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Transport and Fate of Aqueous Film Forming Foam in an Urban Estuary

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Abstract

The deployment of aqueous film forming foams (AFFF) used for firefighting during emergencies and training often releases per- and polyfluoroalkyl substances (PFAS) into the environment. In October 2018, first responders in Providence, RI, USA applied an AFFF during a fuel spill. Due to the proximity of the incident to the upper reaches of Narragansett Bay (NB), an unknown quantity of gasoline and AFFF entered the estuary via surface runoff and stormwater drains. Water samples near the spill were collected approximately 15 hours after the incident and analyzed for 24 PFAS. Minor increases in measured PFAS concentrations were observed relative to pre- and post-spill samples at monitoring sites near the incident, except 6:2-fluorotelomer sulfonate (6:2-FTS) that peaked post-spill (max 311 ng/L). After performing the total oxidizable precursor (TOP) assay on water samples and the AFFF concentrate, significant increases in perfluorocarboxylic acids (PFCAs) were observed. One compound, 6:2-fluorotelomer mercaptoalkylamido sulfonate (6:2-FTSAS), was identified as a major component of the AFFF used. Peak areas of 6:2-FTSAS and the degradation product 6:2-FTSAS-sulfoxide corresponded to observed increases in the TOP assay results and were useful as tracers of AFFF in surrounding waters. Elevated levels of PFAS at the time of sampling were limited to a confined area of the Providence River due to river flow and tidal action. Observed concentrations were also compared to hydrodynamic model results, and results confirmed rapid dissipation of AFFF components with distance from the spill. However, modeled results did not capture possible secondary releases of AFFF from local municipal stormwater and sewer infrastructure, as observational data suggest. The multiple lines of evidence of PFAS present in surface waters permitted a better assessment of the potential environmental impacts from products such as AFFF for which the chemical composition is largely unknown.

Keywords: aqueous film forming foam (AFFF), per- and polyfluoroalkyl substances (PFAS), surface water, 6:2-fluorotelomer sulfonate (6:2-FTS), 6:2-fluorotelomer mercaptoalkylamido sulfonate (6:2-FTSAS), class B foam
1 Introduction

Fluorosurfactants are a group of synthetic organic compounds within the broader class of per- and polyfluoroalkyl substances (PFAS) and became available commercially in the 1950s. Like other surfactants, fluorosurfactants have a hydrophobic “tail” and a hydrophilic “head” as part of their chemical structure (Pabon and Corpart, 2002). Due to the physico-chemical properties of fluorosurfactants (i.e. lowering of aqueous surface tension, thermal and chemical stability), these compounds excel when applied to suppress or extinguish liquid fuel fires, where using only water would be ineffective (Kissa, 2001). By 1972, AFFFs synthesized by the electrochemical fluorination process contained perfluorooctane sulfonate (PFOS) and other homologs, and were in widespread use by the US Navy (Gipe and Peterson, 1972). AFFFs based on the fluorotelomerization process were first listed on the US military’s qualified products list in 1973 (Korzeniowski et al., 2018). Historically, compounds manufactured by these methods had fluorocarbon backbones ($C_nF_{2n+1}$) where $n$ ranged from four to ten and were primarily composed of long chain PFAS greater than six perfluorocarbon atoms (Améduri and Boutevin, 1997). PFOS was eliminated from AFFFs voluntarily by the primary manufacturer and via the U.S. Environmental Protection Agency’s (EPA) significant new use rule which provided for the continued production of PFOS only in limited applications (USEPA, 2002). Similarly, in the 2010/15 PFOA Stewardship Program, the manufacturers of PFAS containing products (including AFFFs) committed to eliminating compounds that degrade to perfluorooctanoic acid (PFOA) or other long chain homologs (USEPA, 2006). Modern AFFF formulations for fuel or solvent fire suppression are proprietary mixtures which typically contain one or more fluorotelomer surfactants based on six carbon chemistries (i.e. $C_6F_{13}$ tail) as a minor constituent (<2 %) and other hydrocarbon or protein-based surfactants (up to 20%), polar solvents (up to 20%) and water (>60%) in the formulation (Korzeniowski et al., 2018; Pabon and Corpart, 2002; Ruyle et al., 2021).

While AFFFs were originally designed for military use, they have also been used extensively by municipal fire departments, airports, as well as chemical and hydrocarbon storage and processing facilities (Hu et al., 2016; Moody and Field, 2000). Fluorosurfactants produced by telomerization have been shown to ultimately degrade to perfluoroalkyl carboxylic acids (PFCAs) such as perfluorooctanoic acid (PFOA) and perfluorohexanoic acid (PFHxA) along with other intermediate perfluoroalkyl degradation products (Wallington et al., 2006; Wang et al., 2011; Weiner et al., 2013). The long-term use of AFFFs during training and emergency response has resulted in the widespread contamination of ground and surface waters near industrial sites, airports, and military bases (Hu et al., 2016). Further,
Hundreds of individual fluorinated AFFF compounds have been identified in commercial AFFF products (Backe et al., 2013; Barzen-Hanson et al., 2017; D’Agostino and Mabury, 2014; Place and Field, 2012). As a result, many of these compounds or their degradation products have been detected in groundwater and drinking water (Backe et al., 2013; Boone et al., 2019; Gebbink et al., 2017; Houtz et al., 2013; Hu et al., 2016; Moody et al., 2003). Due to the high mobility of PFAS in aqueous media, AFFF has also been measured in inshore and offshore surface waters (Benskin et al., 2012; Miranda et al., 2021; Möller et al., 2010; Nguyen et al., 2017; Zhao et al., 2012). Finally, quantification of the PFAS constituents present in aqueous samples post spill remains unachievable due to the lack of analytical standards for PFAS present within modern AFFFs.

In some cases, AFFF compounds or their degradation products have been identified and found to bioaccumulate in invertebrates, fish, reptiles, birds and mammals in both freshwater and marine environments (Ahrens and Bundschuh, 2014; Gebbink et al., 2016; Langberg et al., 2019; Moe et al., 2012; Munoz et al., 2017; Palmer et al., 2019; Robuck et al., 2020; Shi et al., 2019) and have associated adverse health effects in humans and model organisms (Shi et al., 2018; Sunderland et al., 2019). For example, research has shown adverse impacts to liver function on downstream fish populations following another spill event (Oakes et al., 2010). AFFF components have also been detected in Arctic environments and organisms (Benskin et al., 2012; Yamashita et al., 2005), far afield from their point of use and reminiscent of the global transport of conventional persistent organic pollutants (Wania and MacKay, 1996), albeit by different mechanisms (Johansson et al., 2019). While a number of toxicity studies have investigated effects of legacy foams, few toxicity studies on fluorotelomer based foams have been performed to date, and information on the impacts and effects of AFFF deployed during emergency response in estuaries and coastal areas remains limited.

As part of an existing research program, the US EPA Atlantic Coastal Ecological Sciences Division had previously planned PFAS monitoring throughout Narragansett Bay (northeastern USA). The night before scheduled monitoring, a tanker truck overturned in Providence (RI, USA) and a significant amount of gasoline was released which required the application of AFFF. The primary objective of this effort was to determine the occurrence, behavior, and fate of AFFF present in Narragansett Bay waters immediately following the spill incident by grab samples of surface water following the spill. A second goal was to compare field results to a modeled tracer using a hydrodynamic model developed for use in NB. A third goal was to use the total oxidizable precursor (TOP) assay to convert unidentified PFAS into measurable compounds to better assess the total amount of PFAS present in NB. Finally, we also
searched prior published results of AFFF composition to identify major foam components useful for tracking AFFF residues in NB.

2 Methods

2.1 Study location and sample collection

The port of Providence, Rhode Island is located at the head of Narragansett Bay (NB) and the waterfront on the Providence River is heavily industrialized, with a number of petroleum storage and distribution facilities. In addition, the city hosts numerous industries which may contribute to PFAS concentrations within NB, including metal coating/plating, textile mills, paint/coating/adhesive manufacturing, paper manufacturing, waste and sewage treatment (Zhang et al., 2016).

On the evening of October 3, 2018, a tanker truck departing a petroleum distribution center in the waterfront area overturned soon after leaving the location. This accident resulted in the leakage of approximately 40,000 liters of automotive gasoline onto city streets (Figure 1). As part of the emergency response activities, approximately 4,500 liters of alcohol resistant AFFF concentrate (Thunderstorm W833A (Williams Fire & Hazard Control, Port Arthur, TX)) was diluted and applied by firefighters to the spill for vapor suppression and ignition prevention. Although approximately 68,000 liters of AFFF, water and gasoline mixture were collected during cleanup efforts, an unknown quantity of gasoline and dilute AFFF infiltrated the pervious surfaces nearby the spill and entered the Providence River via stormwater drains as runoff (RIDEM, 2019). Due to the mixture of private and public stormwater and sewer infrastructure in the city, and the amount of AFFF applied to the spill, AFFF also may have penetrated infrastructure (e.g. manhole covers) which discharges stormwater indirectly to the Providence River via the local wastewater treatment plant (WWTP).

Sampling of the surface waters of the Providence River occurred approximately 15 hours after the start of the incident. The spill roughly coincided with high tide and samples were collected during the ebb of the next high tide. Winds were low (<5 m/s) during the period between the spill and sample collection at both the head and mouth of the Providence River (Supplemental Figure 1). Freshwater input to the upper Providence River was higher than average during sampling, with total flow from the major tributaries on the day of the spill of 90 m$^3$/s (Supplemental Table 1) and monthly average flow over the previous ten years of 22 m$^3$/s (USGS, 2019). Ungauged contributions to streamflow data were not accounted for and were considered negligible. Nine surface water samples along a north-south transect in the area of the spill were collected (Figure 1). Surface samples were collected from a depth
of 0.5 meters in pre-cleaned one-liter HDPE bottles and kept on ice in the field and stored at 4 °C in the dark upon returning to the lab. The FP station (Figure 1) was part of monthly monitoring performed independently of this investigation and comparisons to conditions pre- and post-spill were therefore possible at this location.

A sample of the AFFF concentrate applied to the spill was donated by the Rhode Island Department of Environmental Management and diluted in methanol at concentrations ranging from 19 ng/mL to 19 μg/mL for evaluation and characterization by mass spectrometry analysis. No public information on the exact composition of this product is available in the marketplace, the scientific literature or from the manufacturer. The product safety datasheet states that it contains “polyfluorinated alkyl polyamide” between a 1% and 5% concentration.

2.2 Water Sample Preparation and Analysis

Water samples were analyzed for 24 PFAS that have certified calibration standards, consisting of eleven PFCAs, seven perfluoroalkane sulfonic acids (PFSAs), one perfluoroalkane sulfonamide (FASA), two perfluoroalkane sulfonamido-acetic acids (FASAAs) and three n:2 fluorotelomer sulfonates (FTS) as shown in Table 1. After collection, water samples (500 mL aliquots) were fortified with 10 ng isotopically labeled internal standards (Wellington Laboratories, Guelph, Canada) and extracted via weak anion exchange sorbent material (Oasis WAX 150 mg, Waters Corp, Milford MA). Solid phase extraction cartridges were conditioned using 6 mL of methanol with 0.1% ammonium hydroxide, followed by 6 mL of methanol and 6 mL of C18 polished PFAS free water (MilliQ, Millipore Sigma, Burlington, MA). Samples were loaded onto the cartridges at 5 mL/min and cartridges were washed with PFAS free water and dried for 15 min by nitrogen gas. Cartridges were eluted with 6 mL of methanol followed by 6 mL of methanol modified with 0.1% ammonium hydroxide (Taniyasu et al., 2005). All solid phase extraction steps were automated using an AutoTrace 280 system (Thermo Scientific, Waltham, MA), modified to remove most fluoropolymer components. Sample extracts were then taken gently to dryness (EZ2 Plus, Genevac, Warminster, PA) and constituted with 1 mL of 75:25 water: methanol with 2 mM ammonium acetate.

In addition to the targeted analysis of water samples described using individual calibration standards, a total oxidizable precursor (TOP) analysis was conducted following a slightly modified procedure from Houtz and Sedlak (2012). TOP is a procedure that uses a heat and persulfate mediated
hydroxyl radical reaction to convert unknown or “precursor” PFAS compounds, which cannot be individually identified due to the lack of commercial standards, to PFCAs for which standards are available. TOP samples were oxidized by the addition of 160 mM of sodium hydroxide (Sigma Aldrich, St. Louis, MO), 60 mM of potassium persulfate (Sigma Aldrich, St. Louis, MO) and heated for 6 hours at 85 °C in a water bath (Memmert, Eagle, WI). After cooling, samples were adjusted to pH 5—7 using concentrated trace metal grade hydrochloric acid (J.T. Baker, Center Valley, PA) and fortified with 10 ng of internal standard before extraction following the same procedure previously described for water samples. This procedure was performed on field collected samples and diluted AFFF used in the spill response. AFFF dissolved in methanol was added to 100 mL of PFAS free water at zero salinity (DIW) and artificial seawater at a salinity of 30 ppt (ASW). Both DIW and ASW were amended with 1000 ng of the AFFF for assessment via the TOP assay. According to the manufacturer’s safety data sheet at this concentration of AFFF, 10–50 ng of the unidentified PFAS portion of the AFFF may be present per 100 mL. Water samples (100 mL) collected in October 2018 from sites near the spill were also oxidized using the same TOP procedure as the AFFF samples. Samples from before the spill (July 2018) and after (December 2018) at the FP station were also extracted for the targeted analytes and subjected to TOP analysis for comparison to samples from the date of the spill. All oxidations were performed in triplicate and averaged between 6.9 – 43 %RSD for reported compounds.

Samples were analyzed by ultra-high-performance liquid chromatography coupled to a tandem quadrupole mass spectrometer (MS/MS) system (Xevo TQD, Waters Corporation). Compounds were eluted using a water:methanol gradient modified with 2 mM ammonium acetate (Supplemental Table 2). PFAS analytes were detected by the MS/MS system using multiple reaction monitoring mode with specific ionization conditions optimized for each target analyte and quantified by isotope dilution (Supplemental Table 3). Detection and reporting limits were determined individually for each compound (Supplemental Table 4). An eleven-point calibration curve was performed and coefficients of determination (R²) were ≥0.99 for all compounds reported. Extraction recoveries for reported analytes ranged from 71 – 123 %, with the exception of PFNS (40 %).

All statistical analysis on water PFAS concentrations was performed in SigmaPlot 14 (SyStat Software, Inc., San Jose, CA).

2.3 Hydrodynamic Model

Hydrodynamic simulations of the Providence River were performed using the Regional Ocean Modeling System (ROMS) finite difference numerical model (Haidvogel et al., 2008; Shchepetkin and
McWilliams, 2005). The model is three-dimensional and includes stratification, rivers, tides, and atmospheric forcing. A non-reactive virtual dye (VD) tracer was added near the spill site to simulate the transport of PFAS, but does not account for any PFAS-specific chemical properties and was not intended to directly predict PFAS concentration, only a proxy for relative distribution. The VD acts as a neutrally buoyant, conservative Lagrangian tracer, tracking both the advection and diffusion of a non-reactive chemical within the water. The VD was added to the top four model vertical layers on October 3, 2018 18:30 EDT and fifteen terrain-following “sigma” layers were used which expand or contract while following changes in the local bathymetry. At the point of injection, the four virtually dyed layers correspond to approximately the top 1 m of the water column. Atmospheric forcing was obtained from the NOAA North American Mesoscale model. River discharge was added to the model using river gauge observations from USGS and accounted for ungauged downstream flow. Tidal forcing was applied at the open boundaries using depth-integrated velocities and surface elevations from a tidal model of the North Atlantic (Szpilka et al., 2016). The temperature and salinity fields in the model were initialized using a full-year 2018 hindcast spin-up run. Modeled temperature, salinity, surface elevation (tides) and currents were each validated over an annual cycle and showed high levels of agreement with observations (Ullman et al., 2019). Further details on model construction are available in the SI.

3 Results and Discussion

3.1 Targeted PFAS

Spatial Analysis. Results of the targeted analysis for all stations (Table 2) showed concentrations ranging from below detection to 6.3 ng/L for individual PFCAs and from below detection to 8.1 ng/L for individual PFSA during the October 3, 2018 sampling (Table 2). The six station transect within the Providence River showed increases in concentrations of perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) upriver from transect station PR1 at the river mouth to PR5 which was located near the outfall of the WWTP (Figure 2A & 2B). Most PFCA and PFSA compounds decreased in concentration from PR5 to PR6 which was located nearest to the spill, with the exception of PFNA. Concentrations of 8:2-FTS followed a similar trend to the PFCA and PFSA compounds and were at their highest concentrations at PR5 and decreased to the north and south, suggesting the proximity of a nearby source (Figure 2B). Concentrations of FOSA and the FTS compounds other than 8:2-FTS
continuously decreased upriver. Concentrations of 6:2-FTS were the highest of all compounds and decreased from 311 ng/L at PR1 to 18 ng/L at PR6. Analysis of the AFFF used indicated 6:2-FTS was not present in this foam. However, it has been confirmed as a minor component in several AFFF products (Backe et al., 2013; Place and Field, 2012), some industrial processes (e.g. metal plating operations) replaced PFOS with 6:2-FTS, and previous research has shown elevated 6:2-FTS levels in the bay (Zhang et al., 2016).

Overall, concentrations of total combined PFCAs and PFSAs ranged between 15 ng/L and 26 ng/L in the Providence River transect sites and were highest at PR5 nearby the outfall of the local WWTP. Levels of PFAS in this range have previously been reported in NB surface waters (Zhang et al., 2016).

A sample of the AFFF applied to the spill was diluted and analyzed using the described method for targeted PFAS analysis. None of the targeted analysis compounds were above detection limits, confirming that the AFFF was not a source of the targeted compounds. However, if the precursor components of the AFFF deployed during the spill were oxidized or degraded before application, a quantifiable amount of PFCAs or PFSAs might be expected in the targeted analysis. The absence of these compounds in the diluted foam confirms that PFAS components in the AFFF used had not degraded significantly in the period before their application and environmental release from this event.

Temporal Analysis. Monthly monitoring for PFAS throughout NB enabled temporal comparisons at stations in proximity to the spill transect stations before and after the spill event. Comparisons were possible at the FP site for July, October (spill event) and December 2018. Concentrations of PFBA, PFPeA, PFHxA, PFHpA, PFOA, and 6:2-FTS showed higher concentrations in October relative to July and December 2018 samples (Figure 3A). Of all compounds present at the FP site in October, 6:2-fluorotelomer sulfonate (6:2 FTS) was observed at the highest concentrations compared to pre- and post-spill conditions. 6:2 FTS concentrations at the FP site increased 5-fold between July (13 ng/L) and October (71 ng/L) and decreased by nine-fold between October and December (8 ng/L). Explanation of the elevated levels of 6:2-FTS at sites in close proximity to the spill event was not readily apparent. Analysis of the AFFF used during this event showed no measurable levels of 6:2-FTS leading to several scenarios for its presence in the surface water at levels far exceeding those observed during pre- and post-conditions. First, it is possible that a second unknown AFFF was also applied to the gasoline spill which contained this compound as an active constituent, however we believe this is unlikely based on firsthand accounts (RIDEM, 2019). Second, degradation of components in the AFFF used may have resulted in production of 6:2-FTS post-application, as has been recently shown in bench level testing.
Third, and least likely, an unknown source may have discharged 6:2-FTS concurrently and coincidentally but unrelated to the spill response.

**AFFF in the Providence River.** As previously noted, comparisons of the pre- and post-spill results of the targeted analytes do not show highly elevated levels of PFAS in the Providence River with respect to the spill event and the AFFF used did not contain measurable amounts of PFAS present in the targeted analysis list. To further investigate the cause of the observed increase in the PFAS upriver from PR1, a diluted aliquot of the deployed AFFF was also directly infused to the mass spectrometer to identify prominent spectra and transitions of compounds for which published data exists. Significant mass spectral intensity was observed at 586 m/z (Supplemental Figure 4) with five corresponding characteristic MS/MS fragment ions of (m/z 90, 104, 135, 152 and 206) most dominant in intensity (Supplemental Figure 5). This spectra and resulting product ions are consistent with 6:2 fluorotelomer-mercaptoalkylamido sulfonate (6:2-FTSAS) a ubiquitous component of AFFF formulations alternatively known as 6:2-fluorotelomer thioamido sulfonate or 6:2-fluorotelomer thioether amido sulfonate (6:2FtTAoS) and 6:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate (6:2-FTTh-PrAd-DiMeEtS) (Backe et al., 2013; Field et al., 2003; Harding-Marjanovic et al., 2015; Mejia-Avendaño et al., 2017; Place and Field, 2012; Ruyle et al., 2021; Weiner et al., 2013). Water samples extracted for the targeted analysis were reanalyzed for 6:2-FTSAS and 6:2-FTSAS-sulfoxide, a known degradation product of 6:2-FTSAS previously identified in both sterile and activated sludge biodegradation treatments (Weiner et al., 2013) and aerobic soil microcosms (Harding-Marjanovic et al., 2015; Yi et al., 2018). Results showed high peak areas decreasing in intensity with distance from the WWTP outfall area (Figure 4), with 6:2-FTSAS-sulfoxide peak areas following the same trend but approximately an order of magnitude lower in intensity. The highest signals occurred directly adjacent to the WWTP outfall, suggesting that some AFFF applied to city streets which entered the Providence River near PR6 via surface runoff or stormwater drains north of the WWTP outfall was not the source of elevated peak areas at the time of sampling at PR5 nearer to the WWTP outfall. Intriguingly, while 6:2-FTSAS decreased in intensity downriver, 6:2-FTS increased in concentration downriver. This behavior was unexpected as most industrial effluent contributing to 6:2-FTS concentrations in the Providence River enter from points further north at the head of the river. While biodegradation experiments using freshwater activated sludge bottle experiments and freshwater microcosms have shown that 6:2-FTSAS degrades to 6:2-FTS (Harding-Marjanovic et al., 2015; Weiner et al., 2013), the timescales reported for transformation were longer than the typical travel time of surface water flows observed during this study. However, 6:2-FTSAS may also degrade more directly by S-dealkylation via P-450 enzymatic activity (Weiner et al.,...
This observation makes speculation regarding increased degradation rates of this compound in seawater systems relative to freshwater systems tempting as marine microorganisms are efficient processors of both inorganic and organic sulfur compounds (Moran and Durham, 2019). The presence of 6:2-FTSAS and 6:2-FTSAS-sulfoxide, identified by their characteristic mass transitions, were useful as tracers of AFFF discharge to the PR and greatly aided the determination of the ultimate fate of AFFF applied to city streets. Unfortunately, these compounds do not have commercially available authentic standards and therefore were not quantifiable during this study.

3.2 Total oxidizable precursors

TOP analysis was performed on water from the transect stations sampled approximately 12 hours after the spill occurred. Concentrations of all PFCAs clearly increased upriver with a maximum at the PR5 station and decreased again at site PR6 further to the north (}
Figure 5). From PR3 station and further north to station PR6, the highest concentrations were observed for PFPeA, followed closely by PFHxA and PFBA. Outside of this area, post-TOP compound concentrations showed no clear pattern. While many PFCAs were not present at the southernmost stations, all PFCAs were present at the FP, PR5 and PR6 stations. The concentrations of PFBA, PFPeA and PFHxA present relative to the other PFCAs indicate upper NB received the discharge of precursor compound(s) with a six-carbon backbone or longer associated with AFFF (Barzen-Hanson et al., 2017; Houtz et al., 2016). This data reflects stated industry trends of eliminating the inclusion of eight-carbon chemistries in AFFF products (USEPA, 2006) and the increased utilization of six-carbon compounds in contemporary AFFFs (Ruyle et al., 2021).

To confirm that the observed levels from the TOP analysis of the transect site samples were not common to the Providence River and were associated with the AFFF deployment, TOP analysis was also performed on the water samples collected at the 3 monthly monitoring sites in the Providence River from July, October and December 2018. Results showed highly elevated levels of several compounds only during the October sampling at the Fields Point Reach station (Figure 3B). The highest concentrations were of PFPeA (859 ng/L) followed by PFHxA (533 ng/L), PFBA (447 ng/L), PFHpA (200 ng/L), PFOA (118 ng/L) and PFNA (44 ng/L). After the TOP assay, PFCA concentrations were all below 8 ng/L at Fields Point in July and December and were below 8 ng/L for all sampling periods at the other two Providence River stations (Supplemental Figure 3).

Stormwater flow in the immediate area around the spill is also collected, channeled and discharged into the river through a series of private stormwater systems located on industrial facilities along the waterfront. The lower relative concentrations between the PR5 and PR6 sites (Figure 5) suggests that any discharge of foam from the private stormwater system had subsided and was diluted by surface freshwater flow and tidal action between the occurrence of the spill and sample collection. The elevated PFAS concentrations following TOP assay of the FP and PR5 samples from October suggests that some quantity of the deployed AFFF was not only washed into to the stormwater systems in the vicinity of the incident which discharge directly to NB nearby PR6. Due to the amount of diluted AFFF deployed (~45,000 L) some pooling in the road and penetration of liquids through sewer manifolds clearly occurred. Stormwater south of the spill area rarely discharges directly to the Providence River due to the construction of interceptors which divert public stormwater and combined sewer overflows to the local WWTP where it is treated and discharged to the Providence River. Gas monitoring at the head of the treatment works indicated the presence of gasoline, but levels were low enough not to
affect treatment operations. While the presence of gasoline in the treatment works was limited post spill, the detection of gasoline at the treatment plant headworks suggests that a mixture of spilled gasoline, water and AFFF applied to the spill was partially routed to the WWTP.

The TOP procedure was also conducted on the AFFF at three different diluted concentrations in PFAS free de-ionized water (DI) and artificial seawater. Results showed a linear response across the range for the shorter chain PFCAs with Pearson’s correlations above 0.8 and p-values below 0.05 (Supplemental Table 5). The manufacturer statement indicated that level of PFAS in the AFFF was 1-5% of a proprietary compound, and it was therefore assumed that approximately 10–50 ng out of every 1000 ng of AFFF was a PFAS compound. However, a quantitative mass balance was impossible, as identities and molecular weights of all potential precursor compounds present in the AFFF are required for a complete mass computation. When normalized to AFFF oxidized in each treatment, total PFCAs produced from the TOP procedure performed on the AFFF varied widely with 107 mg PFCAs per gram AFFF with a 45 % relative standard deviation.

Not all PFAS compounds present in the AFFF or water samples may be oxidizable by the TOP method, and compounds may also oxidize to PFAS not part of the 24-compound targeted analysis list such as perfluoro acetic and propionic acids. In addition, natural degradation pathways of PFAS precursors may differ from those that occur when using the TOP method. Regardless, results of the TOP assay help to improve the understanding of potential exposure from unknown PFAS.

3.3 Hydrodynamic Model

Water grab samples at the same time and sampling locations and used to assess the fate of AFFF discharged to NB were compared with patterns of dispersion and transport of virtual dye (VD) from a point source location within the Providence River. The model results showed a decline in VD concentration moving both north and south from station PR5 concurring with the observational PFAS results. It is interesting, though not unexpected, that the observational data typically show higher PFAS concentrations at PR3 than PR4, which is 4 km south of the VD source (spill location). This is due to the extreme vertical and lateral gradients in subtidal flow the Providence River has been shown to exhibit (Kincaid, 2001, 2012, 2018), which may separate a water parcel and associated PFAS or other contaminants into distinct sections. Though situated significantly further southward, station PR3 lies near the shoals along the western edge of the shipping channel, where a remarkably stable jet flushes
water (and contaminants) southward (Kincaid, 2001, 2012). The starkest contrast between the model output and observation was the overprediction of the VD concentrations in the southern Providence River (at PR2 and PR1) relative to measured PFAS concentrations which trended toward zero. The model sequence of the VD (Figure 6) shows rapid southward advection within the first 3.5 hours after release. The VD was released during an ebb tide (concurrent to the spill event) when winds were toward the northeast and the following flood tide was not enough to transport the dye out of the lower Providence River, as seen during the high tide 9.5 hours after release (Figure 6c) when the VD was expected to reach its maximum northward extent. At the sampling time (Figure 6d), VD north of Fields Point had collected on the western shore while dye south of Fields Point appeared to converge on the shallow shoals.

The model predicts a large percentage of VD makes it south, past the mouth of the Pawtuxet River by the time of sampling. The channel in this area trends from northeast to southwest, towards and past the Pawtuxet River mouth (west side of the channel near PR3), and prior results have shown this is an important hydrodynamic dividing point for chemical plumes from the north (Kincaid, 2012). Numerous factors are predicted to control the relative percentages of VD that either a) passes south of this point or b) gets caught in the ES gyre. Even subtle differences in local winds, runoff and mixing can strongly influence this chemical choke point. In this model run, there was a large percentage of VD predicted to make it south of the Pawtuxet mouth and into lower Providence River as quickly as 1-2 tidal cycles after the release (Figure 6d-f). These southern samples, and the mismatch between model predictions and observations at these southern stations, provide strong constraints for future model studies aimed at improving coupled physics, chemical transport and ecosystem processes within the ROMS models of Narragansett Bay. Specifically, they provide a valuable data-model comparison point for improving simulations of both along-shoal and shoal-channel exchange processes between ES and extensive southwestern shoal waters between the two prominent points on the southwestern side of the PR.

The mismatch between the model and the data could indicate a secondary source of contaminants from the delayed discharge of AFFF from the gasoline spill. This would represent an indirect source to NB via the WWTP outfall, as multiple AFFF discharge sources could account for the discrepancies between the modeled and measured data. One possible source of the model’s overprediction of the observed data trend in the lower PR could result from a premature release time of the VD. If the model dye were released later by several hours, it could have started on a flood tide, which would have advected northward. Wind-driven transport at the surface may also have influenced transport, as
The transport of PFAS concentrated in the surface may have been more affected by the northward winds in the hours before sampling to a greater degree than the primarily tidal-driven model results. Finally, we note that the VD acts as a conservative tracer and should not be expected to account for compound-specific physicochemical properties. The fate of PFAS discharged to upper NB was likely not only subject to dispersion by hydrodynamic forces but complicated further by physical dispersion of the fluorosurfactant AFFF components as a result of partitioning to the air-sea interface and by the surface tension gradient between the two fluids (Marangoni effect) which forces mass transfer along the fluid interface. This effect also may have led to dispersion of AFFF fluorosurfactants laterally within the local sewer and stormwater infrastructure.

4. Conclusions

The results show that while concentrations of the 24 PFAS compounds were near or below the MRL in the Providence River area sampled during July and December 2018, the spill event and response of October 3rd certainly contributed additional PFAS to the Providence River. This is shown by increased concentrations of PFAS along the Providence River transect, and at the Fields Point site in October relative to July and December. The AFFF component 6:2 FTSAS was also identified in the PR and was useful as a tracer in the Providence River, allowing for conceptual understanding of dilution and transport within upper NB. The TOP assay provided key information on PFAS present but not measured by targeted analysis and was essential to detecting the AFFF residues present from the spill. Evidence of a large amount of AFFF entering the river is further strengthened by the high peak areas of 6:2-FTSAS and 6:2-FTSAS-sulfoxide in the northernmost transect stations and solidified by the extremely high PFAS levels present after conducting the TOP assay. Based on accounts of the response to this incident, it is likely that some of the deployed AFFF was diluted and washed not only into stormwater infrastructure which discharges directly into NB, but also to stormwater and sewer infrastructure which contribute to influent at the local WWTP and discharged to the PR after treatment. Considering characteristic hydraulic residence times of the WWTP, our sampling likely captured near peak discharge concentrations close to the outfall. From the transect data, rapid dilution of residual AFFF in the Providence River was apparent as water moved towards the river mouth (PR1). Spatial trends of chemical measurements were also supported by modeled hydrodynamic data but key differences between modeled output and observations strengthened the case for secondary sources of AFFF post spill.
From an ecosystem perspective, the rapid drop in concentrations of PFAS compounds from the AFFF source area (Fields Point) to the lower end of the transect in the river shows the effects of rapid dilution from hydrodynamics in the PR and reflects PFAS concentrations routinely observed in previous monitoring studies. This dilution from both freshwater inflow and tidal exchange limited the spatial and temporal extent of elevated levels of PFAS present post spill. In contrast, concentrations of PFAS at the southernmost site reflects the effects of dilution of all upstream sources and shows that targeted PFAS analysis is not always sufficient when determining total PFAS loads present in the environment. In urbanized embayments where chemical spills may occur, such as the Providence River, it is important to consider impacts from infrastructure and the hydrodynamic conditions which can influence the duration and severity of an event.

5. Acknowledgments

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6. References

Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater.

Environmental Science & Technology 51, 2047-2057. 10.1021/acs.est.6b05843.


7. Figures

Figure 1 – Map of surface water station locations in the Providence River (PR), which has an overall freshwater flow from North to South. Inset map shows the greater Narragansett Bay area.
Figure 2 – Concentrations of selected PFCAs in samples collected from the Providence River transect (A). Concentrations of selected PFSAs, in samples collected from the Providence River transect (B). 6:2-FTS on the right axis, all others on the left axis.
Figure 3 – Concentrations of select PFAS at the Fields Point Reach site measured by targeted analysis (A) and TOP assay results (B) in July, October and December 2018.
Figure 4 – Peak areas of 6:2-FTSAS with distance from the local WWTP outfall. Southernmost stations did not have detectable levels.
Figure 5 – Concentrations of PFCAs present in samples collected from the Providence River transect after TOP oxidations.
Figure 6 - Snapshots of surface dye concentration from the ROMS model. Colorbar shows the log10 of dye concentration in kg/m³. Initial dye patch highlighted with yellow box in (a). Red triangles mark the sampling locations. Grey line drawn on 10 m depth contour to show location of dredged ship channel. In the top right of each frame, the tidal height timeseries is shown with current time marked by a red circle. Wind direction and speed are shown with grey arrows. Note also that (d) shows the time of the sampling used in Supplemental Figure 7.

Supplemental Figure 1 - Wind speed and tidal data 24 h time period shown from the approximate time of the spill (October 3, 2018). Data from Conimicut Light (station # 8452944) at the mouth of the Providence River (A), and Providence (station # 845400) at the head of the Providence River (B).

Supplemental Figure 2 - Concentrations of select PFAS at the Fields Point Reach station in July, October (during spill event) and December 2018.

Supplemental Figure 3 - Concentrations of select PFCAs present during monthly sampling at the FP WR site after TOP analysis.

Supplemental Figure 4 - AFFF MS Infusion – 586 m/z identified as candidate compound

Supplemental Figure 5 - MS Infusion – Products of 586 m/z

Supplemental Figure 6 - Time-mean surface dye concentration from ROMS model over first 5 model days. Colorbar shows the log10 of dye concentration in kg/m³. Red triangles mark the sampling locations. Grey line drawn on 10 m depth contour.
Supplemental Figure 7 - ROMS model surface dye concentration (kg/m³) at the nine sampling locations.

### 8. Tables

Table 1 – PFAS targeted analytes list and acronyms.

<table>
<thead>
<tr>
<th>Compound (CAS #)</th>
<th>Abbreviation</th>
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<td>Perfluorobutanoic acid (375-22-4)</td>
<td>PFBA</td>
</tr>
<tr>
<td>Perfluorpentanoic acid (2706-90-3)</td>
<td>PFPeA</td>
</tr>
<tr>
<td>Perfluorohexanoic acid (307-24-4)</td>
<td>PFHxA</td>
</tr>
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<td>Perfluoroheptanoic acid (375-85-9)</td>
<td>PFHpA</td>
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<td>Perfluorooctanoic acid (335-67-1)</td>
<td>PFOA</td>
</tr>
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<td>Perfluorononanoic acid (375-95-1)</td>
<td>PFNA</td>
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<td>Perfluorodecanoic acid (335-76-2)</td>
<td>PFDA</td>
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Table 2 – PFAS concentrations (ng/L) at the Fields Point Reach (FP) station in July, October and December 2018. PFAS concentrations from the Providence River Transect are from October 2018 only. N-MeFOSAA, N-EtFOSAA, PFDS, PFDoA, PFTrDA and PFTeDA were below the MDL in all samples and are not shown. All concentrations are ng/L.

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<th>Date</th>
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<th>PFBS</th>
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Supplemental Table 1 - Daily Freshwater river flow to the upper Providence River from the Blackstone, Ten Mile and Moshassuck Rivers during the time of the spill.

Supplemental Table 2 - LC mobile phase gradient conditions.

Supplemental Table 3 - Optimized mass spectrometer settings for reported PFAS compounds.

Supplemental Table 4 - Detection and reporting limits of the reported PFAS compounds.

Supplemental Table 5 - Correlation to Amount of Thunderstorm Digested