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

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1 Abstract

2 The deployment of aqueous film forming foams (AFFF) used for firefighting during emergencies and
3 training often releases per- and polyfluoroalkyl substances (PFAS) into the environment. In October
4 2018, first responders in Providence, RI, USA applied an AFFF during a fuel spill. Due to the proximity of
5 the incident to the upper reaches of Narragansett Bay (NB), an unknown quantity of gasoline and AFFF
6 entered the estuary via surface runoff and stormwater drains. Water samples near the spill were
7 collected approximately 15 hours after the incident and analyzed for 24 PFAS. Minor increases in
8 measured PFAS concentrations were observed relative to pre- and post-spill samples at monitoring sites
9 near the incident, except 6:2-fluorotelomer sulfonate (6:2-FTS) that peaked post-spill (max 311 ng/L).
10 After performing the total oxidizable precursor (TOP) assay on water samples and the AFFF concentrate,
11 significant increases in perfluorocarboxylic acids (PFCAs) were observed. One compound, 6:2
12 fluorotelomer mercaptoalkylamido sulfonate (6:2-FTSAS), was identified as a major component of the
13 AFFF used. Peak areas of 6:2-FTSAS and the degradation product 6:2-FTSAS-sulfoxide corresponded to
14 observed increases in the TOP assay results and were useful as tracers of AFFF in surrounding waters.
15 Elevated levels of PFAS at the time of sampling were limited to a confined area of the Providence River
16 due to river flow and tidal action. Observed concentrations were also compared to hydrodynamic
17 model results, and results confirmed rapid dissipation of AFFF components with distance from the spill.
18 However, modeled results did not capture possible secondary releases of AFFF from local municipal
19 stormwater and sewer infrastructure, as observational data suggest. The multiple lines of evidence of
20 PFAS present in surface waters permitted a better assessment of the potential environmental impacts
21 from products such as AFFF for which the chemical composition is largely unknown.

22

23 **Keywords:** aqueous film forming foam (AFFF), per- and polyfluoroalkyl substances (PFAS), surface water,
24 6:2-fluorotelomer sulfonate (6:2-FTS), 6:2- fluorotelomer mercaptoalkylamido sulfonate (6:2-FTSAS),
25 class B foam

26

27 1 Introduction

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

50 While AFFFs were originally designed for military use, they have also been used extensively by
51 municipal fire departments, airports, as well as chemical and hydrocarbon storage and processing
52 facilities (Hu et al., 2016; Moody and Field, 2000). Fluorosurfactants produced by telomerization have
53 been shown to ultimately degrade to perfluoroalkyl carboxylic acids (PFCAs) such as perfluorooctanoic
54 acid (PFOA) and perfluorohexanoic acid (PFHxA) along with other intermediate perfluoroalkyl
55 degradation products (Wallington et al., 2006; Wang et al., 2011; Weiner et al., 2013). The long-term use
56 of AFFFs during training and emergency response has resulted in the widespread contamination of
57 ground and surface waters near industrial sites, airports, and military bases (Hu et al., 2016). Further,

58 hundreds of individual fluorinated AFFF compounds have been identified in commercial AFFF products
59 (Backe et al., 2013; Barzen-Hanson et al., 2017; D’Agostino and Mabury, 2014; Place and Field, 2012). As
60 a result, many of these compounds or their degradation products have been detected in groundwater
61 and drinking water (Backe et al., 2013; Boone et al., 2019; Gebbink et al., 2017; Houtz et al., 2013; Hu et
62 al., 2016; Moody et al., 2003). Due to the high mobility of PFAS in aqueous media, AFFF has also been
63 measured in inshore and offshore surface waters (Benskin et al., 2012; Miranda et al., 2021; Möller et
64 al., 2010; Nguyen et al., 2017; Zhao et al., 2012). Finally, quantification of the PFAS constituents present
65 in aqueous samples post spill remains unachievable due to the lack of analytical standards for PFAS
66 present within modern AFFFs.

67 In some cases, AFFF compounds or their degradation products have been identified and found to
68 bioaccumulate in invertebrates, fish, reptiles, birds and mammals in both freshwater and marine
69 environments (Ahrens and Bundschuh, 2014; Gebbink et al., 2016; Langberg et al., 2019; Moe et al.,
70 2012; Munoz et al., 2017; Palmer et al., 2019; Robuck et al., 2020; Shi et al., 2019) and have associated
71 adverse health effects in humans and model organisms (Shi et al., 2018; Sunderland et al., 2019). For
72 example, research has shown adverse impacts to liver function on downstream fish populations
73 following another spill event (Oakes et al., 2010). AFFF components have also been detected in Arctic
74 environments and organisms (Benskin et al., 2012; Yamashita et al., 2005), far afield from their point of
75 use and reminiscent of the global transport of conventional persistent organic pollutants (Wania and
76 MacKay, 1996), albeit by different mechanisms (Johansson et al., 2019). While a number of toxicity
77 studies have investigated effects of legacy foams, few toxicity studies on fluorotelomer based foams
78 have been performed to date, and information on the impacts and effects of AFFF deployed during
79 emergency response in estuaries and coastal areas remains limited.

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

89 searched prior published results of AFFF composition to identify major foam components useful for
90 tracking AFFF residues in NB.

91 2 Methods

92 2.1 Study location and sample collection

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

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

110 Sampling of the surface waters of the Providence River occurred approximately 15 hours after the
111 start of the incident. The spill roughly coincided with high tide and samples were collected during the
112 ebb of the next high tide. Winds were low (<5 m/s) during the period between the spill and sample
113 collection at both the head and mouth of the Providence River (Supplemental Figure 1). Freshwater
114 input to the upper Providence River was higher than average during sampling, with total flow from the
115 major tributaries on the day of the spill of 90 m³/s (Supplemental Table 1) and monthly average flow
116 over the previous ten years of 22 m³/s (USGS, 2019). Ungauged contributions to streamflow data were
117 not accounted for and were considered negligible. Nine surface water samples along a north-south
118 transect in the area of the spill were collected (Figure 1). Surface samples were collected from a depth

119 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
120 dark upon returning to the lab. The FP station (Figure 1) was part of monthly monitoring performed
121 independently of this investigation and comparisons to conditions pre- and post-spill were therefore
122 possible at this location.

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

129

130 2.2 Water Sample Preparation and Analysis

131 Water samples were analyzed for 24 PFAS that have certified calibration standards, consisting of
132 eleven PFCAs, seven perfluoroalkane sulfonic acids (PFSA), one perfluoroalkane sulfonamide (FASA),
133 two perfluoroalkane sulfonamido-acetic acids (FASAAs) and three n:2 fluorotelomer sulfonates (FTS) as
134 shown in Table 1. After collection, water samples (500 mL aliquots) were fortified with 10 ng
135 isotopically labeled internal standards (Wellington Laboratories, Guelph, Canada) and extracted via
136 weak anion exchange sorbent material (Oasis WAX 150 mg, Waters Corp, Milford MA). Solid phase
137 extraction cartridges were conditioned using 6 mL of methanol with 0.1% ammonium hydroxide,
138 followed by 6 mL of methanol and 6 mL of C18 polished PFAS free water (MilliQ, Millipore Sigma,
139 Burlington, MA). Samples were loaded onto the cartridges at 5 mL/min and cartridges were washed
140 with PFAS free water and dried for 15 min by nitrogen gas. Cartridges were eluted with 6 mL of
141 methanol followed by 6 mL of methanol modified with 0.1% ammonium hydroxide (Taniyasu et al.,
142 2005). All solid phase extraction steps were automated using an AutoTrace 280 system (Thermo
143 Scientific, Waltham, MA), modified to remove most fluoropolymer components. Sample extracts were
144 then taken gently to dryness (EZ2 Plus, Genevac, Warminster, PA) and reconstituted with 1 mL of 75: 25
145 water: methanol with 2 mM ammonium acetate.

146 In addition to the targeted analysis of water samples described using individual calibration
147 standards, a total oxidizable precursor (TOP) analysis was conducted following a slightly modified
148 procedure from Houtz and Sedlak (2012). TOP is a procedure that uses a heat and persulfate mediated

149 hydroxyl radical reaction to convert unknown or “precursor” PFAS compounds, which cannot be
150 individually identified due to the lack of commercial standards, to PFCAs for which standards are
151 available. TOP samples were oxidized by the addition of 160 mM of sodium hydroxide (Sigma Aldrich,
152 St. Louis, MO), 60 mM of potassium persulfate (Sigma Aldrich, St. Louis, MO) and heated for 6 hours at
153 85 °C in a water bath (Memmert, Eagle, WI). After cooling, samples were adjusted to pH 5–7 using
154 concentrated trace metal grade hydrochloric acid (J.T. Baker, Center Valley, PA) and fortified with 10 ng
155 of internal standard before extraction following the same procedure previously described for water
156 samples. This procedure was performed on field collected samples and diluted AFFF used in the spill
157 response. AFFF dissolved in methanol was added to 100 mL of PFAS free water at zero salinity (DIW)
158 and artificial seawater at a salinity of 30 ppt (ASW). Both DIW and ASW were amended with 1000 ng of
159 the AFFF for assessment via the TOP assay. According to the manufacturer’s safety data sheet at this
160 concentration of AFFF, 10–50 ng of the unidentified PFAS portion of the AFFF may be present per 100
161 mL. Water samples (100 mL) collected in October 2018 from sites near the spill were also oxidized using
162 the same TOP procedure as the AFFF samples. Samples from before the spill (July 2018) and after
163 (December 2018) at the FP station were also extracted for the targeted analytes and subjected to TOP
164 analysis for comparison to samples from the date of the spill. All oxidations were performed in triplicate
165 and averaged between 6.9 – 43 %RSD for reported compounds.

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

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

177 2.3 Hydrodynamic Model

178 Hydrodynamic simulations of the Providence River were performed using the Regional Ocean
179 Modeling System (ROMS) finite difference numerical model (Haidvogel et al., 2008; Shchepetkin and

180 McWilliams, 2005). The model is three-dimensional and includes stratification, rivers, tides, and
181 atmospheric forcing. A non-reactive virtual dye (VD) tracer was added near the spill site to simulate the
182 transport of PFAS, but does not account for any PFAS-specific chemical properties and was not intended
183 to directly predict PFAS concentration, only a proxy for relative distribution. The VD acts as a neutrally
184 buoyant, conservative Lagrangian tracer, tracking both the advection and diffusion of a non-reactive
185 chemical within the water. The VD was added to the top four model vertical layers on October 3, 2018
186 18:30 EDT and fifteen terrain-following “sigma” layers were used which expand or contract while
187 following changes in the local bathymetry. At the point of injection, the four virtually dyed layers
188 correspond to approximately the top 1 m of the water column. Atmospheric forcing was obtained from
189 the NOAA North American Mesoscale model. River discharge was added to the model using river gauge
190 observations from USGS and accounted for ungauged downstream flow. Tidal forcing was applied at the
191 open boundaries using depth-integrated velocities and surface elevations from a tidal model of the
192 North Atlantic (Szpilka et al., 2016). The temperature and salinity fields in the model were initialized
193 using a full-year 2018 hindcast spin-up run. Modeled temperature, salinity, surface elevation (tides) and
194 currents were each validated over an annual cycle and showed high levels of agreement with
195 observations (Ullman et al., 2019). Further details on model construction are available in the SI.

196

197 3 Results and Discussion

198 3.1 Targeted PFAS

199 *Spatial Analysis.* Results of the targeted analysis for all stations (Table 2) showed concentrations ranging
200 from below detection to 6.3 ng/L for individual PFCAs and from below detection to 8.1 ng/L for
201 individual PFSA during the October 3, 2018 sampling (Table 2). The six station transect within the
202 Providence River showed increases in concentrations of perfluorobutanoic acid (PFBA),
203 perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA) and
204 perfluorooctane sulfonate (PFOS) upriver from transect station PR1 at the river mouth to PR5 which was
205 located near the outfall of the WWTP (Figure 2A & 2B). Most PFCA and PFSA compounds decreased in
206 concentration from PR5 to PR6 which was located nearest to the spill, with the exception of PFNA.
207 Concentrations of 8:2-FTS followed a similar trend to the PFCA and PFSA compounds and were at their
208 highest concentrations at PR5 and decreased to the north and south, suggesting the proximity of a
209 nearby source (Figure 2B). Concentrations of FOSA and the FTS compounds other than 8:2-FTS

210 continuously decreased upriver. Concentrations of 6:2-FTS were the highest of all compounds and
211 decreased from 311 ng/L at PR1 to 18 ng/L at PR6. Analysis of the AFFF used indicated 6:2-FTS was not
212 present in this foam. However, it has been confirmed as a minor component in several AFFF products
213 (Backe et al., 2013; Place and Field, 2012), some industrial processes (e.g. metal plating operations)
214 replaced PFOS with 6:2-FTS, and previous research has shown elevated 6:2-FTS levels in the bay (Zhang
215 et al., 2016).

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

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

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

241 (Gonzalez et al., 2021). Third, and least likely, an unknown source may have discharged 6:2-FTS
242 concurrently and coincidentally but unrelated to the spill response.

243 *AFFF in the Providence River.* As previously noted, comparisons of the pre- and post-spill results of the
244 targeted analytes do not show highly elevated levels of PFAS in the Providence River with respect to the
245 spill event and the AFFF used did not contain measurable amounts of PFAS present in the targeted
246 analysis list. To further investigate the cause of the observed increase in the PFAS upriver from PR1, a
247 diluted aliquot of the deployed AFFF was also directly infused to the mass spectrometer to identify
248 prominent spectra and transitions of compounds for which published data exists. Significant mass
249 spectral intensity was observed at 586 m/z (Supplemental Figure 4) with five corresponding
250 characteristic MS/MS fragment ions of (m/z 90, 104, 135, 152 and 206) most dominant in intensity
251 (Supplemental Figure 5). This spectra and resulting product ions are consistent with 6:2 fluorotelomer-
252 mercaptoalkylamido sulfonate (6:2-FTSAS) a ubiquitous component of AFFF formulations alternatively
253 known as 6:2-fluorotelomer thioamido sulfonate or 6:2-fluorotelomer thioether amido sulfonate (6:2-
254 FtTAoS) and 6:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate (6:2-FTTh-PrAd-DiMeEtS)
255 (Backe et al., 2013; Field et al., 2003; Harding-Marjanovic et al., 2015; Mejia-Avenidaño et al., 2017; Place
256 and Field, 2012; Ruyle et al., 2021; Weiner et al., 2013). Water samples extracted for the targeted
257 analysis were reanalyzed for 6:2-FTSAS and 6:2-FTSAS-sulfoxide, a known degradation product of 6:2-
258 FTSAS previously identified in both sterile and activated sludge biodegradation treatments (Weiner et
259 al., 2013) and aerobic soil microcosms (Harding-Marjanovic et al., 2015; Yi et al., 2018). Results showed
260 high peak areas decreasing in intensity with distance from the WWTP outfall area (Figure 4), with 6:2-
261 FTSAS-sulfoxide peak areas following the same trend but approximately an order of magnitude lower in
262 intensity. The highest signals occurred directly adjacent to the WWTP outfall, suggesting that some
263 AFFF applied to city streets which entered the Providence River near PR6 via surface runoff or
264 stormwater drains north of the WWTP outfall was not the source of elevated peak areas at the time of
265 sampling at PR5 nearer to the WWTP outfall. Intriguingly, while 6:2-FTSAS decreased in intensity
266 downriver, 6:2-FTS increased in concentration downriver. This behavior was unexpected as most
267 industrial effluent contributing to 6:2-FTS concentrations in the Providence River enter from points
268 further north at the head of the river. While biodegradation experiments using freshwater activated
269 sludge bottle experiments and freshwater microcosms have shown that 6:2-FTSAS degrades to 6:2-FTS
270 (Harding-Marjanovic et al., 2015; Weiner et al., 2013), the timescales reported for transformation were
271 longer than the typical travel time of surface water flows observed during this study. However, 6:2-
272 FTSAS may also degrade more directly by S-dealkylation via P-450 enzymatic activity (Weiner et al.,

273 2013). This observation makes speculation regarding increased degradation rates of this compound in
274 seawater systems relative to freshwater systems tempting as marine microorganisms are efficient
275 processors of both inorganic and organic sulfur compounds (Moran and Durham, 2019). The presence
276 of 6:2-FTSAS and 6:2-FTSAS-sulfoxide, identified by their characteristic mass transitions, were useful as
277 tracers of AFFF discharge to the PR and greatly aided the determination of the ultimate fate of AFFF
278 applied to city streets. Unfortunately, these compounds do not have commercially available authentic
279 standards and therefore were not quantifiable during this study.

280

281 3.2 Total oxidizable precursors

282 TOP analysis was performed on water from the transect stations sampled approximately 12 hours after
283 the spill occurred. Concentrations of all PFCAs clearly increased upriver with a maximum at the PR5
284 station and decreased again at site PR6 further to the north (

285 Figure 5). From PR3 station and further north to station PR6, the highest concentrations were
286 observed for PFPeA, followed closely by PFHxA and PFBA. Outside of this area, post-TOP compound
287 concentrations showed no clear pattern. While many PFCAs were not present at the southernmost
288 stations, all PFCAs were present at the FP, PR5 and PR6 stations. The concentrations of PFBA, PFPeA and
289 PFHxA present relative to the other PFCAs indicate upper NB received the discharge of precursor
290 compound(s) with a six-carbon backbone or longer associated with AFFF (Barzen-Hanson et al., 2017;
291 Houtz et al., 2016). This data reflects stated industry trends of eliminating the inclusion of eight-carbon
292 chemistries in AFFF products (USEPA, 2006) and the increased utilization of six-carbon compounds in
293 contemporary AFFFs (Ruyle et al., 2021).

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

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

316 affect treatment operations. While the presence of gasoline in the treatment works was limited post
317 spill, the detection of gasoline at the treatment plant headworks suggests that a mixture of spilled
318 gasoline, water and AFFF applied to the spill was partially routed to the WWTP.

319 The TOP procedure was also conducted on the AFFF at three different diluted concentrations in
320 PFAS free de-ionized water (DI) and artificial seawater. Results showed a linear response across the
321 range for the shorter chain PFCAs with Pearson's correlations above 0.8 and p-values below 0.05
322 (Supplemental Table 5). The manufacturer statement indicated that level of PFAS in the AFFF was 1-5%
323 of a proprietary compound, and it was therefore assumed that approximately 10–50 ng out of every
324 1000 ng of AFFF was a PFAS compound. However, a quantitative mass balance was impossible, as
325 identities and molecular weights of all potential precursor compounds present in the AFFF are required
326 for a complete mass computation. When normalized to AFFF oxidized in each treatment, total PFCAs
327 produced from the TOP procedure performed on the AFFF varied widely with 107 mg PFCAs per gram
328 AFFF with a 45 % relative standard deviation.

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

334

335 3.3 Hydrodynamic Model

336 Water grab samples at the same time and sampling locations and used to assess the fate of AFFF
337 discharged to NB were compared with patterns of dispersion and transport of virtual dye (VD) from a
338 point source location within the Providence River. The model results showed a decline in VD
339 concentration moving both north and south from station PR5 concurring with the observational PFAS
340 results. It is interesting, though not unexpected, that the observational data typically show higher PFAS
341 concentrations at PR3 than PR4, which is 4 km south of the VD source (spill location). This is due to the
342 extreme vertical and lateral gradients in subtidal flow the Providence River has been shown to exhibit
343 (Kincaid, 2001, 2012, 2018), which may separate a water parcel and associated PFAS or other
344 contaminants into distinct sections. Though situated significantly further southward, station PR3 lies
345 near the shoals along the western edge of the shipping channel, where a remarkably stable jet flushes

346 water (and contaminants) southward (Kincaid, 2001, 2012). The starkest contrast between the model
347 output and observation was the overprediction of the VD concentrations in the southern Providence
348 River (at PR2 and PR1) relative to measured PFAS concentrations which trended toward zero. The
349 model sequence of the VD (Figure 6) shows rapid southward advection within the first 3.5 hours after
350 release. The VD was released during an ebb tide (concurrent to the spill event) when winds were
351 toward the northeast and the following flood tide was not enough to transport the dye out of the lower
352 Providence River, as seen during the high tide 9.5 hours after release (Figure 6c) when the VD was
353 expected to reach its maximum northward extent. At the sampling time (Figure 6d), VD north of Fields
354 Point had collected on the western shore while dye south of Fields Point appeared to converge on the
355 shallow shoals.

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

370 The mismatch between the model and the data could indicate a secondary source of contaminants
371 from the delayed discharge of AFFF from the gasoline spill. This would represent an indirect source to
372 NB via the WWTP outfall, as multiple AFFF discharge sources could account for the discrepancies
373 between the modeled and measured data. One possible source of the model's overprediction of the
374 observed data trend in the lower PR could result from a premature release time of the VD. If the model
375 dye were released later by several hours, it could have started on a flood tide, which would have
376 advected northward. Wind-driven transport at the surface may also have influenced transport, as

377 transport of PFAS concentrated in the surface may have been more affected by the northward winds in
378 the hours before sampling to a greater degree than the primarily tidal-driven model results. Finally, we
379 note that the VD acts as a conservative tracer and should not be expected to account for compound-
380 specific physicochemical properties. The fate of PFAS discharged to upper NB was likely not only subject
381 to dispersion by hydrodynamic forces but complicated further by physical dispersion of the
382 fluorosurfactant AFFF components as a result of partitioning to the air-sea interface and by the surface
383 tension gradient between the two fluids (Marangoni effect) which forces mass transfer along the fluid
384 interface. This effect also may have led to dispersion of AFFF fluorosurfactants laterally within the local
385 sewer and stormwater infrastructure.

386

387 4. Conclusions

388 The results show that while concentrations of the 24 PFAS compounds were near or below the MRL
389 in the Providence River area sampled during July and December 2018, the spill event and response of
390 October 3rd certainly contributed additional PFAS to the Providence River. This is shown by increased
391 concentrations of PFAS along the Providence River transect, and at the Fields Point site in October
392 relative to July and December. The AFFF component 6:2 FTSAS was also identified in the PR and was
393 useful as a tracer in the Providence River, allowing for conceptual understanding of dilution and
394 transport within upper NB. The TOP assay provided key information on PFAS present but not measured
395 by targeted analysis and was essential to detecting the AFFF residues present from the spill. Evidence of
396 a large amount of AFFF entering the river is further strengthened by the high peak areas of 6:2-FTSAS
397 and 6:2-FTSAS-sulfoxide in the northernmost transect stations and solidified by the extremely high PFAS
398 levels present after conducting the TOP assay. Based on accounts of the response to this incident, it is
399 likely that some of the deployed AFFF was diluted and washed not only into stormwater infrastructure
400 which discharges directly into NB, but also to stormwater and sewer infrastructure which contribute to
401 influent at the local WWTP and discharged to the PR after treatment. Considering characteristic
402 hydraulic residence times of the WWTP, our sampling likely captured near peak discharge
403 concentrations close to the outfall. From the transect data, rapid dilution of residual AFFF in the
404 Providence River was apparent as water moved towards the river mouth (PR1). Spatial trends of
405 chemical measurements were also supported by modeled hydrodynamic data but key differences
406 between modeled output and observations strengthened the case for secondary sources of AFFF post
407 spill.

408 From an ecosystem perspective, the rapid drop in concentrations of PFAS compounds from the AFFF
409 source area (Fields Point) to the lower end of the transect in the river shows the effects of rapid dilution
410 from hydrodynamics in the PR and reflects PFAS concentrations routinely observed in previous
411 monitoring studies. This dilution from both freshwater inflow and tidal exchange limited the spatial and
412 temporal extent of elevated levels of PFAS present post spill. In contrast, concentrations of PFAS at the
413 southernmost site reflects the effects of dilution of all upstream sources and shows that targeted PFAS
414 analysis is not always sufficient when determining total PFAS loads present in the environment. In
415 urbanized embayments where chemical spills may occur, such as the Providence River, it is important to
416 consider impacts from infrastructure and the hydrodynamic conditions which can influence the duration
417 and severity of an event.

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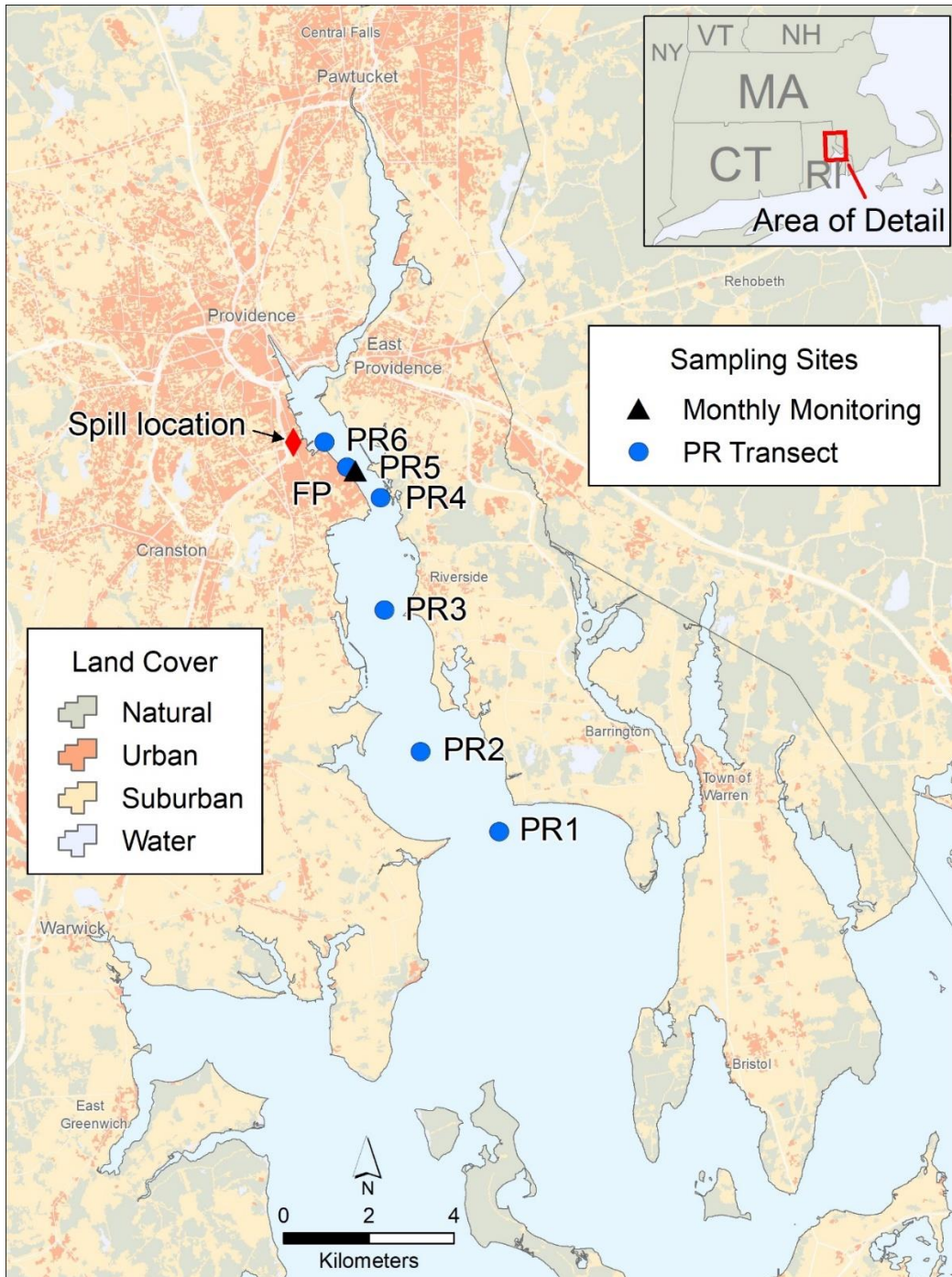
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611 7. Figures

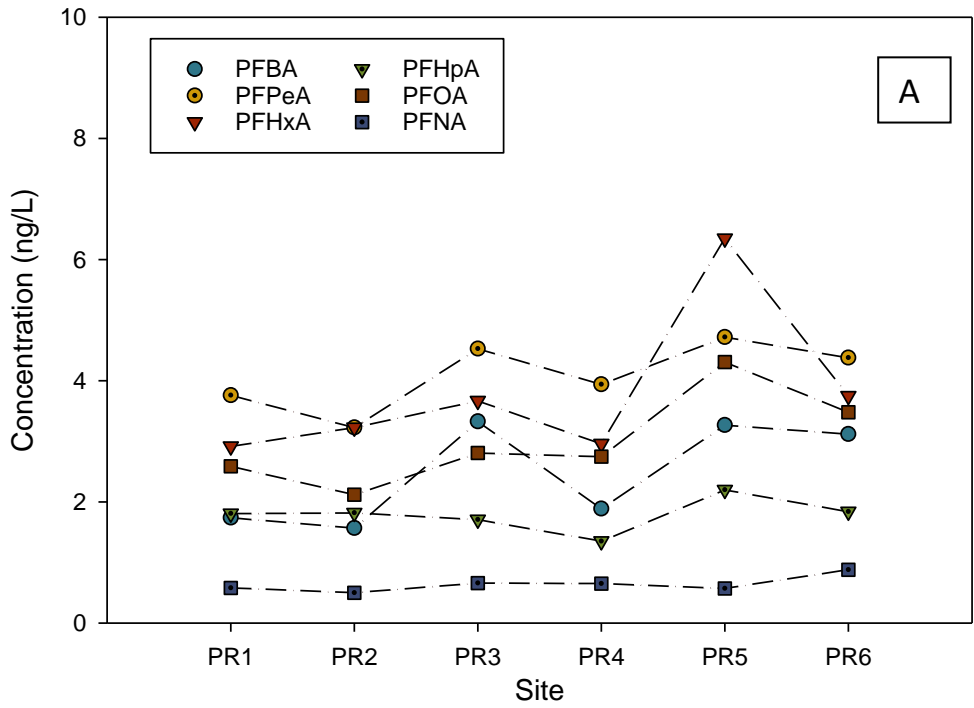
612 Figure 1 – Map of surface water station locations in the Providence River (PR), which has an overall
613 freshwater flow from North to South. Inset map shows the greater Narragansett Bay
614 area.



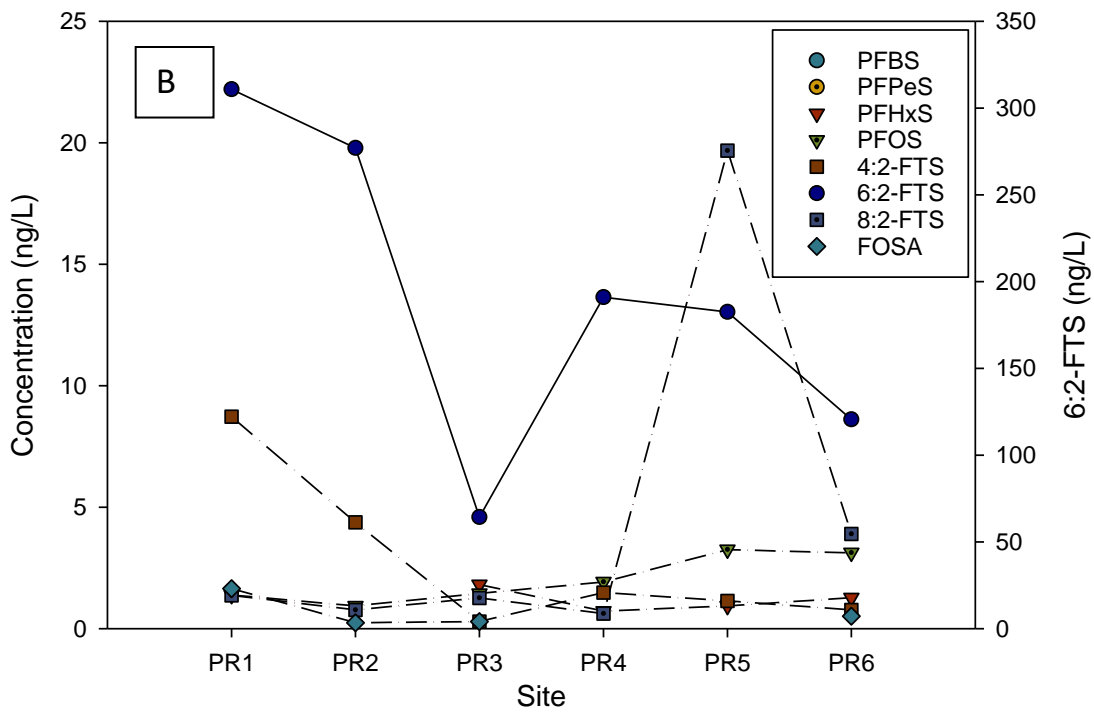
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Figure 2 – Concentrations of selected PFCAs in samples collected from the Providence River transect (A). Concentrations of selected PFSA, in samples collected from the Providence River transect (B). 6:2-FTS on the right axis, all others on the left axis.



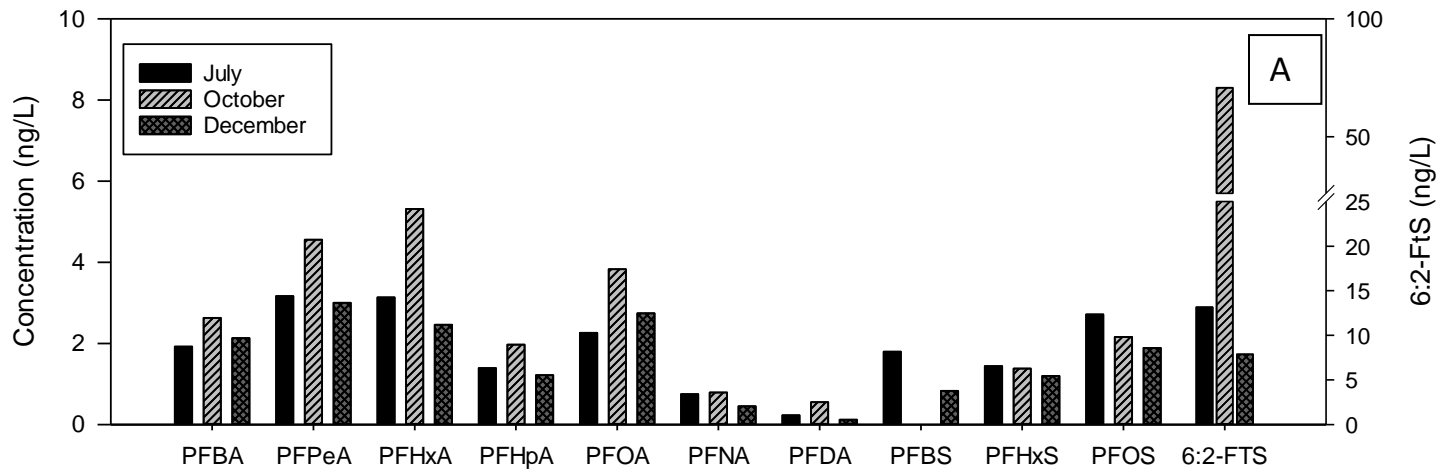
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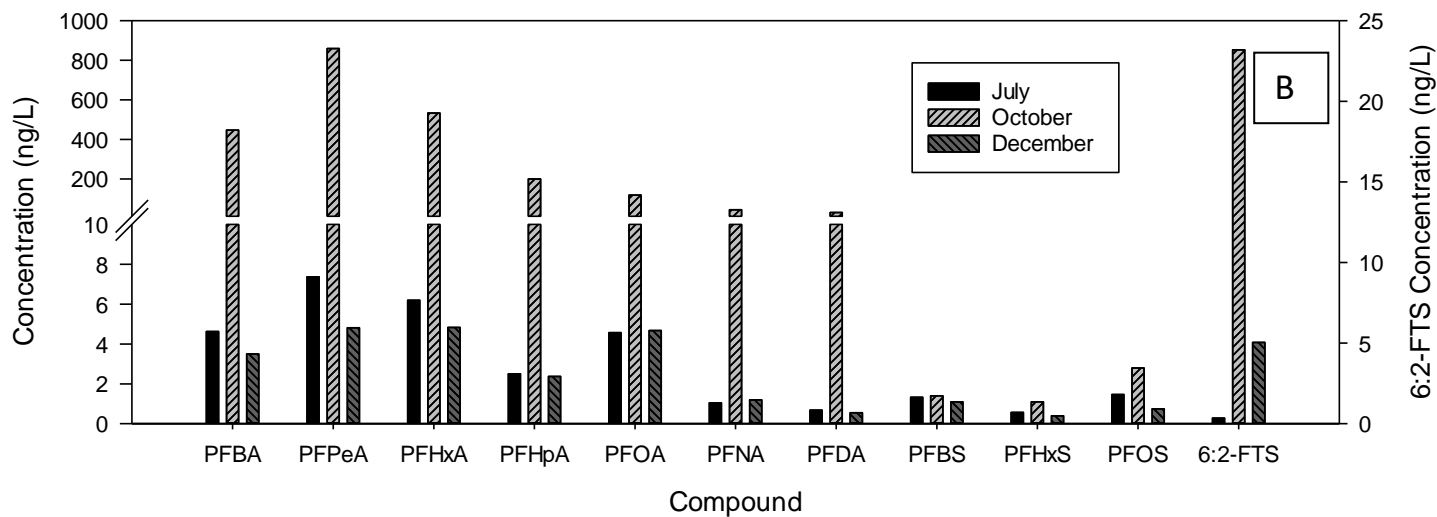
622 Figure 3 – Concentrations of select PFAS at the Fields Point Reach site measured by targeted analysis
 623 (A) and TOP assay results (B) in July, October and December 2018.

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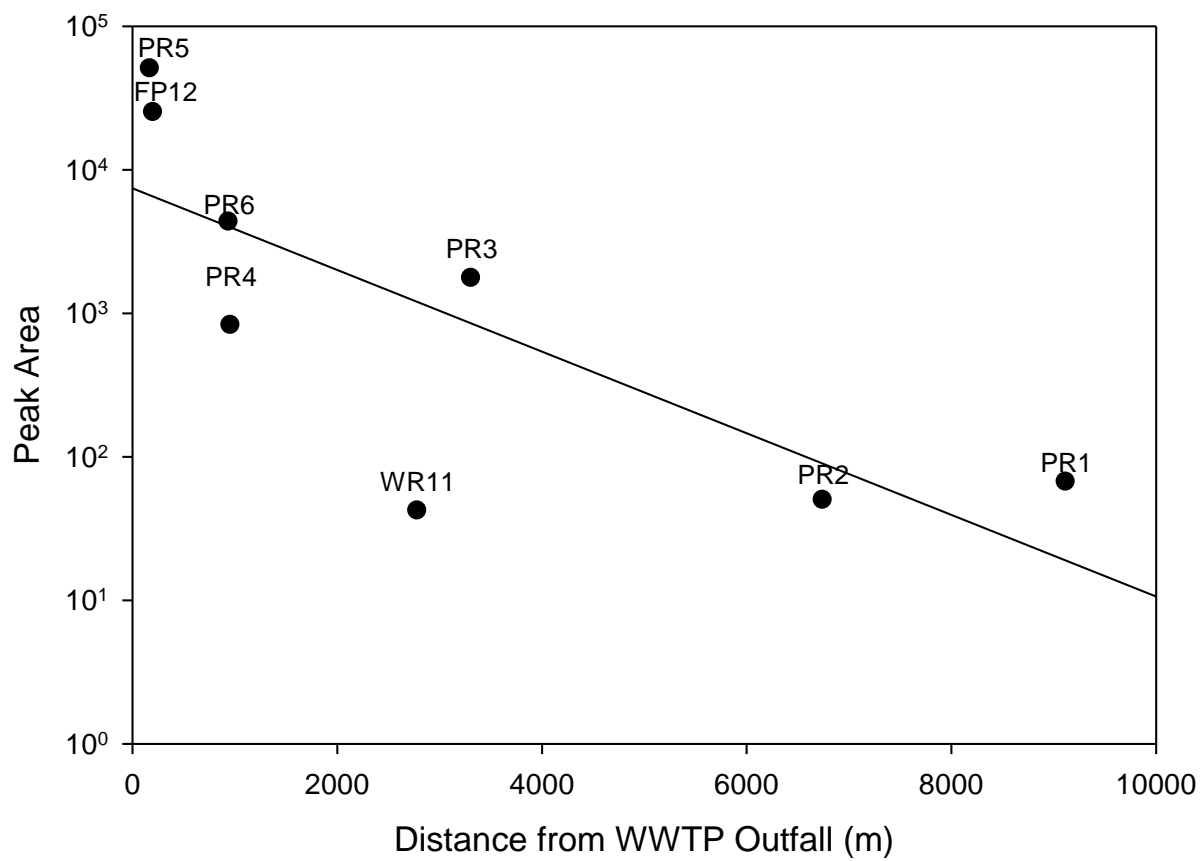
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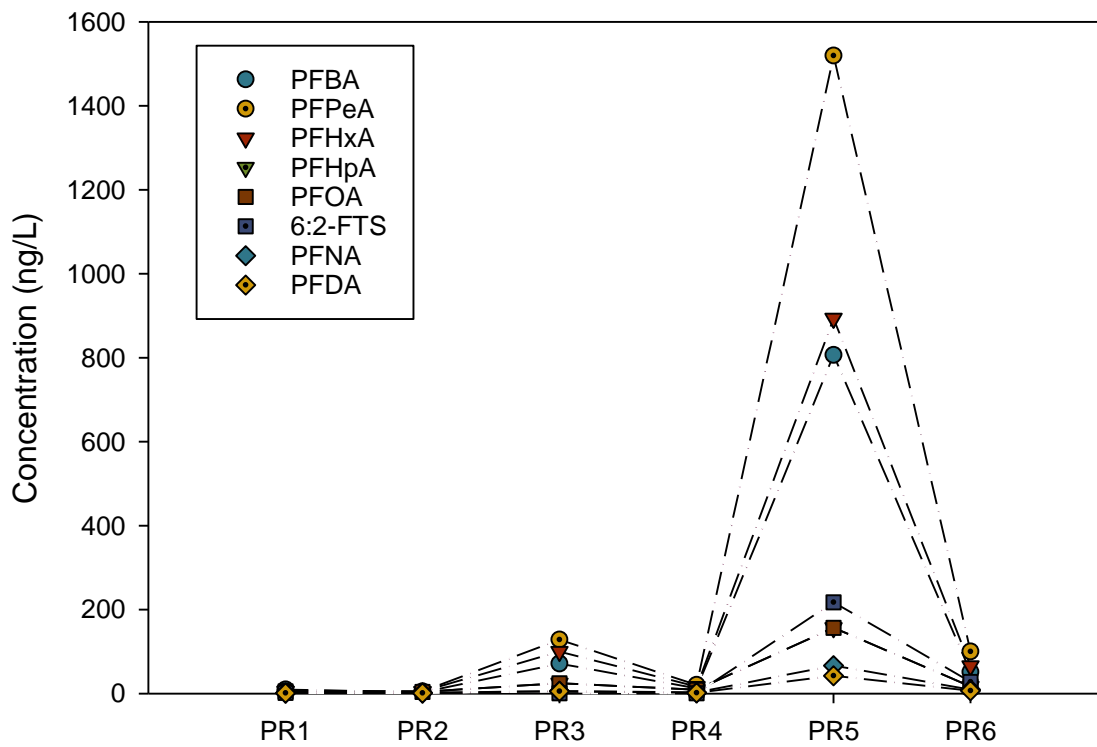
Figure 4 – Peak areas of 6:2-FTSAS with distance from the local WWTP outfall. Southernmost stations did not have detectable levels.



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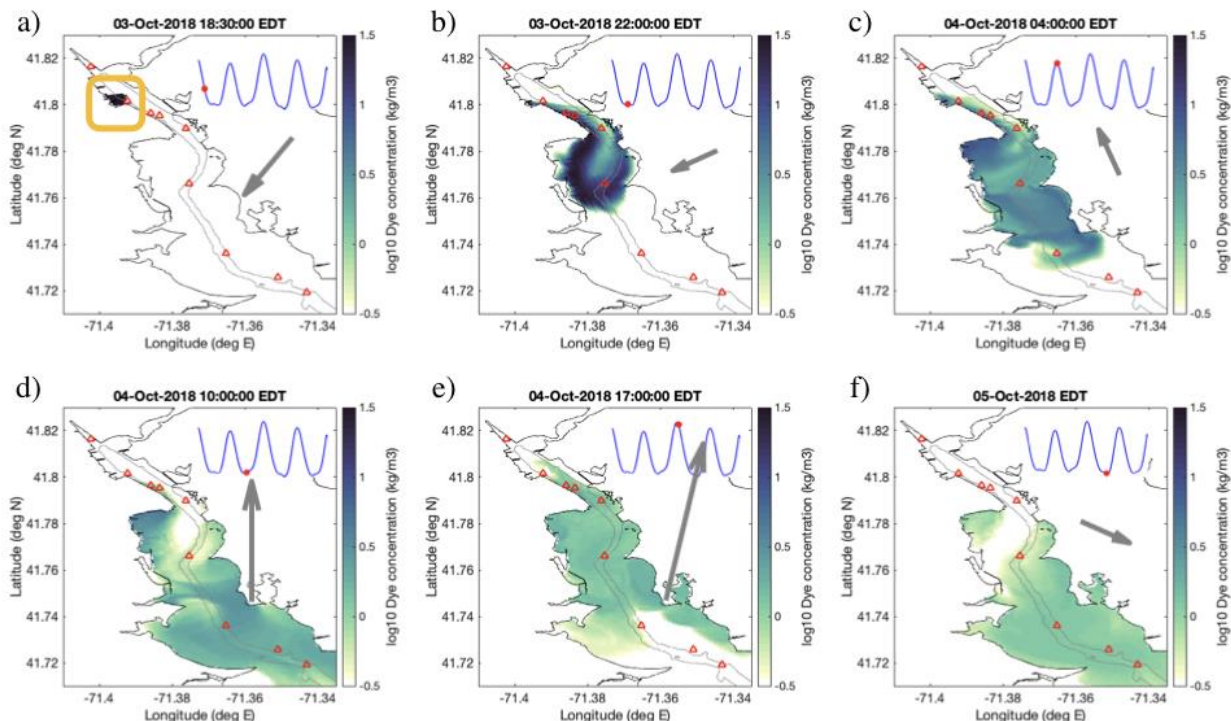
Figure 5 – Concentrations of PFCAs present in samples collected from the Providence River transect after TOP oxidations.



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640 Figure 6 - Snapshots of surface dye concentration from the ROMS model. Colorbar shows the log₁₀
 641 of dye concentration in kg/m³. Initial dye patch highlighted with yellow box in (a). Red
 642 triangles mark the sampling locations. Grey line drawn on 10 m depth contour to show
 643 location of dredged ship channel. In the top right of each frame, the tidal height
 644 timeseries is shown with current time marked by a red circle. Wind direction and speed
 645 are shown with grey arrows. Note also that (d) shows the time of the sampling used in
 646 Supplemental Figure 7.



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

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

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

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

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

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

662 Supplemental Figure 7 - ROMS model surface dye concentration (kg/m³) at the nine sampling
663 locations.

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665 8. Tables

666 Table 1 – PFAS targeted analytes list and acronyms.

Compound (CAS #)	Abbreviation
Perfluorobutanoic acid (375-22-4)	PFBA
Perfluoropentanoic acid (2706-90-3)	PFPeA
Perfluorohexanoic acid (307-24-4)	PFHxA
Perfluoroheptanoic acid (375-85-9)	PFHpA
Perfluorooctanoic acid (335-67-1)	PFOA
Perfluorononanoic acid (375-95-1)	PFNA
Perfluorodecanoic acid (335-76-2)	PFDA
Perfluoroundecanoic acid (2058-94-8)	PFUdA
Perfluorododecanoic acid (307-55-1)	PFDoA
Perfluorotridecanoic acid (72629-94-8)	PFTTrDA
Perfluorotetradecanoic acid (376-06-7)	PFTeDA
Perfluoro-1-octanesulfonamide (754-91-6)	FOSA
N-methylperfluoro-1-octanesulfonamidoacetic acid (2355-31-9)	N-MeFOSAA
N-ethylperfluoro-1-octanesulfonamidoacetic acid (2991-50-6)	N-EtFOSAA
Perfluorobutanesulfonate (375-73-5)	PFBS
Perfluoropentanesulfonate (2706-91-4)	PFPeS
Perfluorohexanesulfonate (355-46-4)	PFHxS
Perfluoroheptanesulfonate (375-92-8)	PFHpS
Perfluorooctanesulfonate (1763-23-1)	PFOS
Perfluorononanesulfonate (68259-12-1)	PFNS
Perfluorodecanesulfonate (335-77-3)	PFDS
4:2-fluorotelomer sulfonate (1432486-88-8)	4:2-FTS
6:2-fluorotelomer sulfonate (88992-47-6)	6:2-FTS
8:2-fluorotelomer sulfonate (1383439-45-9)	8:2-FTS

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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.

Date	Station	PFBA	PFPeA	PFBS	PFHxA	4:2-FTS	PFPeS	PFHpA	PFHxS	PFOA	6:2-FTS	PFHpS	PFNA	FOSA	PFOS	PFDA	8:2-FTS	PFNS	PFUdA
11-July-2018	FP	1.92	3.17	1.80	3.14	<MDL	<MDL	1.39	1.44	2.26	13.14	<MDL	0.75	<MDL	2.72	0.23	<MDL	0.64	<MDL
04-Oct-2018	PR1	1.74	3.76	<MDL	2.92	8.73	<MDL	1.81	<MDL	2.59	310.88	<MDL	0.58	1.65	1.38	0.25	1.37	<MDL	<MDL
	PR2	1.57	3.23	<MDL	3.23	4.38	<MDL	1.82	<MDL	2.12	277.08	<MDL	0.50	0.24	0.93	0.15	0.77	<MDL	<MDL
	PR3	3.33	4.53	<MDL	3.67	0.29	<MDL	1.71	1.82	2.81	64.37	<MDL	0.66	0.29	1.45	<MDL	1.26	<MDL	<MDL
	PR4	1.89	3.94	<MDL	2.96	1.48	<MDL	1.35	0.72	2.75	191.00	<MDL	0.65	<MDL	1.93	0.22	0.62	<MDL	<MDL
	PR5	3.27	4.72	<MDL	6.35	1.14	<MDL	2.20	0.93	4.31	182.54	<MDL	0.57	<MDL	3.26	0.51	19.68	<MDL	<MDL
	PR6	3.12	4.38	<MDL	3.75	0.77	<MDL	1.84	1.27	3.48	120.66	<MDL	0.88	0.51	3.13	0.29	3.90	<MDL	<MDL
	FP	2.63	4.56	<MDL	5.32	<MDL	<MDL	1.97	1.38	3.83	70.84	<MDL	0.79	<MDL	2.16	0.55	5.54	<MDL	<MDL
12-Dec-2018	FP	2.13	3.00	0.83	2.46	<MDL	0.18	1.22	1.20	2.74	7.88	0.03	0.45	<MDL	1.89	0.12	<MDL	<MDL	0.07

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682 Supplemental Table 1 - Daily Freshwater river flow to the upper Providence River from the
683 Blackstone, Ten Mile and Moshassuck Rivers during the time of the spill.

684 Supplemental Table 2 - LC mobile phase gradient conditions.

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

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

687 Supplemental Table 5 - Correlation to Amount of Thunderstorm Digested

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