in removing PFAS from wastewater effluent (Yu et al., 2009, e.g.).

The City of Altamonte Springs (City), an inland utility in Central Florida, completed an investigation of CBAT for direct potable reuse (DPR) at their Altamonte Springs Regional Water Reclamation Facility (ASRWRF). Called pureALTA, the permanent 20 gallon-per-minute (gpm) demonstration pilot uses a multi-barrier pathogen and pollutant removal process—ozone (O3) combined with biological activated carbon filtration (BAC), UF, GAC, and UV AOP—to treat filtered, unchlorinated secondary effluent to drinking water standards (data provided in Appendix).

Extensive water quality data were collected from this pilot to demonstrate that it meets regulatory requirements for potable reuse projects. Water quality parameters measured included chemicals and pathogens with regulated limits as well as unregulated contaminants and indicator organisms. Data were generated from grab samples collected periodically as well as real-time data from online monitoring. Data were also gathered on perfluoroalkyl acids (PFAAs) and polyfluoroalkyl acids (i.e., precursors to PFAA) after each of pureALTA’s treatment barriers to understand removal across the CBAT train. This study represents one of the first pilot-scale evaluations of PFAS removal in a CBAT process for potable reuse and remains a model for utilities facing similar water quality challenges and considering implementing alternative water supply solutions.

MATERIALS AND METHODS

Pilot design

The City’s ASRWRF uses the modified Ludzack-Ettinger (MLE) process and clarification for secondary treatment followed by deep-bed sand filtration and sodium hypochlorite disinfection for tertiary treatment. Reclaimed water from this facility is used for beneficial reuse. Figure 1 shows a schematic of pureALTA’s process flow as currently installed and operating at the ASRWRF.

Feedwater is sourced downstream of the tertiary filters but before chlorination and pumped to a holding tank. Ozone dose control is based on an “O3:TOC ratio” approach that uses TOC and nitrite concentrations in the influent water to adjust the applied ozone dose administered into the water using mainstream injection with a venturimeter, as shown in Equation (1).
Nitrite averaged 0.11 mg/L in the feed water, while TOC ranged from 5.7 to 6.2 mg/L. The “O₃:TOC Ratio” setpoints tested during the pilot ranged from 0.8 to 1.3.

A contact time of 3 min is allowed to mix the ozone and feed water before the resulting ozonated water is applied to the BAC filter, which has a hydraulic loading rate of 2.9 gpm per square foot (ft²) and an empty bed contact time (EBCT) of 15 min. The filter contains 6 feet of exhausted carbon (bituminous coal-based, Calgon Filtrasorb 820) media with a high surface area for developing biological layers in the media bed. The media was procured from a local utility’s water treatment plant, where it had been in operation for approximately 2 years before use at pureALTA. Before testing commenced at pureALTA, the filter was allowed to acclimate to ozonated feedwater for 4 weeks. Xylem, Inc. provided a custom-built product of their Oxelia™ system for the ozone and BAC processes.

Following the BAC filter, the water passes through a single hollow-fiber UF membrane module containing polyvinylidene fluoride fibers with a nominal pore size of 0.01 micrometers (μm) and a 775-ft² surface area provided by Toray Industries, Inc (model HFU-2020N). To control biofouling, monochloramine made from sodium hypochlorite and ammonium sulfate at a chlorine-to-ammonia ratio of 4 is added to UF feed water.

Adsorption is achieved via GAC filtration using an 8 x 30 U.S. Sieve Series mesh bituminous coal-based activated carbon media of 0.8–1 mm effective size. A single Calgon Carbon Disposorb GAC filter filled with Calgon F300 provides an EBCT of 14.3 min at 17 gpm.

Finally, UV disinfection is provided in a closed-vessel reactor provided by Trojan Technologies (model Swift SC D06) using low-pressure, high-output UV lamps, and a dose of 900 millijoules per square centimeter (mJ/cm²). Hydrogen peroxide is added to the UV feed water for hydroxyl radical generation for AOP.

2.2 Analytical methods

2.2.1 Perfluoroalkyl acids

Samples were collected six times during the year-long study under varying pilot conditions. Samples were analyzed as described by Glover et al. (2018). Briefly, a modified version of EPA Method 537 was used on all samples and field blanks collected for PFNA analysis. Samples were extracted via automated solid-phase extraction using hydrophilic–lipophilic balance...
cartridges and preconditioned with methyl tert-butyl ether (MTBE), methanol, and water. Extractions were then eluted with methanol and a methanol/MTBE mix and concentrated with nitrogen gas before being stored at approximately \(-20^\circ\mathrm{C}\) until analysis via isotope-dilution liquid-chromatography tandem mass spectrometry. Table 1 shows the PFAA compounds analyzed and their corresponding method reporting limits (MRLs).

### 2.2.2 | Total oxidizable precursor assay

Samples were also analyzed via the total oxidizable precursor (TOP) assay, as described by Glover et al. (2018). Briefly, high concentrations of hydroxyl radicals were generated through the thermolysis of persulfate. Samples were exposed to a temperature of 85\(^\circ\mathrm{C}\) for 6 h in a water bath at pH >11, followed by subsequent cooling and pH adjustment between 5 and 9. The molar concentration of nontargeted PFAA precursors was calculated by subtracting the molar concentration of targeted PFAAs and PFCAs. Results were validated by measuring the PFOA yield from oxidized targeted PFAA precursors per a method adapted from Houtz and Sedlak (2012).

### 2.2.3 | Total organic carbon

TOC was analyzed at multiple points in the treatment train using grab samples and online monitoring. Grab samples were analyzed using Standard Method 5310B while optical-based probes were used for real-time TOC monitoring at the ozone influent, BAC filtrate, and GAC filtrate. YSI’s (a Xylem, Inc. company) NicaVIS 701 IQ NI and CarboVIS 701 IQ probes were used on the ozone influent and BAC filtrate, respectively. For a brief period during the study, a Hach BioTector B3500c online TOC analyzer was installed on the GAC filtrate, which was eventually replaced with a permanent YSI CarboVIS 701IQ probe.

### 3 | RESULTS

#### 3.1 | Source water characterization

The average PFAA concentration in pureALTA’s feedwater was measured at 67 ng/L. As shown in Figure 2, of the 11 PFAAs sampled, perfluoropentanoic acid (PFPeA) was measured at the highest average of 23 ng/L, contributing to 35% of the PFAA loading, while perfluorohexanoic acid (PFHxA) averaged at 17 ng/L, contributing 26%, thus showing the dominance of short-chain PFAAs. Meanwhile, PFOA and PFOS were measured at averages of 8.8 and 3.4 ng/L, respectively, far below their 70 ng/L federal HAL as individual or combined concentrations.

The overall low levels of PFAAs are not entirely uncommon for wastewater sources with primarily residential and commercial dischargers (Buck et al., 2011; Coggan et al., 2019). The ASRWRF has one permitted significant industrial user, a metal-finishing company that provides zinc plating, electroless nickel plating, and copper plating, among other services. Electroplating processes use PFAS as a chemical fume suppressant to prevent hexavalent chromium vapor evaporation (Glüge et al., 2020). PFOS has historically been used in metal-plating operations but, in 2015, the EPA banned PFOS-based fume suppressants (U.S. Federal Register, 2012). As an alternative, mist suppressants now contain the PFAA precursor 6:2 fluorotelomer sulfonate (6:2 FtS), a compound susceptible to chemical and biological transformation into PFAAs. Targeted PFAA precursors, which included 6:2 FtS, made up only 0.5% of the total PFAAs measured in the feedwater as compared to TOP assay results and nontargeted PFAA precursors made up nearly 65% of the total PFAA loading, with the remainder being targeted PFAAs.
3.2 | PFAS removal through pureALTA treatment processes

As shown in Figure 3, pureALTA’s results showed changes in PFAA speciation and total quantity at each steady-state treatment stage.

During the sampling events, O₃:TOC ratio setpoints ranged between 0.8 and 1.3, corresponding to an ozone dose range of 5.0–8.6 mg/L. Studies show that, although ozone is effective in oxidizing PFAAs (Crone et al., 2019; Glover et al., 2018; Schröder & Meesters, 2005), it may increase the concentration of targeted PFAAs by oxidizing precursors (Dickenson et al., 2015; Sari et al., 2020). PFBS increased by an average of 31% after ozonation. PFPeA increased by 9% at higher ozone doses (above 7 mg/L). PFHxA increased by an average of 11% at lower ozone doses (below 6.5 mg/L) and by 18% at higher doses (above 7 mg/L). PFHpA increased by 15% and 27% at lower and higher doses, respectively. TOP assay results from one sampling event indicated a total concentration of nontargeted PFAA precursors at 359 pM in the filtered secondary effluent and 301 pM in the ozone-treated water. Generally, more precursors were found to oxidize to targeted PFAAs at higher ozone doses.

BAC filtration achieved 25%, 63%, 15%, and 57% removal of PFHxS, PFOS, PFNA, and PFDA, respectively. Biological filtration has been reported as not being particularly effective in removing PFAAs in water treatment (Dickenson et al., 2015). With only 2 years of operation at a water treatment plant before being used at pureALTA, some adsorptive capacity remaining on the carbon in the BAC filter may explain the removal of these compounds. Concentration of PFBS, PFPeA, PFHxA, and PFHpA increased by 23%, 71%, 53%, and 54%, respectively, after BAC filtration. One potential explanation for this increase through BAC is that competitive sorption effects result in a release of previously sorbed shorter-chain PFAAs, and more sorption sites are being occupied by longer-chain PFAAs.

PFOS and PFDA decreased by 88% and 37% to their MRLs after the UF step. The removal mechanism in this step is suspected to be sieving of particle-adsorbed PFAAs. PFHxA and PFPeA continued to increase in concentration by 19% and 41%, respectively.

GAC adsorption is an effective treatment process for PFAA removal, depending on carbon capacity, EBCT, and carbon change-out frequency (Appleman et al., 2013; Appleman et al., 2014; Crone et al., 2019; Dickinson et al., 2015; Glover et al., 2018; Holliday, 2020). At pureALTA, each sampling event corresponded to a different bed volume (BV) in the GAC bed, and these results are discussed in Figure 4.

UV AOP did not show any additional removal of these compounds owing to their low reaction rates with hydroxyl radicals (Hori et al., 2004). PFAA concentration in pureALTA’s advanced treated water (ATW) remained the same as that in the GAC filtrate.

3.3 | PFAA and TOC breakthrough in GAC

The State of Florida has a 3 mg/L TOC limit in the ATW for indirect potable reuse projects (Florida Administrative Code, 2012). In the absence of rules for DPR, this limit was applied to the pureALTA project.

This demonstration facility’s process controls are designed to optimize performance for TOC removal. The ozone process was controlled according to influent TOC and nitrite concentrations to sufficiently oxidize contaminants that exert an ozone demand while breaking down TOC into assimilable organic carbon (AOC). Studies and
existing full-scale applications have shown that ozonating BAC feedwater to make AOC increases TOC removal by up to 35% via biodegradation (City of Altamonte Springs, 2018; City of San Diego, 2015). The TOC in pureALTA’s feed water was recorded at an average of 6 mg/L, which decreased by approximately 30% after the BAC filtration process. The GAC was changed out once during the study, at approximately 6 months, or 12,000 BV.

Figure 4 shows the breakthrough of TOC and PFAAs with increasing BVs in the GAC system; a GAC media change-out was completed between the third and fourth sample. TOC removal was recorded at 44% through the GAC at BV <4000, 34% at BVs <8500, and 26% at BVs >10,000 indicating exhaustion of the GAC media resulting in decreased removal over time.

Data showed PFBA below the MRL of 5 ng/L in pureALTA’s feedwater, which remained unchanged through the treatment process, except at BVs higher than 6500, after which PFBA was detected at an average of 5.4 ng/L. This result may be attributed to the GAC media desorbing low levels of PFBA formed from precursors. PFBS decreased by an average of 77% at BVs <4000, 54% at BVs <8500, and 33% at BVs >10,000 in the GAC filtrate. Similar to PFBS, other short-chain PFAAs were seen to be better removed at lower BVs, with removal efficiency dropping closer to carbon exhaustion. PFOA, PFOS, and PFNA were under their MRLs in GAC filtrate for all BV conditions, indicating how the saturation of free sorption sites on the media affects removal and confirming the media’s preference for long-chain compounds like PFOA and PFOS with higher molecular weights (Salveson et al., 2018). Total PFOA and PFOS concentration across all BV conditions was measured at an average of 7.8 ng/L, nearly nine times lower than the EPA HAL of 70 ng/L.

In both GAC operational runs at the highest BV data point available, PFBS, PFPeA, PFHxA, and PFHxS were between 67%, 88%, 73%, and 26% breakthrough, respectively. A similar decline in removal was observed by Belkouteb et al. (2020) who found that PFHxA showed the fastest breakthrough followed by PFBS. Breakthrough for PFHxA in Belkouteb et al. (2020), however, occurred at much higher BVs, between 20,000 and 30,000. This difference between that study and pureALTA data is possibly due to the smaller effective size of the Calgon F400 media (0.6–0.7 mm) with a larger surface area compared to the Calgon F300 (0.8–1 mm) used at pureALTA (Wu et al., 2020; Yu et al., 2009). While studies were not performed to definitively establish the difference in PFAA breakthrough characteristics for different GAC media at pureALTA, several other factors such as pore size distribution of the media or background water quality may impact breakthrough performance. PFOA, PFOS, PFNA, and PFDA were generally at or below their MRLs with increasing BVs. TOC breakthrough of approximately 78%, which corresponds with the regulatory limit of 3 mg/L, was observed above 10,000 BVs.

A question of interest for the CBAT approach is to determine whether TOC or PFAS breakthrough will dictate GAC change-out frequency, which is a major cost consideration for this treatment approach. For this project, the 3 mg/L TOC limit triggers GAC change-out at
approximately 10,000 BV whereas influent PFOS and PFOA are already below the HAL of 70 ng/L and thus TOC is clearly the limiting parameter.

However, the potential future regulation of short-chain PFAAs (and/or PFOS and PFOA at lower levels) may dictate carbon media change-out in the future. A more detailed evaluation of this comparison is shown in the breakthrough curves plotted in Figures 5 and 6. A linear regression shows a good fit for normalized TOC \( R^2 = 96\% \), total PFAA \( R^2 = 88\% \), and short-chain PFAA \( R^2 = 75\% \) breakthrough, and a moderate fit for the long-chain PFAA data \( R^2 = 31\% \) with increasing BVs. This provides a basic tool for quick estimations on BVs and GAC change-out requirements depending on target contaminant-removal rates. A rough approximation of complete breakthrough \( (C/C_0 = 1) \) was linearly extrapolated for both parameters. For both total PFAAs and TOC, this occurred at approximately 17,500 BVs and an estimated operation time of 175 days. Short-chain PFAAs, however, showed complete breakthrough at a very low BV of 2000. This evaluation illustrates that the question of which parameter, TOC, or PFAAs, will control GAC change-out frequency (and thus, a significant portion of the operating cost of a CBAT facility) is likely not only dependent on site-specific incoming water quality but also highly dependent on PFAAs treatment goals, specifically related to short-chain PFAAs.

Finally, one challenge associated with monitoring PFAA breakthrough in any system is the lag time between sample collection and obtaining analytical results. Thus, understanding the relative breakthrough of TOC to various PFAAs at a given site is helpful to predict their breakthrough. Figure 7 explores this correlation. In it, data were evaluated in three ways: (1) total PFAAs, (2) sum of short-chain PFAAs, and (3) sum of long-chain PFAAs. As expected, the first and second datasets are consistent as the overwhelming mass fraction of PFAAs at this point in the treatment train are short-chain. Whereas TOC breakthrough is likely a poor predictor of short-chain PFAA breakthrough, the correlation with long-chain PFAAs is strong. This speaks both to the potential suitability of TOC as a surrogate for long-chain compound breakthrough, as well as confirms the conclusions taken from Figures 5 and 6 in an alternative way: there is not yet a clear answer to the question of whether TOC or short-chain PFAAs will drive GAC change-out frequency (and thus, cost) in future CBAT projects.

### 4 CONCLUSIONS

The combination of ozonation, BAC, UF, GAC adsorption, and UV AOP showed complete removal of long-chain PFAAs, such as PFOA and PFOS, in ATW at or under the HAL. Ozone, BAC, and UF showed an increase in PFAAs to varying levels as caused by the transformation of precursors. GAC adsorption was identified as a critical treatment process to remove both TOC and PFAAs with varying impacts on removal efficiencies based on media age and BVs. Correlating PFAA breakthrough to TOC breakthrough showed a relationship with long-chain PFAA offering a site-specific predictive modeling tool to the City to anticipate carbon change-out frequency for these long-chain compounds.

As of July 2021, pureALTA has been online for four and a half years and continues to operate, providing opportunities for continued research and community engagement.
engagement. The ASRWRF is currently undergoing process changes that will modify its MLE process to a four-stage Bardenpho process that meets the following water quality criteria for advanced wastewater treatment, as defined by the Florida statutes (§403.086): 5 mg/L biochemical oxygen demand, 5 mg/L total suspended solids, 3 mg/L total nitrogen, and 1 mg/L total phosphorus. This upgrade will remove nutrients and organic loading to more stringent levels, improving pureALTA’s feedwater quality. These process changes are expected to impact operational decisions for the demonstration facility such as prolonging the GAC bed life, positively impacting finished ATW quality and overall advanced treatment costs.

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CONFLICT OF INTEREST
The authors declare no potential conflict of interest.
DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

AUTHOR CONTRIBUTIONS
Pranjali Kumar: Conceptualization; resources; data curation; formal analysis; supervision; validation; investigation; visualization; writing – original draft; project administration; writing – review and editing. Laura Rodriguez-Gonzalez: Formal analysis; writing – original draft. Andy Salveson: Supervision. David Ammerman: Supervision; project administration. Eva Steinele-Darling: Conceptualization; resources; supervision; validation; project administration; writing – review and editing.

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