Assessment of PFAS fate, transport, and treatment inhibition associated with a simulated AFFF release within a WASTEWATER treatment plant

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HIGHLIGHTS

- A simulated AFFF release was associated with minimal adverse impacts on wastewater treatment.
- Fluorotelomer precursor degraded to 6:2 FTS, identified intermediates, & terminal PFAS.
- Removal of 70% of AFFF associated PFAS compounds after four days.

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ABSTRACT

Sequencing batch reactors (SBRs) were operated for 36 days to simulate the potential wastewater treatment impacts as well as fate and transport of per- and polyfluoroalkyl substances (PFAS) that could be associated with a release of alcohol resistant aqueous film forming foam (AR-AFFF) from on-site methanol fire suppression systems. The results of this study indicate that two days of exposure to AFFF were associated with small reductions in mixed liquor solids content and nitrification rates. No impacts on denitrification or biological phosphorus removal were observed. The addition of AFFF was associated with increases in 6:2 fluorotelomer sulfonate (6:2 FTS) in influent, effluent, and solids samples in the SBR. The following biotransformation pathway is proposed: an unidentified fluorotelomer precursor quickly degraded to 6:2 FTS, which then slowly degraded to several identified degradation intermediates and terminal, short-chain perfluorocarboxylic acid products. Data for 6:2 FTS, which was used as a proxy for AFFF-associated PFAS, were extrapolated to estimate that a removal of approximately 70% of AFFF via effluent and solids wasting would occur after 4 days at a full-scale treatment plant. This information can be used to better understand potential impacts on downstream processes, including potable reuse and biosolids production.

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1. Introduction

Aqueous film forming foam (AFFF) can be used to quickly suppress Class B fires by creating a surfactant film on top of the fuel source; this film aids in cooling the fuel source and preventing vapor formation and re-ignition. These firefighting foams, which were first developed in the 1960s, have been linked to environmental contamination surrounding sites known to use AFFF as well as within wastewater treatment plants that have historically accepted AFFF waste (e.g. Baduel et al., 2017; Dauchy et al., 2017, 2019; Houtz et al., 2013, 2016, 2018; Moody and Field, 1999, 2000). Foam formulations typically contain a proprietary mixture of a solvent and both hydrocarbon and fluorocarbon surfactants (Moody and Field, 2000). It is well known that AFFF formulations differ between manufacturers; in fact, the same product can have different formulations from year to year. Much of the work surrounding AFFF has focused on per- and polyfluoroalkyl substance (PFAS) content, fate, and transport. This increased interest can be attributed to the environmental persistence of PFAS, potential for bioaccumulation in humans and wildlife, and association with deleterious health outcomes (e.g. Awad et al., 2011; Cousins et al., 2016; DeWitt et al., 2019; McCarthy et al., 2017; ATSDR, 2018;
Sunderland et al., 2019).

Historically, AFFF contained long-chain PFAS such as PFOS, PFOA, or their precursors (e.g., N-polyoxyethylene-N-propyl perfluorooctane sulfonamide) (Buck et al., 2012; Kishi and Aral, 2008). However, as concern increased around the likelihood that long-chain PFAS would bioaccumulate and the potential for regulation of these long-chain compounds increased, manufacturers began to phase out AFFF containing long-chain PFAS. During this transition, industry representatives report that they increased production of fluorotelomers, especially those known to breakdown to form predominantly 6:2 fluorotelomer sulfonate (6:2 FTS) (Cortina and Korzeniowski, 2008). This assertion is supported in the literature, with likely degradation pathways resulting in 6:2 FTS formation from compounds known to be in AFFF and other consumer products both in groundwater environments and wastewater treatment plants (Brunton and Sedlak, 2017; Field and Seow, 2017; Harding-Marjanovic et al., 2015; Houtz et al., 2018). 6:2 FTS can further degrade into short-chain PFAAs (Harding-Marjanovic et al., 2015). Research surrounding short-chain PFAS and fluorotelomer precursors is ongoing, including adequate identification and understanding potential risk associated with their presence in the environment, water sources, and wastewater residuals.

AFFF presence in the environment can present several challenges for wastewater facilities that were not historically designed to treat PFAS. Due to the limited number of commercial standards available and diverse characteristics of emerging PFAS, many certified methods quantitate fewer than 30 of the numerous PFAS (e.g. EPA Methods 537, 537.1, 533). However, non-targeted analyses have tentatively identified hundreds of PFAS and thousands of PFAS have been registered in the global market (McCord and Strynar, 2019; Wang et al., 2017). Polyluoralkyl substances that can transform to PFAAs in the natural environment or during water and wastewater treatment have been called precursors (Houtz and Sedlak, 2012). Biological treatment within wastewater plants can convert precursors invisible to quantitative methods in the influent into visible terminal PFAAs in the effluent and cause these treatment plants to look like sources of PFAS (Arvaniti et al., 2012). The Total Oxidizable Precursor (TOP) assay was developed to indirectly and non-specifically quantify precursors that may biotically or abiotically degrade into PFAAs (Houtz and Sedlak, 2012).

Hampton Roads Sanitation District (HRSD) serves approximately 1.7 million people within a 3100 square mile service area in southeast Virginia. The combined capacity of HRSD’s 16 wastewater treatment plants is slightly under 250 million gallons per day (MGD). Due to concerns that AFFF presence could inhibit effective settling within wastewater treatment plants, HRSD has maintained a strict zero discharge policy towards AFFF since the mid-1970s. More recently, concerns over PFAS impacts on water reuse activities at HRSD have further supported this long-standing zero-discharge policy.

Although external sources of AFFF are prohibited from entering HRSD’s collection system, several of HRSD’s treatment plants have AFFF fire suppression systems on site. These fire suppression systems are required when methanol is stored on site for supplemental carbon addition for denitrification within the wastewater treatment plant. The storm drains near the AFFF systems at each facility connect back to the treatment headworks. Therefore, either an accidental triggering of the fire suppression system or a methanol-based fire suppression response could introduce AFFF into the wastewater plant. Methanol is often considered the most cost effective source of supplemental carbon for utilities with advanced biological nutrient removal (BNR) processes; therefore, a better understanding of how AFFF fire suppression systems could impact treatment, final effluent, and wastewater residual quality is a widely applicable question.

While many studies have investigated different aspects of the interactions between AFFF, PFAS, and wastewater treatment, few have taken an integrated approach to understand both treatment impacts and fate and transport associated with realistic concentrations of AFFF in wastewater treatment. Fate and transport of AFFF associated PFAS compounds through full-scale facilities have been reported in several studies (Houtz et al., 2016, 2018). In addition, some studies have documented negligible impacts on wastewater treatment associated with AFFF presence (Erten-Unal et al., 1998), while others have documented impacts on effective settling, denitrification, and anaerobic digestion microbial communities (Fitzgerald et al., 2019; Hingley, 2011; Saam et al., 1979). Several studies have also focused directly on wastewater treatment impacts when PFAS were added directly, rather than as part of an AFFF formulation (e.g. Yang et al., 2020; Yu et al., 2018). Studies are still needed that tie together both the wastewater treatment challenges associated with AFFF as well as PFAS fate and transport that could impact wastewater effluent, water reuse activity, and/or wastewater residual production.

In order to better understand the fate and transport of AFFF-associated PFAS through wastewater treatment as well as potential impacts to wastewater treatment, a bench-scale sequencing batch reactor (SBR) study was conducted. Three main questions were addressed as part of this study: (1) Is AFFF presence associated with wastewater treatment inhibition? (2) What are the fate, transport, and biodegradation of AFFF-associated PFAS after a release? and (3) What is the expected residence time of PFAS within a treatment plant after an AFFF release?

2. Methods

2.1. Sequencing batch reactors (SBRs)

Four SBRs were configured to mimic a full-scale 5-stage Bar-denpho treatment train to understand potential inhibition of nitrification, denitrification, and/or biological phosphorus removal (Bio-P) associated with AFFF presence. Reactors were 30 L and submerged in a water bath to maintain a constant temperature of 15 °C. All reactors were operated with a 24-h hydraulic residence time (HRT) and an 18-day solids residence time (SRT) was targeted using the Garrett wasting method. Cycle operating parameters are included in Table S1.

At least one SRT was allowed to pass after seeding SBRs with mixed liquor from the Virginia Initiative Plant (VIP, Norfolk, VA) before AFFF was added to SBRs. Raw water was collected every 2–3 days from the VIP, coarse filtered through mesh (~0.5 mm² openings), and added to individual 55-gallon drums used to feed each of the SBRs. In order to simulate a short duration release of AFFF from an on-site system, AFFF was added to the feed during raw water drum changes at the beginning of the experiment; subsequent raw water additions to the feed drums were made without the addition of AFFF. The two AFFF formulations tested here are those present at HRSD treatment plants: Ansulite Low Viscosity 3X3 alcohol resistant (AK)-AFFF (used at three facilities) and Chemguard Ultraguard CUG (used at one facility).

2.2. Determining realistic AFFF concentrations for SBR studies

AFFF concentrate dilution factors were calculated using flow rates specific to each treatment plant and methanol fire suppression system. This protocol is described in supplementary protocol 1 and Table S2. Based on the calculated dilution factors, it was evident that two dilutions would be important for understanding AFFF dynamics at HRSD plants: a 500 times dilution (as was calculated for Ansulite at AB) and a 2000 times dilution (as was calculated for...
Ansolite at VIP/NP and Chemguard at YR). Therefore, in this study the four SBRs had the following AFFF treatments administered: control (no AFFF), 2000X Ansolite dilution, 2000X Chemguard dilution, and 500X Ansolite dilution.

2.3. Bulk nutrient and water quality parameters

Routine analysis of several parameters in influent and effluent were used to assess each AFFF treatment in addition to mixed liquor volatile suspended solids (MLVSS) content within each SBR. Influent and effluent parameters included: total suspended solids (TSS), chemical oxygen demand (COD), soluble chemical oxygen demand (sCOD), and total Kjeldahl nitrogen (TKN).

Nutrient profiles were conducted prior to and after addition of AFFF to each reactor to better understand the potential for AFFF presence to be associated with BNR inhibition. Hach TNT analyses for NH₄⁻N, NO₃⁻N, NO₂⁻N, and PO₄-P were conducted on samples after filtering through a 0.45 μm membrane filter. A detailed summary of analyses completed at each time point during a profile is included in Table S5. Nitrification rates were calculated based on the removal of NH₄⁻N within the first and second aerobic time frames. Nitrite-N levels were assessed to ensure that removal of NH₄⁻N was accurately representing nitrification rates (i.e. no nitrite oxidizing bacteria (NOB) inhibition was evident in reactors). Denitrification rates were calculated based on the removal of NO₃⁻N over time within the first and second anoxic time frames. Bio-P was assessed based on both the release of PO₄-P during the anaerobic time frame and the overall removal of PO₄-P throughout the entire 8-h profile.

2.4. Fate and transport of AFFF-Associated PFAS

In order to maximize sample resolution for PFAS measurements over time, only one SBR was selected for PFAS analysis. Although it does not represent the worst-case scenario for an AFFF release, the 2000X dilution of Ansolite was selected for in-depth analysis because it was the most representative of real-world conditions at HRSD treatment plants. Based on flow modeling, three out of four plants would see 2000X AFFF in influent if a fire suppression system were triggered. Although one plant would see a 500X concentration of AFFF in influent, future plans for water reuse at this plant would incorporate blending with wastewater effluent from another treatment plant before water reuse treatment, which would dilute it by at least another factor of four, thus the selection of the 2000X dilution SBR for PFAS testing. Samples were collected once in the week prior to AFFF addition and on days 1, 2, 3, 4, 5, 8, 10, 11, 15, 17, 19, 22, 24, 29, and 36 after AFFF addition. On each date, influence prior to the SBR cycle feed as well as effluent and mixed liquor samples from within the reactor at the end of a treatment cycle were collected. These samples were analyzed for target PFAS and the TOP assay as described below; all aqueous analyses were conducted by The Southern Nevada Water Authority (SNWA) and all solids analyses were conducted by Eurofins Eaton Analytical.

2.5. Sample collection and analytical methods

Aqueous (i.e., influent and effluent) samples were collected in amber high-density polyethylene (HDPE) bottles, preserved with 0.05% ascorbic acid and shipped to SNWA for analysis. Samples were held at 4 °C until they were analyzed for 27 PFAS compounds using liquid chromatography with tandem mass spectrometry (LC-MS/MS) (Table S4). Samples with observable turbidity (i.e., influent but not effluent samples) were filtered prior to extraction with pre-ashed 90 mm glass fiber filters; method validation studies indicated no impact from filtration on measured concentrations of target analytes (Table S5). Two analytical methods were used for PFAS determination: (1) isotope-dilution LC-MS/MS following automated solid phase extraction (ASPE) was used where isotopically labelled analogs of PFAS were commercially available, (2) whereas external calibration, direct-injection LC-MS/MS was used for analytes where isotopically labelled analogs were not commercially available (Table S4). This second, direct injection was applied for these analytes because ASPE losses and matrix effects could not be corrected confidently without isotopically labelled analogs.

ASPE (Method 1) was performed using a Dionex AutoTrace 280 workstation (Thermo Fisher Scientific). Samples were acidified to < pH 2 with concentrated sulfuric acid, then spiked with isotopically labelled standards prior to extraction. 500-mL samples were processed in batches of six. Pre-packed 200 mg, 6 cc HLB cartridges (Waters Corporation) were sequentially conditioned with MTBE, methanol, and reagent water before sample loading. After loading, cartridges were rinsed with reagent grade water and dried for 30 min with nitrogen gas. Target analytes were eluted with methanol into conical vials (Dionex), and extracts concentrated to a final volume of 500 μL with nitrogen gas.

Analyses were separated using a 50 × 4.6 mm Kinetex C18 column with a 2.6 μm pore size (Phenomenex) and a binary gradient consisting of 5% and then ammonium acetate (v/v) in water (A) and 100% methanol (B) at a flow rate of 500 μL/min. An Agilent G1312A binary pump and an HTC-PAL auto sampler (CTC Analytics) with an injection volume of 2 μL were used for all analyses. Potential contaminants from LC system were separated from analyte peaks by installing a 100 × 4.6 mm Kinetex C18 column with a 2.6 μm pore size (Phenomenex) in-line upstream from the injector valve. Tandem mass spectrometry was performed using an API 4000 triple-quadrupole mass spectrometer (Applied Biosystems). Using ESI negative ionization, optimal compound-dependent parameters were determined for a primary and secondary MS/MS transitions of target analytes and source-dependent parameters optimized. The concentration of each analyte was calculated from primary transitions by isotope dilution using relative isotope-target ratios against calibrators prepared in methanol. Method reporting limits (MRLs) were based on method detection limits (MDL) calculated from seven replicate measurements of deionized water samples fortified with analytes and extracted as described above; MRLs for each analyte were set conservatively at least five times the MDL, and higher as needed in consideration of known and unanticipated background sources.

For direct injection with external calibration LC-MS/MS (Method 2), samples were spiked with isotopically labelled ([13C5] perfluoropentanoic acid (PFPeA)) to a final concentration of 2.5 μg/L prior to LC-MS/MS analysis. Analyses were separated using a 50 × 4.6 mm Kinetex C18 column with a 2.6 μm pore size (Phenomenex) and a binary gradient consisting of 5.0 mM ammonium acetate (v/v) in water (A) and 100% methanol (B) at a flow rate of 500 μL/min. An Agilent G1312A binary pump and an HTC-PAL auto sampler (CTC Analytics) with an injection volume of 10 μL was used for all analyses. Tandem mass spectrometry with ESI negative ionization was performed as described above for Method 1. The concentration of each analyte was calculated from primary transitions by external calibration against calibrators prepared in reagent water. Peak area counts for ([13C5] PFPeA) were monitored for positive confirmation of sample injection. MRLs and MDLs were determined as described above for Method 1.

Mixed liquor samples were collected in HDPE bottles, frozen for approximately one month and then shipped to Eurofins Laboratory where they were held at 0 °C until analysis. At Eurofins, the mixed liquor samples were centrifuged and the solid portion was collected for the analysis of 32 PFAS compounds using a Modified EPA 537 method on an LC-MS/MS with and without the TOP assay. See
Table S6 for a summary of all PFAS compounds analyzed in aqueous and solid samples. Aqueous data are reported in ng/L; solid data are reported in ng/g dry solids units.

2.6. Total oxidizable precursor (TOP) assay method and validation for aqueous samples

The TOP assay was employed to verify a material balance around the precursor compounds. This assay generates hydroxyl radicals by the thermal breakdown of persulfate under basic conditions (Houtz and Sedlak, 2012). These hydroxyl radicals oxidize precursors into PFAAs, but do not degrade PFAAs. By comparing concentrations of PFAAs and known precursor in samples prior to oxidation with the concentrations of PFAAs post-TOP assay, the quantity of unidentified precursors can be estimated. It should be noted, however that the TOP assay will not always yield a complete mass balance. For example, precursors that degrade to unmeasured ultra-short-chain PFAAs or perfluoroethers would be undetected (Martin et al., 2019; Zhang et al., 2019).

The TOP assay was conducted on aqueous samples using the methods described by Glover et al. (2018). Total precursors were calculated by subtracting the ambient (i.e., pre-TOP assay) PFAA concentrations from the PFAA concentrations after the TOP assay. Identified precursors were calculated by multiplying the molar concentrations of quantified polyfluorinated compounds (e.g., 6:2 FTS) in the ambient samples by their average molar yields according to Houtz and Sedlak (2012). Unidentified precursors were calculated as the difference between total precursors and identified precursors.

Prior to using the TOP assay on aqueous samples from the SBR, a method validation was conducted (Glover et al., 2018). One liter each of 1 µg/L 8:2 fluorotelomer sulfonic acid (8:2 FTS) and N-methylperfluorooctane sulfonamidooctacetic acid (N-MeFOSAA) in deionized water were oxidized in the TOP assay. For 8:2 FTS, the molar yields of perfluorobutanoic acid (PFBA), PFPeA, perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), and PFOA were 14%, 16%, 19%, 23%, and 20%, respectively, within the 95% confidence intervals of the molar yields reported by Houtz and Sedlak (2012). For N-MeFOSAA, the molar yield of PFOA was 75%, below the 95% confidence interval reported by Houtz and Sedlak (2012) but within the 95% confidence interval reported by Martin et al. (2019).

2.7. Relative residence time of PFAS

In order to assess downstream implications of an unexpected addition of PFAS-containing AFFF to a full-scale treatment plant, the experimental results presented here can be extrapolated. However, comparison of the SBR data to full scale treatment needs to be done in equivalent time units—HRT and SRT. The HRT of each SBR was 24 h and the targeted SRT was 18 days, with raw water feed drums re-filled every two to three days. This can be compared to an approximate HRT of 18 h and approximate SRT of 10 days at one of HRSD’s full-scale plants that utilizes a 5-stage Bardenpho configuration (NP). Thus, while the actual time length of the HRT and SRT vary between reactor and full-scale treatment, comparisons between the HRT and SRT of each system can be made directly.

An additional consideration for extrapolating SBR results is how the AFFF was added to each reactor. Each of the three raw water barrels were spiked with AFFF on day 1 and this water remained in place and fed the reactors for two days. Afterward, the feed barrels were thoroughly rinsed and re-filled with unspiked raw water. Thus, the number of HRTs and SRTs required to return to lower PFAS content within the reactors should be calculated starting on day 3 when the AFFF source was removed.

3. Results and discussion

3.1. Profiles to understand potential for biological nutrient removal (BNR) inhibition

Table 1 shows a summary of changes documented within SBRs after AFFF addition. A time series of MLVSS in all four SBRs is shown in Fig. S1. MLVSS fluctuated in all SBRs between approximately 1200 mg/L and 2000 mg/L, with the exception of one control SBR mixed liquor sample collected on 8/29/2019. It is likely that this sample was an outlier, however, it has been included for completeness. After the addition of AFFF on 8/26/2019, the MLVSS for all four reactors dropped. However, it should be noted that the 500X Anulsirte SBR had the largest decrease seen over a two-day period (−645 mg/L). This reduction in mixed liquor content was likely due to increased foaming seen in the 500X Anulsirte reactor after the AFFF addition (Fig. S2). Despite the apparent foaming, sludge volume index (SVI) measurements did not change appreciably pre- and post-AFFF addition to SBRs (Fig. S3). Although the SVI in the 500X Anulsirte reactor did increase to 140 mL/g prior to the addition of AFFF, settling with an SVI at that level would be adequate.

Effluent and influent TSS, COD, sCOD, and TKN for all four SBRs can be seen in Figs. S4 and S5, respectively. No measurable changes were seen in influent TSS or TKN in any of the SBRs after the addition of AFFF on 8/26/19. The addition of AFFF was coupled with an increase in both total and soluble COD in the 500X Anulsirte SBR, which had the highest volume of AFFF added. No measurable COD changes were documented for the 2000X AFFF dilution SBRs or the control SBR. Indeed, AFFF does have a COD signature. Anulsirte samples diluted 500X in high purity water have a COD of approximately 1000 mg/L and Anulsirte samples diluted 2000X in high purity water have a COD of approximately 200 mg/L. It is likely that the additional COD associated with the 2000X Anulsirte addition was not enough to overcome the routine background fluctuations in COD, while the 500X Anulsirte addition was detectable in influent because of the higher COD addition associated with this spike.

Effluent TSS, COD, sCOD, and TKN did not appear to change measurably after addition of 2000X dilutions of Anulsirte and Chemguard. However, as was seen in the influent for the 500X Anulsirte dilution, effluent COD and effluent sCOD in that reactor showed noticeable, short-duration increases. Effluent TKN in the 500X Anulsirte dilution reactor also showed a short duration spike after AFFF addition. These increases are further supported by slight reductions in nitrification rates in both the first and second aerobic time frames after the addition of the 500X Anulsirte dilution (Fig. 1).

Other than this short duration decrease in nitrification that occurred when the highest concentrations of AFFF were added, no other notable nitrification inhibition was observed. Similarly, denitrification rates did not appear to change after AFFF was added to the SBRs (Fig. 2). On the profile date prior to adding AFFF, PO₄-P levels measured in the raw water feeding the SBRs was considerably higher than normal (Fig. 3). Although the polyphosphate-accumulating organisms (PAOs) in the SBRs, continued to release in the anaerobic zone, the aerobic HRT may have not been long enough to allow for complete uptake of released PO₄-P at the cooler temperatures. This resulted in high effluent PO₄-P on the profile date preceding AFFF addition. Influent PO₄-P levels returned to normal in the profile following AFFF additions and no significant reductions in Bio-P activity were noted post-AFFF addition.

Based on the profile data and routine analyses conducted during this study, it appears that the presence of the two types of AFFF HRSD maintains on-site are not associated with substantial treatment upsets. In the SBR spiked with the highest concentration of
Table 1
Summary of impacts on parameters measured within each SBR. NC indicates that no change was documented as a result of AFFF addition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control</th>
<th>Ansulite 500X</th>
<th>Ansulite 2000X</th>
<th>Chemguard 2000X</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLVSS</td>
<td>NC</td>
<td>Reduction</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>TSS</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>COD &amp; sCOD</td>
<td>NC</td>
<td>Influent Increase</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>TKN</td>
<td>NC</td>
<td>Effluent Increase</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>Nitrification</td>
<td>NC</td>
<td>Reduction</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>Denitrification</td>
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<td>NC</td>
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<td>NC</td>
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<tr>
<td>Biological P Removal</td>
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</table>

Fig. 1. Specific nitrification rates for first and second aerobic stages in all four SBRs.

Fig. 2. Specific denitrification rates for first and second anoxic stages in all four SBRs.
AFFF (Ansulite 500X), a short-lived reduction in nitrification rates was documented. Effluent TSS levels did not increase after AFFF addition (Fig. S5), however a reduction in MLVSS content post AFFF addition was documented, most notably in the 500X dilution Ansulite reactor (Fig. S1). It is therefore likely that the reduction in MLVSS was due to entrapment of the solids in foam that collected at the top of the reactor (see Fig. S2), rather than via the reactor effluent. As MLVSS is often used as a proxy for biomass in activated sludge, it is likely that loss of MLVSS via foaming may have reduced the active nitrifier population in the 500X dilution Ansulite reactor, which resulted in reduced nitrification rates for a short period.

Both denitrification and Bio-P appeared to be unaffected by the presence of AFFF. This is in direct contrast to results presented in Hingley (2011), in which the presence of the same Chemguard AFFF as used in this study was associated with denitrification inhibition in SBRs. This difference could be attributed to differences in experimental methods. Hingley (2011) continually added AFFF over the entire course of the experiment. Though not expressly stated in the methods, one would presume that this decision was made to simulate treatment conditions if a wastewater utility elected to allow AFFF into its collection system (i.e. conditions without a zero-discharge policy). The current study only added AFFF to SBR raw water feed drums once, in order to simulate a release of an on-site fire suppression system. It is possible that had AFFF been routinely added in this study, similar impacts as those seen in Hingley (2011) could have been documented. However, because HRSD does not intend to lift the AFFF zero-discharge policy, testing long term fluxes of AFFF is no longer necessary.

3.2. Fate and transport of AFFF-Associated PFAS

Of the 27 PFAS compounds tested for in aqueous samples, a total of ten PFAS were detected in pre-TOP analyses, one precursor compound and nine terminal PFAAs. The predominant PFAS detected in both aqueous and solid samples pre-TOP was 6:2 FTS (Fig. 4). A clear spike in 6:2 FTS in all matrices can be seen post AFFF addition to the reactor. Solids 6:2 FTS concentrations went from ND (LOQ = 260 ng/g) before AFFF addition to a maximum of 79,000 ng/g two days after AFFF addition. The majority of the 6:2 FTS in solid samples was removed somewhere between 10 and 14 days after AFFF addition, after which it decreased slightly, but not completely by the last day of sampling (6600 ng/g). Post-TOP assay, PFCAs with 4–10 carbons were analyzed and PFCAs with 4–7 carbons were detected.

Influent 6:2 FTS concentrations went from 31 ng/L pre-AFFF addition to a maximum of 550 ng/L two days after AFFF was added. Effluent 6:2 FTS concentrations were also 31 ng/L before AFFF was added and peaked at 9200 ng/L two days after AFFF addition. An additional peak in effluent 6:2 FTS should be noted on 9/4/2019, which is drastically greater than the surrounding sample dates (670,000 ng/L). It is probable that this was due to contamination as the same dramatic increase was not seen in the post-TOP assay effluent samples collected on the same date and should be considered an outlier in the dataset (Fig. 5).

Since influent but not effluent samples were filtered prior to extraction, some fraction of PFAS may not have been observed in the influent samples due to sorption to the particulate phase. However, this analytical artifact is likely minor for the target analytes and would not explain the higher 6:2 FTS in the effluent than influent. Zhao et al. (2020) measured a log distribution coefficient (Kd) between suspended particles and the dissolved phase in river water of 2.65 ± 0.24. Munoz et al. (2019) measured a similar log Kd of 2.4 ± 0.2 between suspended particles and estuary water. Assuming a log Kd of 2.65 and a typical influent TSS concentration of 100 mg/L, the percent of influent 6:2 FTS in the particulate phase would be around 4%. Kd may differ between wastewater influent and river or estuary water, but this data was not available for...
wastewater in the literature to the best of our knowledge. Regardless, any 6:2 FTS sorbed to influent particles would be expected to exit the system via the sludge wasting stream rather than desorb and exit via the effluent.

PFAS dynamics documented in this study show evidence of a degradation pathway in which one or more precursor PFAS compounds were readily broken down to 6:2 FTS. If 6:2 FTS was present in the Ansulite AFFF concentrate, it would be expected that influent concentrations of 6:2 FTS would be higher than effluent concentrations, but this was not the case. Rather, pre-TOP data show that 6:2 FTS concentrations in the influent were much lower than the effluent concentration (Fig. 4). This 6:2 FTS increase indicates that 6:2 FTS was produced through the degradation of an unidentified precursor in the AFFF. The TOP assay data showed the opposite trend, with as much as 9 times higher total precursors in the influent than the effluent, particularly shortly after AFFF addition (Fig. 5). Assuming average PFCA molar yields from Houtz and Sedlak (2012), the PFCA formation in the influent and effluent were over 600 and 9 times greater than could be explained by the measured polyfluorinated compounds, respectively (Fig. 5).

Although these dynamics have been documented for non-AR foams in soil microcosms (Harding-Marjanovic et al., 2015) and
within a small, high rate treatment plant (~0.5 MGD and 1.5–3 h HRT, Houtz et al., 2018), this study is the first to show evidence of a similar breakdown pathway for an AR-AFFF within a biological nutrient removal (BNR) wastewater treatment design with a considerably longer HRT.

Previous studies have found that other Ansul products that contain high concentrations of 6:2 fluorotelomer thioamido sulfonate (6:2 FtTAoS), commonly referred to by its trade name Lodyne, can quickly degrade into 6:2 FTS when exposed to microbial activity or strong oxidation (Bruton and Sedlak, 2017; Harding-Marjanovic et al., 2015; Houtz et al., 2018). In this study, 6:2 FtTAoS was not quantified because standards were not yet available, so it is not known whether this was the precursor compound that led to increased 6:2 FTS levels in SBRs. However, the idea that there are classes of precursors in newer formulations of AFFF that result in 6:2 FTS formation has been confirmed by industry representatives (Cortina and Korzeniowski, 2008).

Additional support for Ansulite AR-AFFF precursor breakdown to 6:2 FTS can be seen upon inspection of 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) data, which are available for influent and effluent, but were not quantified in solid samples. This compound is a known precursor to 6:2 FTS that has been added to certain recent AFFF formulations and has been shown to aerobically degrade into short chain PFAAs in activated sludge microcosms (D’Agostino and Mabury, 2017; Shaw et al., 2019). The fact that there was more 6:2 FTAB in the influent than in the effluent following Ansulite addition indicates that it was potentially breaking down into other compounds like 6:2 FTS (Fig. 6). However, the concentrations of 6:2 FTAB in the influent (320–360 ng/L) cannot explain the 9200 ng/L 6:2 FTS spike seen in the reactor effluent. Thus, another precursor compound that was not directly measured in this study is likely leading to the large 6:2 FTS spike that was documented.

It appears that 6:2 FTS was not broken down readily via wastewater treatment; lower detections in aqueous and solids matrices occurred due to losses via effluent discharge and solids wasting (Fig. 7). This is evident based on the molar mass balance of 6:2 FTS with known degradation intermediates (6:2 Fluorotelomer unsaturated carboxylic acid (6:2 FtUCA), 5:3 Fluorotelomer carboxylic acid (5:3 FtCA)) and short chain, terminal perfluoroalkyl carboxylic acid (PfCA) products of 6:2 FTS degradation—perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), and perfluorohexanoic acid (PFHxA) Perfluorohexanoic acid (PFHpA; Wang et al., 2011; Houtz and Sedlak, 2012; Harding-Marjanovic et al., 2015; Bruton and Sedlak, 2017). While the flux of 6:2 FTS is shown to reach a maximum two days after AFFF addition and then decline, the sum of intermediates (only measured in aqueous samples) and terminal, short chain PFCAs (PFBA, PFPeA, PFHxA, PFHpA) in the same samples make up a much smaller proportion of the total PFAS content (Fig. 7). In addition, 75% of the 6:2 FTS was removed from reactor solids within one SRT after initial AFFF addition. Polyfluorinated compounds with 6:2 fluorotelomer moieties generally have comparable TOP assay molar yields (Boiteux et al., 2016; Houtz and Sedlak, 2012; Martin et al., 2019). Thus, the decrease in TOP assay precursors in the SBR indicates that a substantial fraction of the unidentified precursor(s) sorbed to the solids and were removed by solids wasting as well. Indeed, some studies have found that polyfluorinated compounds can sorb more readily to sludge than their perfluorinated counterparts (Arakaki et al., 2017).

The 6:2 FTS dynamics documented here fit well with what has been previously seen in other studies. While precursor compounds can be rapidly biotransformed aerobically to 6:2 FTS, degradation of 6:2 FTS under normal environmental conditions is often much slower (Bruton and Sedlak, 2017; Harding-Marjanovic et al., 2015; Wang et al., 2011; Zhang et al., 2016). Desulfonation, which is required to break down 6:2 FTS, is very slow and appears to be the rate limiting step in its breakdown to short chain PFCAs (Wang et al., 2011; Zhang et al., 2016). According to the degradation pathway proposed by Harding-Marjanovic et al. (2015), desulfonation of 6:2 FTS will result in 6:2 FtUCA. Further transformation of 6:2 FtUCA will result in either 5:3 FtCA or terminal short chain

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**Fig. 6.** Influent and effluent concentrations of 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) over time. Times of AFFF addition as well as one hydraulic residence time (HRT: length of time liquid will remain in a treatment process, calculated as tank volume divided by flow rate) after AFFF addition are denoted by dashed lines.
PFCAs (PFBA, PFPeA, PFHxA, or PFHpA; Harding-Marjanovic et al., 2015).

Other than 6:2 FTS and its known precursors and degradation products, four additional terminal PFAAs were detected throughout this study in influent and effluent samples but did not show large changes pre- and post AFFF spike (Fig. S6). In addition, five terminal PFAA compounds were detected in solid samples, but did not seem to fluctuate with the addition of AFFF to the reactor (Fig. S7). It is probable that these compounds represent background PFAS concentrations within the aqueous and solid matrices.

3.3. Relative residence time of PFAS

One of the first steps in understanding implications for downstream processes after an unintended AFFF release to a treatment plant is to determine how long the PFAS will remain in the system at high concentrations. Because 6:2 FTS was the predominant PFAS compound measured within SBRs, it was used as a proxy for AFFF-associated PFAS in the system. Five HRTs after AFFF was removed from the raw water feed drums on 8/28/19, 6:2 FTS concentrations had fallen to 30% of the highest measured concentration in the reactor effluent. In addition, 0.44 SRTs after AFFF was no longer being added to reactors, 6:2 FTS concentrations had been reduced to 29% of the highest measured solids concentrations. At the end of the experiment, 36 days after AFFF addition (= 36 HRTs and ~2 SRTs), detectable levels of 6:2 FTS still remained in solids, but were 8% of the maximum concentration detected. Extrapolating these data to operational time scales at HRSD’s Nansemond Plant (Suffolk, VA), which is a full-scale 5-stage Bardenpho plant, would result in an approximate four-day requirement (3.75 based on HRT; 4.44 based on SRT) for 70% of the maximum PFAS concentrations to move out of the system.

4. Conclusions

Here we investigated potential treatment impacts associated with short-duration fluxes of two types of AFFF into a simulated wastewater treatment process. Such an event would likely be associated with minimal treatment upsets; MLVSS loss due to foaming during aeration and short-duration nitrification rate reductions were observed in test reactors spiked with high concentrations of AFFF. In addition, an AFFF release would be accompanied by a flux of fluorotelomer precursors that would be rapidly degraded under aerobic conditions to 6:2 FTS and more slowly to terminal PFCAs. It is estimated that in a comparable full-scale treatment plant, 6:2 FTS concentrations in effluent and solids would be reduced by 70% in approximately four days. If an accidental release of AFFF were to occur, this information would be useful to staff for operational adjustments to downstream processes like potable reuse and biosolids production. In addition, the PFAS dynamics documented here, particularly those surrounding 6:2 FTS are likely still applicable to the lower concentrations of PFAS that are typically documented at wastewater plants.

Credit author statement

Dana Gonzalez: conceptualization, methodology, writing-original draft, investigation; Kyle Thompson: writing-review & editing, methodology, investigation; Oscar Quiñones: writing-review & editing, methodology, investigation; Eric Dickenson: supervision, writing-review & editing, methodology; Charles Bott: supervision, writing-review & editing, methodology, resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Reference to a specific document with natural text.
Bio-P: Biological phosphorus removal: Wastewater treatment configuration used to remove phosphorus that uses an anaerobic zone where polyphosphate-accumulating organisms (PAOs) uptake volatile fatty acids (VFA) and release phosphorus; in the aerobic zone following the anaerobic zone, phosphorus is taken up again and results in low effluent phosphorus concentrations.

BNR: Biological nutrient removal: Typically refers to wastewater treatment configurations that enhance the removal of nitrogen and/or phosphorus.

COD: Chemical oxygen demand: Laboratory measurement that is used to as an indirect measurement of the amount of organic matter in a sample.

sCOD: Soluble chemical oxygen demand: COD test performed after filtration, which removes particulate compounds before analysis.

HRT: Hydraulic residence time: Length of time liquid will remain in a treatment process. Calculated as tank volume divided by flowrate.

MLVSS: Mixed liquor volatile suspended solids: Organic fraction of particulate matter in a sample.

NOB: Nitrite oxidizing bacteria: Group of bacteria involved in nitrification that oxidize nitrite to nitrate.

PAO: Polyphosphate-accumulating organisms: see Bio-P above.

SBR: Sequencing batch reactor: Reactors that are used to treat wastewater in a single basin sequentially rather than in a flow-through system.

SRT: Solids residence time: Measure of the amount of time solids will remain in a treatment process. Calculated as total mass of solids divided by the mass of solids wasted each day.

SVI: Sludge volume index: Laboratory analysis that is used to assess the settleability of sludge. Calculated as settled sludge volume divided by mixed liquor suspended solids concentration.

TKN: Total Kjeldahl nitrogen: Total concentration of organic nitrogen and ammonia nitrogen.

TSS: Total suspended solids: Laboratory measurement used to describe dry weight of particulate material in a sample.