Published in final edited form as:

Environ Pollut. 2020 October ; 265(Pt B): 115009. doi:10.1016/j.envpol.2020.115009.

Temporal and spatial analysis of per and polyfluoroalkyl substances in surface waters of Houston ship channel following a large-scale industrial fire incident

Noor A. Aly^{1,2}, Yu-Syuan Luo^{1,2}, Yina Liu^{3,4}, Gaston Casillas^{1,5}, Thomas J. McDonald⁵, James M. Kaihatu⁶, Mikyoung Jun⁷, Nicholas Ellis⁸, Sarah Gossett⁸, James N. Dodds⁹, Erin S. Baker⁹, Sharmila Bhandari^{1,2}, Weihsueh A. Chiu^{1,2}, Ivan Rusyn^{1,2}

¹Interdisciplinary Faculty of Toxicology, Texas A&M University, College Station, TX

²Department of Veterinary Integrative Biosciences, Texas A&M University, College Station, TX

³Geochemical and Environmental Research Group, Texas A&M University, College Station, TX

⁴Department of Oceanography, Texas A&M University, College Station, TX

⁵Department of Environmental and Occupational Health, Texas A&M University, College Station, TX

⁶Zachry Department of Civil & Environmental Engineering, Texas A&M University, College Station, TX

⁷Department of Statistics, Texas A&M University, College Station, TX

⁸Galveston Bay Foundation, Houston, TX

⁹Department of Chemistry, North Carolina State University, Raleigh, NC

Abstract

Firefighting foams contain per- and polyfluoroalkyl substances (PFAS) - a class of compounds widely used as surfactants. PFAS are persistent organic pollutants that have been reported in waterways and drinking water systems across the United States. These substances are of interest to both regulatory agencies and the general public because of their persistence in the environment

Author statement:

Noor A. Aly: Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft; Yu-Syuan Luo: Data curation, Formal analysis, Investigation, Methodology; Yina Liu: Data curation, Formal analysis, Methodology, Validation, Writing - original draft, Writing - review & editing; Gaston Casillas: Formal analysis, Investigation, Visualization; Thomas J. McDonald: Funding acquisition, Resources; James M. Kaihatu: Formal analysis, Software, Visualization; Mikyoung Jun: Formal analysis, Software; Nicholas Ellis: Conceptualization, Investigation; Sarah Gossett: Conceptualization, Supervision, Resources; James N. Dodds: Investigation; Erin S. Baker: Funding acquisition, Supervision; Sharmila Bhandari: Formal analysis, Software, Visualization; Weihsueh A. Chiu: Conceptualization, Formal analysis, Funding acquisition, Supervision, Visualization, Writing - review & editing; Ivan Rusyn: Conceptualization, Funding acquisition, Project administration, Supervision, Visualization, Writing - original draft, Writing - review & editing

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

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.

and association with adverse health effects. PFAS can be released in large quantities during industrial incidents because they are present in most firefighting foams used to suppress chemical fires; however, little is known about persistence of PFAS in public waterways after such events. In response to large-scale fires at Intercontinental Terminal Company (ITC) in Houston, Texas in March 2019, almost 5 million liters of class B firefighting foams were used. Much of this material flowed into the Houston Ship Channel and Galveston Bay (HSC/GB) and concerns were raised about the levels of PFAS in these water bodies that have commercial and recreational uses. To evaluate the impact of the ITC incident response on PFAS levels in HSC/GB, we collected 52 surface water samples from 12 locations over a 6-month period after the incident. Samples were analyzed using liquid chromatography–mass spectrometry to evaluate 27 PFAS, including perfluorocarboxylic acids, perfluorosulfonates and fluorotelomers. Among PFAS that were evaluated, 6:2 FTS and PFOS were detected at highest concentrations. Temporal and spatial profiles of PFAS were established; we found a major peak in the level of many PFAS in the days and weeks after the incident and a gradual decline over several months with patterns consistent with the tide- and wave-associated water movements. This work documents the impact of a large-scale industrial fire, on the environmental levels of PFAS, establishes a baseline concentration of PFAS in HSC/GB, and highlights the critical need for development of PFAS water quality standards.

Graphical Abstract

Capsule:

Temporal and spatial analysis of PFAS in surface waters following industrial fire.

Introduction

Per and polyfluoroalkyl substances (PFAS) are synthetic molecules comprising a carbon chain with fluorines attached (Munoz et al., 2017). Their physicochemical properties make them an ideal component of numerous consumer and industrial products, including cookware, water and oil-resistant fabric, and aqueous film forming foams (AFFFs) that are used in fire suppression (ATSDR, 2018; Munoz et al., 2017; NIEHS, 2020). Due to their

widespread use and persistence, PFAS have become an emerging public health challenge globally. Humans are exposed to PFAS by ingesting contaminated water and food, use of various household items (*e.g.*, food containers), by inhalation, and via occupational exposure (Boone et al., 2019; Poothong et al., 2020; U.S. EPA, 2018). It was reported by the Centers for Disease Control and Prevention's National Health and Nutrition Examination Survey (2011–2012) (NHANES, 2012) that PFAS were detected in serum of 97% of Americans (Lewis et al., 2015).

Among the thousands of PFAS known to be produced, only a small number have been investigated in detail using human or animal models (Patlewicz et al., 2019). For example, an epidemiological study conducted by the C8 study panel in the Ohio River Valley that followed both residents and workers exposed to perfluorooctanoic acid (PFOA) from the DuPont chemical plant showed a link to kidney and testicular cancer, ulcerative colitis, thyroid disease, hypercholesterolemia and pregnancy-induced hypertension (Nicole, 2013). The National Toxicology Program has concluded that two of the most-studied PFAS, PFOA and perfluorooctane sulfonate (PFOS), present a hazard to immune system function in humans (NTP, 2016). However, the full extent of the potential health effects of these substances is largely unknown and efforts to systematically review available evidence (Pelch et al., 2019; Sunderland et al., 2019) and collect new toxicity data (Patlewicz et al., 2019) are underway.

Considering the possible adverse health effects due to PFAS exposure, in the early 2000s the United States Environmental Protection Agency (U.S. EPA) published a drinking water advisory for PFOS and PFOA, which ultimately led to the reported discontinuation of production of these substances in the U.S. by some manufacturers (McCord et al., 2018; U.S. EPA, 2016a). However, production of other forms of PFAS is on the rise (Martin, 2019; Ritscher et al., 2018). The U.S. EPA monitored for PFOS, PFOA, perfluorononanoic acid (PFNA), perfluorohexane-sulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), and perfluorobutanesulfonic acid (PFBS) in drinking water between 2013 and 2015 (U.S. EPA, 2016b); however, there are no Maximum Contaminant Levels (MCLs) or regulations established for these chemicals that apply across the U.S. A number of states have established or proposed MCLs for several PFAS. Recently, the U.S. Congress has indicated intent to strengthen regulation of PFAS under the pending decision of the National Defense Authorization Act. Congress proposes to designate all PFAS as hazardous substances under the Comprehensive Environmental Response, Compensation and Liability Act (known as Superfund), as toxic pollutants under the Clean Water Act, and to phase out military use of PFAS-containing AFFFs by 2025 (Johnsen-Harris and Chetwynd, 2019).

PFAS are ubiquitous in the environment and their long-range transport is of interest to researchers and decision-makers (Xu et al., 2013). Many studies have focused on characterization of legacy contaminated sites and the resulting presence of these substances in food, groundwater and air, as well as in human serum and urine. In the past two decades, almost 500 industrial facilities that may be discharging PFAS into the air and water have been identified in the US (Hayes et al., 2019; Pan et al., 2018; Sunderland et al., 2019). Industrial releases and waste site leaching represent fixed long-term PFAS point sources exposure sites; however, far less is known about the extent of the environmental

contamination during singular events. For example it has been documented that during the fire and collapse of the World Trade Center, PFAS were released into the environment (Spratlen et al., 2020; Spratlen et al., 2019), but other instances where PFAS are used such as during industrial fires may present unique one off releases where large concentrations of PFAS can enter the surrounding environment.

PFAS are used in fire-suppressing AFFFs, they can rapidly extinguish hydrocarbon fuel fires as well as form an aqueous film on the fuel surface to prevent evaporation and re-ignition (ITRC, 2017). AFFFs are a proprietary blend of surfactants, many contain PFAS which can be created through electrochemical fluorination or telomerization (Barzen-Hanson et al., 2017). Electrofluorination-based fluorochemicals possess fully fluorinated carbon chains with homologues of varying $[CF_2]$ units. Telomerization-based fluorochemicals possess carbon chains that are not fully fluorinated and typically have homologues of varying $[C_2F_4]$ units (Place and Field, 2012). Noticeable differences in PFAS composition of AFFFs have been documented and most of AFFFs have proprietary formulations that make exposure assessment difficult (Awad et al., 2011; McCord et al., 2018; Mejia-Avendano et al., 2017).

A recent example of a large-scale deployment of AFFF is the petrochemical fire that occurred in the Houston area in March of 2019. Millions of liters of Class B fire-fighting foams were deployed over several days to contain the fire (Thomas, 2019). Although there was a dike wall in place to prevent AFFFs from reaching public waterways, a breach occurred that caused the foams to escape into the Buffalo Bayou, part of the Houston Ship Channel (HSC) that is connected to Galveston Bay (GB). Our study hypothesized that this incident will result in large-scale PFAS contamination in HSC/GB, an area that also is used for recreation. To characterize the extent of the environmental release of PFAS from this disaster, the concentrations of these contaminants in surface water, and the duration of the elevated levels of PFAS, we conducted a temporal and spatial survey of the waters in the HSC/GB. Understanding the extent and spread of PFAS in the environment is important to determine the potential for human exposure during major incidents. In addition, this study provides important information with respect to the patterns of use of both legacy and novel PFAS in firefighting foams.

Materials and Methods

Incident Description.

The tank fires at the Intercontinental Terminals Company (ITC) in Deer Park, TX in the greater Houston area (Figure 1) were discovered at around 10 am on March 17, 2019. The fire originated in an 80,000 barrel (12.7 million liter) aboveground storage tank that held naphtha. Firefighting efforts began shortly after the incident was reported; however, firefighters were unable to contain the fires and leaking naphtha. By March 18, 2019, seven adjacent storage tanks of similar size had caught fire. The fires were completely extinguished by the afternoon of March 20, 2019. On March 22, 2019 a portion of the barrier wall surrounding the tanks failed, releasing a mixture of spilled and AFFF chemicals into the Tucker Bayou that is located less than 500 meters from the site of the fires. The Tucker Bayou merges into the Buffalo Bayou, which in turn merges with the greater HSC/GB estuary. Recovery of the spillage produced about 33,000 barrels (5.2 million liters)

of oil slick and foams mixed with water (Ortiz and Schneider, 2019); however, the full extent of the contamination of the HSC/GB is unknown and it is likely that a wide range of PFAS dispersed into the water.

A number of chemically-diverse AFFFs were used in the ITC response [Supplemental Table 1, Dr. Michael Honeycutt (Texas Commission of Environmental Quality, TCEQ), personal communication] and included ANSULITE 3% (AFC3B), ANSULITE 3×3 AR-AFFF LV (A334-LV), ANSULITE 3×6 AR-AFFF (A364), ANSULITE LOW VISCOSITY 3X3 AR-AFFF Foam Concentrate, Dwight P. Williams Signature Series 1%×3%, THUNDERSTORM W813A 1X3 AR-AFFF, CHEMGUARD ULTRAGUARD 3% AR-AFFF, and UNIVERSAL GOLD 1%/3% Alcohol. U.S. EPA and TCEQ staff were deployed to the area to monitor for gases (hydrogen sulfide, carbon monoxide and oxygen) and volatile organic compounds (naphtha, benzene, xylene and toluene). Air quality was the primary concern immediately following the fires. Water samples were also collected at regular intervals (daily and weekly) to measure metals and semi volatile organic chemicals starting on March 21, 2019 (U.S. EPA, 2019). PFAS analysis was performed only for the water samples collected on March 21, 2019 (U.S. EPA, 2019).

Sample Collection.

Surface water samples were collected from either open water (from a motorized boat) or from several shore-accessible locations as detailed in Table 1. Collection followed the general guidance on sampling as described in the EPA Method 537.1 (Shoemaker and Tettenhorst, 2018). Samples (n=52, 700–1,000 mL each) were collected over 8 field sampling trips (between March 21, 2019 and August 2, 2019) to the HSC/GB area. Because of the emergency nature of the ITC fire and intermittent “shelter in place” orders for some of the sampling sites, not every location had a sample collected on March 21, 22, and 29, 2019. The sampling locations and their relative distance from the ITC incident site are displayed in Figure 1 and summarized in Table 1. Sampling dates and exact locations for each site are detailed in Supplemental Table 3. Samples were collected into one liter pre-washed high-density polyethylene (HDPE) bottles (cat. #1162D42, Thomas Scientific, Swedesboro, NJ) at depths of approximately 0.3 meters. To prevent contamination, clean nitrile gloves were used at every sampling site and bottles were double bagged for transport. Samples were stored on ice or at 4°C until extraction following recommendation by EPA Method 537.1. A deviation from the EPA method consisted of (i) collection of one sample per location and (ii) no addition of preservatives.

PFAS Reference Materials.

Calibration standards and isotopically labeled compounds of perfluorinated carboxylic acids and sulfonates (Supplemental Table 4) were obtained from Wellington Laboratories (Guelph, Ontario).

Sample Preparation.

Sample Extractions.—The procedures for sample extraction were exactly as detailed in Waters Perfluorinated Compound Analysis manual (Silcock et al., 2020). For samples collected in March and April 2019, 50 mL aliquot of each water sample was used for

extraction. For samples collected in June, July and August 2019, 250 mL aliquot of each water sample was used for extraction because we expected lower concentrations of PFAS months after the incident. Samples were decanted into a polypropylene centrifuge tube (cat. #28–106, Genesee Scientific, San Diego, CA) or HDPE bottles (cat. #414004–113, VWR) and extraction standards were added (see below and Supplemental Table 5). Samples were extracted with Oasis weak anion exchange (WAX) cartridges (cat. #186003519, Waters, Milford, MA) in a vacuum manifold exactly as detailed by (Silcock et al., 2020). To determine whether any analytes were lost during sample washes, we collected the 100% methanol wash from the samples and found no detectable PFAS (data not shown). Samples were also prepared without the 100% methanol wash and we observed significant interference from the sample matrix (data not shown). Therefore, the washing step with 100% methanol, before final elution with 0.1% NH_4OH , is a necessary step to further remove salts and other interference matrices from complex environmental samples. Extracted samples were stored at -20°C until analysis.

Due to the unexpected nature of the incident, no pre-extraction standards were available during the first extraction, for these samples the pre-extraction standards were added directly prior to instrumental analysis. A list of the chemicals and solvents used in these experiments can be found in Supplemental Table 5.

Instrumental Analysis.

Liquid chromatography (LC) tandem mass spectrometry (MSMS) data acquisition and quantification were performed using Agilent (Santa Clara, CA) 1260 Infinity II High Speed Pump coupled with a 6470 triple quadrupole MS (Agilent) with electron spray ionization (negative mode). LC conditions were adapted from the PFAS method of (Anumol et al., 2018). Briefly, the chromatographic separation was achieved with a C18 column (Agilent ZORBAX SB C-18, 2.1×50 mm, $1.8 \mu\text{m}$). A flow rate was 0.4 mL/min, 20 μL injection volume and a binary mobile phase gradient consisted of mobile phases A (5 mM ammonium acetate in water) and B (5 mM ammonium acetate in 95% methanol). The gradient was as follows: 10% B held for 0.5 minutes, B increased to 30% by 2 minutes, B increased to 95% by 14 minutes and 100% B by 14.5 minutes. 100% B was then held for 2 minutes to elute strongly retained compounds then switched back to 10% B and held for 6 minutes to equilibrate the stationary phase. Acquisition method details are provided in Supplemental Table 6. MassHunter Acquisition Software (C.01, Agilent) was used for instrument control and data acquisition. MassHunter Quantitative Analysis Software (B.08, Agilent) was used for data processing and analysis. Supplemental Figure 1A shows LC-MS chromatograms for the standards in a mixture of 27 PFAS that were used (see Supplemental Table 4).

The identification of compounds was based on 3 criteria. First, retention time had to match with tolerance of 0.1 min (average standard deviation of retention time was 0.04 min). Second, for MSMS transitions we followed the EPA Method 537.1 criteria that identify a single transition per compound from the reaction monitoring. Additional ions (see Supplemental Table 6) were used to verify all targets based on MSMS transitions detected in our laboratory using pure standards. Third, ratios of quantification and qualification ions had to be at a 20% tolerance. Compound quantification was based on the ratios between native

compounds and isotopically labeled surrogates in the extraction standards, where available. Isotopically labeled fluorotelomer sulfonate (FTS) standards were not available in our laboratory at the time of the analysis. Therefore, the concentrations for FTS are relative and not absolute. However, the patterns through time are informative. Calibration curve mixtures and samples were in the same solvent matrix (96% MeOH) for LC-MSMS analysis.

Quality Assurance/Quality Control for Analysis.

Blanks.

For each batch of extracted samples (6–16 samples in each batch as shown in Supplemental Table 3), at least one procedural blank (ultrahigh purity water in the sample container) was also extracted following the same protocol as the field samples. Additionally, solvent blanks (96% methanol) were also run to track solvent and instrument background. Solvent blanks were run after every 5 field samples to monitor for background and carryover. All analytes in blank (procedural and solvent) samples were below LOQ (data not shown). It should be noted that even after substantial washing, the procedural blanks contained various levels of PFBS. PFBS procedural blank concentrations were consistently below the limit of quantification (LOQ; see Supplemental Table 3), and PFBS signal (*i.e.*, peak area) in solvents blanks was consistently lower than 5% of the lowest calibration standard.

Calibration, Extraction, and Injection Standards.

Calibration stock mixture was created by combining Wellington Laboratories' PFAC-MXC and individual compounds (Supplemental Table 4, Calibration Mix Substances). Calibration curve was created by serial dilution of the stock mixture (Supplemental Table 4). Supplemental Figures 1D and 1E illustrate representative calibration curves for a number of perfluorinated and fluorotelomer standards, respectively. It should be noted that PFBS in the calibration curve (Supplemental Figure 1D) exhibited a response at a concentration of 0 ng/mL suggesting an internal contamination source such as the LC mobile phases used or pump seals and it means this compound cannot be accurately quantified. Representative data on the linearity of the calibration curves are in Supplemental Table 7.

Extraction standards (ES; MPFAC-C-ES) and injection standards (IS, MPFAC-C-IS) were from Wellington Laboratories (Supplemental Table 4, External and Internal Standards). ES were not available during the extraction of the first batch of samples (April 19, 2019 analysis date, Supplemental Table 3). This batch of samples was processed immediately after collection as recommended, not waiting for standards to arrive. Because of the unexpected nature of this disaster, extraction standards were added to these samples before LC-MSMS analysis. The samples were quantified based on the ratio of the target response normalized to the mass labeled extraction standard. ES were spiked into each sample before extraction for all other samples at a 5 ng/mL final concentration (1 mL final elution volume). ES were also spiked into all calibration standards at a final concentration of 5 ng/mL. IS and calibration standards were spiked into all extracted samples prior to injection to the LC-MSMS at a final concentration of 5 ng/mL. IS were used to track potential instrument drift and assess relative recovery of the ES.

Continuing Calibration.

To ensure sample analysis accuracy and consistency within sample batches, a full range calibration curve was run for each sample batch. Additionally, continuing calibration standards from mid and high concentration ranges were run after every 5 field samples throughout the analytical sequence.

LOD and LOQ.

LOD was determined based on a serial dilution method for the standard mix. LOQ was determined based on a serial dilution of the standard mix and calculated concentration was >85% and <115% of accuracy. LOQ values for each analyte are listed in Supplemental Table 3. In the analyses conducted in April and May 2019, substantially higher LOQ values (Supplemental Table 3) were observed as compared to the later analysis dates. This difference may result in a biased comparison of PFAS occurrence among the sampling campaigns. To determine the variability contributed by sample extraction, one of the field samples (SCWS2 collected on April 24, 2019) was extracted twice and analyzed. For all analytes that were above LOQ, except PFBS and L-PFDoS, duplicates were within 20% (Supplemental Table 8). Overall method precision for each analyte was determined by repeated injections of standards (n=3) over 12 hr period. Percent difference between repeat injections was below 20% for each analyte (Supplemental Table 9).

Temporal Analysis.—Because a relatively small number of samples were available for individual PFAS at each sample location, formal time-series analysis could not be performed. However, two statistical analyses were performed to increase confidence in the visual observed trends. If a linear trend was observed (“peak” at first time point), then a linear trend test was performed to confirm that the trend was unlikely to be due to chance. If a “peak” was observed after the first time point, then the data were first differenced to find the change in concentrations between time points, then a change-point test was performed to confirm that change in the “slope” was unlikely to be due to chance. We used these analysis as corroborating evidenc, and did not require formal statistical significance ($p < 0.05$), particularly for the open water locations, due to low sample sizes. Software used was RStudio version 1.2.1335 with R version 3.6.1, and the changepoint R package version 2.2.2 (Killick and Eckley, 2014).

Spatial Analysis.—Spatial interpolation is one of the most often used geographic techniques for spatial query, spatial data visualization, and spatial decision-making in geographic information system (GIS) mapping and environmental science (Fotheringham and Wegener, 1999). In this longitudinal study, surface water samples were taken from the same locations every 6–12 weeks over a course of 6 months. The data on selected PFAS concentrations in these samples were interpolated and visualized using ArcGIS software (v. 10.4, ESRI Inc., Redlands, CA). The total shape file for the Houston Ship Channel was taken from the Houston – Galveston Area Council GIS data set. The specific shape file used for the study was generated from subsections of the shape file for the entirety of the Houston Ship Channel. Sampling locations were spatially joined to the Houston Ship Channel using a Radial Base Function analysis, one of the most accurate spatial interpolation models (Meng et al., 2013). Radial Basis Functions (RBF) are a series of exact interpolation techniques

which create a smooth surface covering each measured data point. RBF is ideal for an area with a large number of data points with gently varying surfaces such as elevation (ArcGIS, 2020). The RBF analysis is part of the “Geospatial Analyst tool” in ArcGIS software.

Concentrations of PFOS and 6:2 FTS from the sampled sites were used as inputs for interpolating the estimated concentrations throughout the study area. The output of the interpolation was visualized using choropleth maps. These maps use themes to shade predetermined areas of maps that represent statistical data, in this case PFAS concentrations. The creation of each choropleth map was based on location inputs along the area of interest. Two different groups of longitudinal choropleth maps were created, one for PFOS and the other for 6:2 FTS. Both choropleth maps have 5 distinct categories of concentration based on quintiles in the data for the entire study. Categories based on both PFOS and 6:2 FTS concentration were displayed by color, with red being the highest concentration and white, the lowest. The RBF smoothing shades the areas of the Houston Ship Channel shape surrounding the sampling location with predicted concentration values. Finally, the choropleth maps were created for each sampling period using a Lambert Conformal Conic projection suitable for the state of Texas. All spatial analyses were performed using ArcMap function in ArcGIS.

Hydrodynamic Modeling.—To determine the possible paths taken by the water masses near the ITC site at the time of the incident and response, the Delft3D model suite (Lesser et al., 2004) was used. The modeling suite is capable of simulating the water motion due to waves, tides and winds. A system of four nested grids was created, starting with one encompassing the entire Gulf of Mexico and ending with a smaller grid enveloping the HSC. The model grids used are shown in Supplemental Figure 3. Grid parameters are shown in Supplemental Table 10. Information from the larger grids (mainly time series of tidal elevations) was saved along the boundaries of the nested grid. Model input included information on waves, winds and tides; tides were run over all four grids, while winds were run only on the smallest domain (Supplemental Figure 3D). The model has been validated (Kim et al., 2019) for the case of hydrodynamics forced by cold front passage near Galveston Island.

Information on the grid configuration, nesting, forcing information and wind-wave calculation is as follows. For tides, we used information (in the form of tidal constituents) from the Inverse Tidal Model (Egbert and Erofeeva, 2002). The constituents from March 15 – April 30, 2019 were applied at the boundaries of the Gulf of Mexico grid to represent tidal motion. Tidal elevations constructed from these constituents were then propagated across the Gulf of Mexico, successively feeding the smaller grids. This insured that the tides in shallow water were properly represented, as tidal constituents in shallow water can be inaccurate (Le Provost, 2001) and thus not suitable for directly forcing a shallow water model. Wind and wave information was obtained from a buoy deployed by the National Data Buoy Center (Station 42035, located at 29.232°N, 94.413°W). Winds were input to the model every 6 hrs, and were assumed constant over the domain of Houston Ship Channel. The computational time step for all models was 1 min.

Simulations for waves in GB and HSC proved to be challenging because the lack of spatially-distributed wind measurements over the Gulf made it impossible to accurately model wind-wave generation to the edge of the GB domain boundary. While the wave conditions at Station 42035 can be used to initialize the model, these are conditions only at one point, and are likely different along the boundary due to variations in water depth. This lack of heterogeneity along the boundary was likely responsible for non-convergence of the wave model within the GB (and consequently the HSC) domains. Alternatively, we made use of wind-wave growth expressions to estimate the wave energy in Galveston Bay without the dedicated wave model. We first assumed that swell wave propagation from the offshore has little impact on the bay because it can only enter through the narrow inlet separating Galveston Island and Bolivar Peninsula. We then used the fetch-limited wave growth formula (Hasselmann et al., 1973) to determine the wave height and period associated with an estimated fetch (length over which the wind can generate waves) of 37 km (the distance from the entrance to Galveston Bay to the edge of the HSC grid) for the highest wind speed in the data (10.7 m/s). This led to a wave height estimate of 1.05 m and a period of 4.56 s. To determine the likely impact of waves on the drogue motion, we assumed that the primary influence of waves on the drogue motion is through the Stokes drift (the mean net transport from waves). Using a simplified expression for this quantity for this maximum wind-wave condition (Dean and Dalrymple, 1991), we determined that the maximum Stokes drift velocity is 0.02 m/s, far smaller than the average tidal velocity and thus can be justifiably neglected.

Results

In the days and months following the fires at the International Terminals Company (ITC) in Houston, TX, surface water samples were collected from 7 shore-accessible and 5 open water locations in HSC/GB area as detailed in Figure 1. Samples (Table 1) were collected upstream (n=3), downstream (n=8), and in close proximity to the incident site (n=1) to determine the spatial distribution and the types of PFAS released at the point source of ITC industrial installation. There were 8 separate sampling campaigns conducted over the course of 6 months (March-August 2019) to determine temporal patterns of PFAS contamination in HSC/GB.

A total of 27 PFAS (see raw data in Supplemental Table 3) were analyzed in all collected samples (Table 1). Supplemental Figure 1B–C shows representative LC-MS chromatograms for samples collected from the open water at location SCWS2, which was closest to the ITC incident, in March (Supplemental Figure 1B) and June (Supplemental Figure 1C) 2019, respectively. A clear trend towards reduction in abundance of the detectable PFAS is evident from these data. Of 27 target PFAS, 15 were detected in amounts over the LOQ in at least one experimental water sample – PFOS, PFBS, PFHpA, PFNA, PFOA, PFHxS, 6:2 FTS, 8:2 FTS, perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA), perfluoropentanesulfonic acid (L-PFPeS), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), and perfluorododecanesulfonic acid (L-PFDoS). The remaining 12 species were below the limit of quantitation in every sample.

Temporal patterns in the concentrations of 6 PFAS that were most abundant across the samples collected at 5 open water locations (Table 1) are shown in Figure 2. In each sample, as expected, there is a clear spike of PFAS, especially 6:2 FTS and PFOS, immediately following the fires. 6:2 FTS peak concentrations reached 1,446 ng/L (sample SCWS1) on March 22nd which is significantly larger than the PFOS peak concentration of 247 ng/L (sample SCWS3). Other detected PFAS had peak concentrations below 50 ng/L. Concentrations were highest at close proximity to the site of the incident (sample location SCWS2) and immediately adjacent to the site (SCWS1). Sample SCWS3 was upstream from the incident site and had similar peak concentrations of 6:2 FTS and PFOS as sample SCWS5, which was the furthest downstream. Levels of these and other detected PFAS remained at comparable levels in April 2019, but declined considerably by June 2019 and remained low in July 2019. All “peaks” were identified by either linear trend or changepoint detection, with p-values ranging between 0.03 and 0.27 due to small sample sizes (n=4 per PFAS per location, Supplemental Figure 2A). Spatial patterns in PFAS concentrations measured using samples collected in this study were similar to those reported by the U.S. EPA in samples collected on March 21, 2019 (Supplemental Table 2).

Temporal patterns in the concentrations of 6 PFAS that were most abundant across the samples collected at 4 shore-accessible areas (Table 1) with the largest number of sampling events are shown in Figure 3. Similar to the open water samples, 6:2 FTS and PFOS were most abundant and were also measured to have similar concentrations to the open water samples. All 4 areas shown were distal to the site of the incident and the levels of all detected PFAS spiked rapidly in the second or third sample taken. The Lynchburg Ferry sampling site was closest to the open water sample SCW5 and the concentrations of 6:2 FTS and PFOS peaked several weeks after the start of the incident. Peak levels of 6:2 FTS were 1,492 ng/L on March 29, 2019. Baytown Nature Center sampling location was further away and downstream from the Lynchburg Ferry location and the peak of PFAS was delayed until April; still, the concentrations of all PFAS reached similar peak levels to other samples. Morgan’s Point and River Terrace Park sampling locations were farthest away from the incident site and concentrations of PFAS peaked in April. All “peaks” were identified by either linear trend or changepoint detection, with all p-values <0.05 (n=6 to 8 per PFAS per location, Supplemental Figure 2B).

Because clear spatial patterns in concentrations of PFAS were observed, we conducted data interpolation as detailed in Methods to estimate water concentrations across HSC/GB estuary based on sampled locations. For this analysis, we chose to construct the maps for March, April, and June 2019 by combining all data available to us for each of these months. To increase the number of observations, we also included data from US EPA that was available for one date in March 2019 (Supplemental Table 2). We chose to map 6:2 FTS and PFOS because these compounds were detected at the greatest concentrations. To enable interpretation of the spatial visualizations across the temporal scale, data for each compound across all samples was divided into quintiles and plotted using red-white color scale (Figure 4). Both PFAS showed similar spatial patterns, with the greatest levels observed in March 2019 at, or near the incident site. Concentrations decreased by April 2019 at or near the incident site with the highest concentrations detected at distal sites downstream. By June

2019, concentrations of both compounds markedly decreased with some detectable levels around the incident site and at several distal locations.

It is noteworthy that we detected PFAS not only at the site of the incident and downstream, but also at several locations that were at a considerable distance upstream in the Houston Ship Channel (sampling locations SCWS3 and SCWS4), as well as in the North-most areas of the Galveston Bay (River Terrace Park location). To confirm that water movements in this part of the estuary can occur in both directions, hydrodynamic analysis was performed (Figure 5) using the Delft3D model as described in Methods. Importantly, the modeling exercise performed in this study was meant to address the question of why PFAS concentrations increased over time in locations that were upstream from the site of the incident. This modeling was not meant to address sediment transport or PFAS sorption, both important processes that can impact PFAS transport (Li et al., 2018; Oliver et al., 2020).

To illustrate the patterns of general water movements in the area of study, a numerical “drogue” – a parcel of water whose motion is tracked – was released at the Buffalo Bayou location closest to the location of the ITC starting March 17, 2019 at midnight, with one additional drogue released each day for seven consecutive days (until midnight March 23, 2019). These dates were chosen to represent the time period that included active firefighting and the subsequent spill of the partially contained foam into the Tucker and Buffalo Bayous (see Methods and Figure 1). The simulated position of each of these seven drogues was tracked until April 30, 2019.

Two maps are shown, one that accounts for the water movement affected by tides (Figure 5A) and one that includes both tide and wind forces (Figure 5B). The dots on the map represent the cumulative path of seven daily drogues at a given point in time (60 min intervals) until April 30, 2019. The drogues move back and forth past the ITC incident site under the influence of the tides (Supplemental Table 11), and tides and winds (Supplemental Table 12). It is noteworthy that the drogues pass by all of the sampling locations. The density of the drogue positions is higher in the upper reaches of the HSC, upstream of the ITC, but there is also some motion toward GB. The trend towards clustering of the drogues in the upper reaches of the HSC is likely due to the relatively shallower water and slower flow velocities in this area. The trend toward GB may be attributed to longer-term tidal components present in the area influencing the water movement beyond the daily periodic trends. It is important to note that the model was simulating a trajectory of a drogue which represents a unit of water in the estuary and not the trajectory of a *contaminant*. The extent of the water mass transport is thus used as a surrogate for the possible extent of contaminant (e.g., PFAS) transport where only advection of the material with the flow occurs. Phenomena that are not modeled may either increase (e.g., via diffusion, turbulent mixing) or decrease (e.g., via sorption or degradation) movement of contaminants.

Discussion

ITC Fire Response Resulted in a Release of PFAS into the Houston Ship Channel

While many of the known sites with routine use of AFFFs have been monitored for PFAS (Ahrens et al., 2015; Lanza et al., 2017), less common is monitoring after specific large-

scale releases. The present case study provides several important inferences regarding temporal and spatial distribution of PFAS after a major firefighting response. Two PFAS were detected in considerable amounts following the fires: PFOS and 6:2 FTS, both of which are known to be constituents or degradation products in AFFF (Houtz et al., 2018). Following a health advisory released by US EPA in 2002, the manufacturing of products containing PFOS and PFOA was discontinued in the U.S. However, many companies creating AFFF already had a supply of formulations containing PFOS in storage. These products became known as legacy AFFF. Legacy AFFF use is not banned by federal law in the U.S.; however, their use is limited to emergency situations. PFOS is also known to be the degradation product of C8 perfluorooctane sulfonamides (Buck et al., 2011). While these are not common constituents of currently manufactured AFFFs, they were also historically used. Degradation of these C8 precursors may be contributing to the observed environmental concentrations of PFOS (Barzen-Hanson et al., 2017; Wang et al., 2009).

AFFF release during the ITC fire occurred from March 17–22, 2019 (KHOU, 2019). The prior recorded release of AFFF in Houston occurred at the Ellington Field Joint Reserve Base in 2018. Water PFOS levels were reported at about 47 ng/L, 6-fold lower than the highest concentrations of PFOS detected after the ITC fires (EWG, 2019). From the temporal analysis, we observed all PFAS decrease over 100-fold in the Houston area over the 6-month sampling period. Similar temporal patterns have been reported at other known AFFF contamination sites (Ahrens et al., 2015; Lanza et al., 2017; Moody et al., 2002), with levels of PFAS decreasing precipitously within months of the known release.

A number of studies reported on surface water levels of diverse PFAS in the estuaries across the world that may have been impacted by continuous industrial discharges. For example, contamination of surface waters in the watershed of the River Rhine by PFAS was found to be dominated by PFBS and PFBA, with PFOS levels to be at around 10 ng/L (Moller et al., 2010). A study of PFAS in the industrially polluted Vaal River in South Africa found that PFPeA was the highest (around 40 ng/L) among 15 substances evaluated (Groffen et al., 2018). In China, various studies reported that surface water PFAS are dominated by the PFOS, PFHxA, PFPeA and PFBA (Cai et al., 2018; Chen et al., 2017). In the US, GenX and related perfluoroalkyl ether acids were detected in the Cape Fear River and in finished drinking water in North Carolina (Hopkins et al., 2018). In our study of a water contamination event associated with a fire-fighting incident, we found 6:2 FTS to be at highest concentrations among 27 PFAS evaluated. This is likely because PFOS precursor-containing AFFFs are not frequently used, but AFFFs containing 6:2 FTS itself or its precursors could have been deployed in greater quantities. 6:2 FTS is a fluorotelomer which is known to be a constituent of some AFFFs, but is used primarily in many industrial applications as a replacement for PFOS (Buck et al., 2011; Coggan et al., 2019; Field and Seow, 2017). Upstream precursors, such as 6:2 fluorotelomer thioether amido sulfonate (6:2 FTSAS) and 6:2 fluorotelomer sulfonamidoalkyl betaine (6:2 FTAB), that are present in certain AFFFs formulations can transform to intermediates including 6:2 FTS (Harding-Marjanovic et al., 2015; Shaw et al., 2019; Weiner et al., 2013). 6:2 FTS is less persistent than PFOS and degrades to perfluorohexanoic (PFHxA) and perfluoroheptanoic (PFHpA) acids (NASF, 2019). Indeed, we found that PFHxA followed closely the temporal patterns of 6:2 FTS ($r^2=0.71$, $p<0.0001$). 6:2 FTS can also generate even shorter-chain perfluoroalkyl

carboxylates such as PFPeA and PFBA via environmental and engineered processes (Martin et al., 2019; Wang et al., 2011). Elevation of these substances may also reflect the influence (e.g., environmental degradation) of other fluorotelomer precursors not targeted in the present study. This may explain why these PFAS were also observed in elevated concentrations in the Houston area waterways after this incident.

PFAS Contaminants Distributed both Up- and Down-stream from the Site of the Incident

Interestingly, PFAS were also detected upstream from the ITC site, this behavior is not uncommon in tidal waterways (Munoz et al., 2017). Our analysis of the tidal movement of water in the HSC showed that water flowed upstream from the ITC incident site. As expected, in the weeks immediately following the fire, the highest levels of PFAS were observed in the HSC near the site; but after a month, these chemicals reached farther areas surrounding the GB before eventually diluting by summer. The water movement modeling undertaken in this study was meant to demonstrate the plausibility of both up- and down-stream transport of contaminated water from the site of the incident and AFFF discharge. The area of the incident is located inland, yet the tides, waves and wind make a major impact on water movement and mixing, as shown by our modeling simulations. These simulations, as well as spatial and temporal patterns in PFAS levels, support convincingly the notion that ITC was the point source for the PFAS detected both up-stream in the Buffalo Bayou and north of the Buffalo Bayou in the GB estuary.

While this water movement modeling was informative, it is not suitable for the purpose of PFAS fate and transport analysis in HSC/GB. Sorption behavior of PFAS is highly complex and could not be explained by a single soil or sediment property (Li et al., 2018). There are currently limited data on the sorption behavior of PFAS in marine or estuarine sediments and the properties controlling their sorption have not been well established (Oliver et al., 2020). Our study did not collect data on organic carbon, pH and sediment content in the surface water samples, properties that are known to have significant effect on PFAS sorption; therefore, additional studies with thorough characterization of the water and sediments are needed to better understand their role in PFAS transport and sorption.

Substantial Gaps Exist Due to Lack of Standards for Characterizing Risk from PFAS Releases

Our study is also highly informative for PFAS exposure characterization. Although no PFAS have federal, enforceable limits set for water contamination, many states sought to fill this gap by developing their own guidance levels. Table 2 compares the PFAS surface water concentrations we observed with the range of available standards/guidance values as compiled by the Interstate Technology and Regulatory Council (ITRC) as of February 20, 2020 (see Supplemental Table 13 for details).

Peak concentrations for five evaluated PFAS (PFOS, 6:2 FTS, PFHxS, PFOA, and PFHpA) exceeded the most stringent standards/guidance values for drinking water. Because the Houston Ship Channel is not known to be used as a source of drinking water, this comparison may be highly conservative on its own. However, because in the case of PFOS, the fish consumption-based standards are similar to or lower than the drinking water-based

standards, exceedance of drinking water standards may still indicate a potential concern, as well as highlighting the need for additional data on bioaccumulation potential for PFAS.

Fish consumption-based standards/guidance values are available for PFOS and PFOA. Based on our observations, we found that many samples were in exceedance of available standards (Supplemental Figure 4). Bioaccumulation factors appear to vary widely across PFAS [e.g., ~70 L/kg for PFOA but ~2400 L/kg for PFOS (Stuchal and Roberts, 2020)], suggesting that extrapolation from water to fish concentrations is highly uncertain without PFAS-specific bioaccumulation data. For PFOS, in particular, the “background” water levels we detected in July-August 2019, which are above the most conservative surface water standards, would translate to 6 ~ 60 ng/g fish concentrations. While sampling of PFAS in fish in the Houston Ship Channel has not been reported, studies in other populated locations have reported levels in this range (Fair et al., 2019; Stahl et al., 2014). Although there are fish advisories warning against the consumption of all fish and crabs from the Houston Ship Channel waterways (DSHS, 2015), it is still common to see anglers in this area, and these results suggest that PFAS should be included in risk assessments of consuming fish from the area (DSHS, 2013).

Several of the locations we sampled were in public parks with shorelines accessible to swimming and/or wading. Thus, we used the drinking water standards to derive an “equivalently protective” standards under an alternative exposure scenario consisting of incidental ingestion while engaging in recreational swimming. As described in Supplemental Table 13, using US EPA Example Exposure Scenarios (U.S. EPA, 2004), the contaminant ingestion rate for a recreational swimmer would be about 260 times less than that for drinking water. With this adjustment, none of the samples had PFAS concentrations above an “equivalent” recreational standard. While exposure to PFAS through this pathway is not likely to be of concern, the ITC fire did impact the lives of many Houston residents. The fire and firefighting response resulted in school closures for over 100,000 students (Ortiz and Schneider, 2019).

Moreover, studies of firefighters using AFFFs show elevated serum concentrations of PFAS following exposure. Since firefighters use heavy inhalation protection it is believed exposure also occurs through ingestion and dermal routes (Laitinen et al., 2014).

Study Limitations and Future Directions

Several important limitations of this work need to be mentioned. First, the unpredicted nature of this disaster created challenges with data analysis. For instance, at the time of sampling in March 2019, the laboratory did not have ready access to the extraction standard to spike during the extraction process. Thus, in order to expedite the analysis of samples, it was decided to proceed without this step. We did add the extraction and injection standards prior to sample analysis. We acknowledge that the lack of extraction standards during sample preparation prevents absolute quantification of the compounds as extraction efficiency and matrix effect cannot be corrected. However, since the sample matrix (water) was identical across all samples, we believe that these data are still informative and provide valuable information for this and future events. For compounds that have both quantifying and qualifying ions, the ratios between the two were used to compare with pure standards to

ensure robust compound identification. While it would have been possible to re-analyze the archived water samples with the optimized analytical method (as opposed to immediate analysis within 1 week of collection as performed here), significant analyte interconversions for certain PFAS in aqueous samples stored at 4°C were observed within 7 days of storage (Woudneh et al., 2019). The same study provides evidence that storage of water samples at -20°C precludes significant degradation of PFAS for up to 180 days (Woudneh et al., 2019).

Second, the analytical background levels of PFBS made it difficult to accurately quantify this compound; however, the remainder of PFAS followed a decreasing trend so one can reasonably assume that if PFBS were in the water samples, it would have followed a similar trend.

Third, the relative sparseness of the sampling locations is a general limitation in spatial interpolation. Large differences in values for co-located samples may not yield smooth interpolation; however, because we quantile ranked the data, these discrepancies were minimized. Overall, while spatial interpolation approaches are highly uncertain, these visualizations are very informative tools for science communication and decision support (Dredger et al., 2007).

Fourth, this study was a targeted analysis of a limited number of PFAS. A wider coverage of known and putative PFAS and their degradation products is now possible using novel non-targeted analytical methods (Dodds et al., 2020). Inclusion of the methods into environmental sampling would likely further refine exposure estimates for these emerging persistent chemicals.

Conclusions

Our results show that the detected PFAS in the Houston Ship Channel over the course of a 6-months study period were likely from the firefighting response to the ITC fires. Although AFFF mixtures contain a proprietary blend of chemicals, we expected that their use in large quantities in the ITC incident would result in detectable concentrations of PFAS. Our finding of considerable temporal and spatial increases in levels of 6:2 FTS and PFOS suggests the usage of both fluorotelomer-based AFFFs (Coggan et al., 2019) and of the legacy electrofluorination-based AFFFs (Moe et al., 2012). While levels of most PFAS were below currently available actionable levels after considering the likely exposure pathways of recreational use, such comparison are severely limited by the absence of health-based water concentration benchmarks for comparison. Of particular concern is that concentrations of PFOS detected in this study exceeded standards based on fish consumption even after returning the “background” levels. At the same time, for most other PFAS, lack of data to estimate bioaccumulation precludes the ability to assess risks from this exposure pathway. Further studies are needed to examine other PFAS that may have been released from the ITC accident because of the diversity of the AFFF formulations that were used (Supplemental Table 1) and the unknown composition of those AFFFs. Additional analytical techniques that may provide high-resolution untargeted analysis of PFAS (Dodds et al., 2020; Liu et al., 2015), or estimate total perfluoroalkyl acid precursors via the total oxidizable precursor assay (Janda et al., 2019) may also be sensible paths towards establishing a more

comprehensive characterization of environmental concentrations of, and human exposures to a wide variety of PFAS.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

The authors thank Dr. Michael Honeycutt (TCEQ) for useful discussions and providing information for Supplemental Table 1. The authors also acknowledge extensive constructive comments from the reviewers that considerably improved this manuscript. This work was funded, in part, by grants P42 ES027704 and P30 ES029067 from the National Institute of Environmental Health Sciences. Noor Aly, Gaston Casillas and Sharmila Bhandari were supported, in part, by a training grant T32 ES026568 from the National Institute of Environmental Health Sciences.

References

- Ahrens L, Norstrom K, Viktor T, Cousins AP, Josefsson S, 2015 Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish. *Chemosphere* 129, 33–38. [PubMed: 24821232]
- Anumol T, Yang DD, Sosienski T, Batoon P, 2018 Analysis of per/polyfluoroalkyl substances (PFASs) in drinking water using the Agilent Ultivo triple quadrupole LC/MS. Agilent, https://www.agilent.com/cs/library/applications/5991-8969EN_PFAS_Application.pdf. Accessed on: October 17, 2019
- ArcGIS, 2020 How Radial Basis Functions Work. ESRI, <https://pro.arcgis.com/en/pro-app/help/analysis/geostatistical-analyst/how-radial-basis-functions-work.htm#GUID-3F6EE7BD-30DE-494E-9007-B1519953A6CE>. Accessed on: February 01, 2020
- ATSDR, 2018 Toxicological Profile for Perfluoroalkyls, in: U.S. Department of Health and Human Services (Ed.). Agency for Toxic Substances and Disease Registry, Atlanta, GA <https://www.atsdr.cdc.gov/toxprofiles/tp200.pdf>. Accessed on: February 01, 2020
- Awad E, Zhang X, Bhavsar SP, Petro S, Crozier PW, Reiner EJ, Fletcher R, Tittlemier SA, Braekevelt E, 2011 Long-term environmental fate of perfluorinated compounds after accidental release at Toronto airport. *Environ Sci Technol* 45, 8081–8089. [PubMed: 21774496]
- Barzen-Hanson KA, Roberts SC, Choyke S, Oetjen K, McAlees A, Riddell N, McCrindle R, Ferguson PL, Higgins CP, Field JA, 2017 Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater. *Environ Sci Technol* 51, 2047–2057. [PubMed: 28098989]
- Boone JS, Vigo C, Boone T, Byrne C, Ferrario J, Benson R, Donohue J, Simmons JE, Kolpin DW, Furlong ET, Glassmeyer ST, 2019 Per- and polyfluoroalkyl substances in source and treated drinking waters of the United States. *Sci Total Environ* 653, 359–369. [PubMed: 30412881]
- Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, de Voogt P, Jensen AA, Kannan K, Mabury SA, van Leeuwen SP, 2011 Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr Environ Assess Manag* 7, 513–541. [PubMed: 21793199]
- Cai Y, Wang X, Wu Y, Zhao S, Li Y, Ma L, Chen C, Huang J, Yu G, 2018 Temporal trends and transport of perfluoroalkyl substances (PFASs) in a subtropical estuary: Jiulong River Estuary, Fujian, China. *Sci Total Environ* 639, 263–270. [PubMed: 29787910]
- Chen H, Han J, Zhang C, Cheng J, Sun R, Wang X, Han G, Yang W, He X, 2017 Occurrence and seasonal variations of per- and polyfluoroalkyl substances (PFASs) including fluorinated alternatives in rivers, drain outlets and the receiving Bohai Sea of China. *Environ Pollut* 231, 1223–1231. [PubMed: 28928021]

- Coggan TL, Moodie D, Kolobaric A, Szabo D, Shimeta J, Crosbie ND, Lee E, Fernandes M, Clarke BO, 2019 An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs). *Heliyon* 5, e02316. [PubMed: 31485522]
- Dean RG, Dalrymple RA, 1991 *Water Wave Mechanics for Engineers and Scientists*. World Scientific, Singapore.
- Dodds JN, Hopkins ZR, Knappe DRU, Baker ES, 2020 Rapid Characterization of Per- and Polyfluoroalkyl Substances (PFAS) by Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS). *Anal Chem* 92, 4427–4435. [PubMed: 32011866]
- Dredger SM, Kothari A, Morrison J, Sawada M, Crighton EJ, Graham ID, 2007 Using participatory design to develop (public) health decision support systems through GIS. *Int J Health Geogr* 6, 53. [PubMed: 18042298]
- DSHS, 2013 Characterization of Potential Adverse health Effects Associated with Consuming Fish from the San Jacinto River-Houston Ship Channel, in: Department of State Health Services (Ed.). Texas Department of State Health Services, Austin, TX <https://dshs.texas.gov/WorkArea/linkit.aspx?LinkIdentifier=id&ItemID=8589999189>. Accessed on: March 15, 2020
- DSHS, 2015 ADV-55 Fish and Shellfish Consumption Advisory for Galveston Bay Estuary, in: Department of State Health Services (Ed.). Texas Department of State Health Services, Austin, TX Accessed on: February 01, 2020
- Egbert GD, Erofeeva SY, 2002 Efficient Inverse Modeling of Barotropic Ocean Tides. *Journal of Atmospheric and Oceanic Technology* 19, 183–204.
- EWG, 2019 PFAS Contamination in the U.S Environmental Working Group, Washington, D.C., https://www.ewg.org/interactive-maps/2019_pfas_contamination/. Accessed on: February 01, 2020
- Fair PA, Wolf B, White ND, Arnott SA, Kannan K, Karthikraj R, Vena JE, 2019 Perfluoroalkyl substances (PFASs) in edible fish species from Charleston Harbor and tributaries, South Carolina, United States: Exposure and risk assessment. *Environ Res* 171, 266–277. [PubMed: 30703622]
- Field JA, Seow J, 2017 Properties, occurrence, and fate of fluorotelomer sulfonates. *Crit Rev Envr Sci Tech* 47, 643–691.
- Fotheringham AS, Wegener M, 1999 *Spatial models and GIS: New and Potential Models*. CRC Press, Boca Raton, FL.
- Groffen T, Wepener V, Malherbe W, Bervoets L, 2018 Distribution of perfluorinated compounds (PFASs) in the aquatic environment of the industrially polluted Vaal River, South Africa. *Sci Total Environ* 627, 1334–1344. [PubMed: 30857097]
- Harding-Marjanovic KC, Houtz EF, Yi S, Field JA, Sedlak DL, Alvarez-Cohen L, 2015 Aerobic Biotransformation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms. *Environ Sci Technol* 49, 7666–7674. [PubMed: 26042823]
- Hasselmann K, Barnett T, Bouws E, Carlson H, Cartwright D, Enke K, Ewing J, Gienapp H, Hasselman D, Kruseman P, Meerburg A, Muller P, Olbers D, Richter K, Sell W, Walden H, 1973 Measurements of wind-wave growth and swell decay during the Joint North Sea Wave Project (JONSWAP). *Deut Hydrogr Z* 8, 1–95.
- Hayes J, Faber S, Andrews D, Lothspeltch A, 2019 PFAS Nation: Toxic Discharges Suspected From Almost 500 Industrial Facilities Across U.S Environmental Working Group, <https://www.ewg.org/news-and-analysis/2019/06/pfas-nation-toxic-discharges-suspected-almost-500-industrial-facilities>. Accessed on: October 14, 2019
- Hopkins ZR, Sun M, DeWitt JC, Knappe DRU, 2018 Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids. *Journal American Water Works Association* 110, 13–28.
- Houtz E, Wang M, Park JS, 2018 Identification and Fate of Aqueous Film Forming Foam Derived Per- and Polyfluoroalkyl Substances in a Wastewater Treatment Plant. *Environ Sci Technol* 52, 13212–13221. [PubMed: 30339382]
- ITRC, 2017 History and Use of Per- and Polyfluoroalkyl Substances (PFAS). Interstate Technology Regulatory Council, Washington, DC, https://pfas-1.itrcweb.org/wp-content/uploads/2017/11/pfas_fact_sheet_history_and_use__11_13_17.pdf. Accessed on: 1/28/2020

- Janda J, Nodler K, Scheurer M, Happel O, Nurenberg G, Zwiener C, Lange FT, 2019 Closing the gap - inclusion of ultrashort-chain perfluoroalkyl carboxylic acids in the total oxidizable precursor (TOP) assay protocol. *Environ Sci Process Impacts* 21, 1926–1935. [PubMed: 31183483]
- Johnsen-Harris B, Chetwynd J, 2019 House passes sweeping PFAS protections: 2025 ban on military use, Superfund cleanup and clean water safeguards. *Environment America*, Denver, CO, <https://environmentamerica.org/news/ame/house-passes-sweeping-pfas-protections-2025-ban-military-use-superfund-cleanup-and-clean>. Accessed on: October 01, 2019
- KHOU, 2019 Timeline: ITC Chemical Tank Fire in Deer Park. KHOU, Houston, TX, <https://www.khou.com/article/news/timeline-itc-chemical-tank-fire-in-deer-park/285-960722df-3907-49c4-91ef-25dc5250dfe1>. Accessed on: February 01, 2020
- Killick R, Eckley IA, 2014 changepoint: An R Package for Changepoint Analysis. *J Stat Softw* 58, 1–19.
- Kim JY, Kaihatu JM, Chang KA, Feagin RA, Huff T, 2019 Estimation of wind wave induced erosion rates in wetlands on Galveston Island based on UAV photogrammetry, Fall Meeting of the American Geophysical Society, San Francisco, CA Accessed on: February 01, 2020
- Laitinen JA, Koponen J, Koikkalainen J, Kiviranta H, 2014 Firefighters' exposure to perfluoroalkyl acids and 2-butoxyethanol present in firefighting foams. *Toxicol Lett* 231, 227–232. [PubMed: 25447453]
- Lanza HA, Cochran RS, Mudge JF, Olson AD, Blackwell BR, Maul JD, Salice CJ, Anderson TA, 2017 Temporal monitoring of perfluorooctane sulfonate accumulation in aquatic biota downstream of historical aqueous film forming foam use areas. *Environ Toxicol Chem* 36, 2022–2029. [PubMed: 28029183]
- Le Provost C, 2001 Ocean Tides, in: Fu LL, Cazenave A (Eds.), *Satellite Altimetry and Earth Sciences: A handbook of Techniques and Applications*. Academic Press, San Diego, CA, pp. 267–301.
- Lesser GR, Roelvink JA, Ven Kester JATM, Stelling GS, 2004 Development and validation of a three-dimensional morphological model. *Coastal Engineering* 51, 883–915.
- Lewis RC, Johns LE, Meeker JD, 2015 Serum Biomarkers of Exposure to Perfluoroalkyl Substances in Relation to Serum Testosterone and Measures of Thyroid Function among Adults and Adolescents from NHANES 2011–2012. *Int J Environ Res Public Health* 12, 6098–6114. [PubMed: 26035660]
- Li Y, Oliver DP, Kookana RS, 2018 A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). *Sci Total Environ* 628–629, 110–120.
- Liu Y, Pereira Ados S, Martin JW, 2015 Discovery of C5–C17 poly- and perfluoroalkyl substances in water by in-line SPE-HPLC-Orbitrap with in-source fragmentation flagging. *Anal Chem* 87, 4260–4268. [PubMed: 25818392]
- Martin D, Munoz G, Mejia-Avendano S, Duy SV, Yao Y, Volchek K, Brown CE, Liu J, Sauve S, 2019 Zwitterionic, cationic, and anionic perfluoroalkyl and polyfluoroalkyl substances integrated into total oxidizable precursor assay of contaminated groundwater. *Talanta* 195, 533–542. [PubMed: 30625579]
- Martin J, 2019 Update on Southern New Hampshire PFAS Investigation. New Hampshire Department of Environmental Services, Concord, New Hampshire, <https://www4.des.state.nh.us/nh-pfas-investigation/?p=1126>. Accessed on: January 15, 2020
- McCord J, Newton S, Strynar M, 2018 Validation of quantitative measurements and semi-quantitative estimates of emerging perfluoroethercarboxylic acids (PFECAs) and hexfluoropropylene oxide acids (HFPOAs). *J Chromatogr A* 1551, 52–58. [PubMed: 29628221]
- Mejia-Avendano S, Munoz G, Vo Duy S, Desrosiers M, Benoi TP, Sauve S, Liu J, 2017 Novel Fluoroalkylated Surfactants in Soils Following Firefighting Foam Deployment During the Lac-Mégantic Railway Accident. *Environ Sci Technol* 51, 8313–8323. [PubMed: 28669179]
- Meng Q, Liu Z, Borders BE, 2013 Assessment of regression kriging for spatial interpolation – comparisons of seven GIS interpolation methods. *Cartogr Geogr Inf Sc* 40, 28–39.
- Moe MK, Huber S, Svenson J, Hagenaars A, Pabon M, Trumper M, Berger U, Knapen D, Herzke D, 2012 The structure of the fire fighting foam surfactant Forafac(R)1157 and its biological and photolytic transformation products. *Chemosphere* 89, 869–875. [PubMed: 22658941]

- Moller A, Ahrens L, Surm R, Westerveld J, van der Wielen F, Ebinghaus R, de Voogt P, 2010 Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. *Environ Pollut* 158, 3243–3250. [PubMed: 20692748]
- Moody CA, Martin JW, Kwan WC, Muir DC, Mabury SA, 2002 Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke Creek. *Environ Sci Technol* 36, 545–551. [PubMed: 11883418]
- Munoz G, Desrosiers M, Duy SV, Labadie P, Budzinski H, Liu J, Sauvé S, 2017 Environmental Occurrence of Perfluoroalkyl Acids and Novel Fluorotelomer Surfactants in the Freshwater Fish *Catostomus commersonii* and Sediments Following Firefighting Foam Deployment at the Lac-Mégantic Railway Accident. *Environmental Science and Technology* 51, 1231–1240. [PubMed: 28056502]
- NASF, 2019 6:2 Fluorotelomer Sulfonate (6:2 FTS) TOXICOLOGY AT A GLANCE. National Association for Surface Finishing, Washington, DC, <https://nasf.org/wp-content/uploads/2019/04/Summary-of-Toxicology-Studies-on-6-2-FTS-and-Detailed-Technical-Support-Documents.pdf>. Accessed on: February 01, 2020
- NHANES, 2012 National Health and Nutrition Examination Survey 2011–2012 Data Documentation, Codebook, and Frequencies Polyfluoroalkyl Chemicals. Center for Disease Control and Prevention, https://www.cdc.gov/Nchs/Nhanes/2011-2012/PFC_G.htm. Accessed on: February 01, 2020
- Nicole W, 2013 PFOA and cancer in a highly exposed community: new findings from the C8 science panel. *Environ Health Perspect* 121, A340. [PubMed: 24284021]
- NIEHS, 2020 Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS). National Institute of Environmental Health Sciences, <https://www.niehs.nih.gov/health/topics/agents/pfc/index.cfm>. Accessed on: October 01, 2019
- NTP, 2016 Immunotoxicity Associated with Exposure to Perfluorooctanoic Acid or Perfluorooctane Sulfonate. National Toxicology Program, Research Triangle Park, NC.
- Oliver DP, Navarro DA, Baldock J, Simpson SL, Kookana RS, 2020 Sorption behaviour of per- and polyfluoroalkyl substances (PFASs) as affected by the properties of coastal estuarine sediments. *Sci Total Environ* 720, 137263. [PubMed: 32145609]
- Ortiz A, Schneider A, 2019 Harris County Prepares To Sue ITC Over Fire At Deer Park Facility. Houston, TX, <https://www.houstonpublicmedia.org/articles/news/2019/03/26/326600/harris-county-to-sue-itc-over-fire-at-deer-park-facility/>. Accessed on: February 01, 2020
- Pan Y, Zhang H, Cui Q, Sheng N, Yeung LWY, Sun Y, Guo Y, Dai J, 2018 Worldwide Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids in Surface Water. *Environ Sci Technol* 52, 7621–7629. [PubMed: 29749740]
- Patlewicz G, Richard AM, Williams AJ, Grulke CM, Sams R, Lambert J, Noyes PD, DeVito MJ, Hines RN, Strynar M, Guiseppi-Elie A, Thomas RS, 2019 A Chemical Category-Based Prioritization Approach for Selecting 75 Per- and Polyfluoroalkyl Substances (PFAS) for Tiered Toxicity and Toxicokinetic Testing. *Environ Health Perspect* 127, 14501. [PubMed: 30632786]
- Pelch KE, Reade A, Wolffe TAM, Kwiatkowski CF, 2019 PFAS health effects database: Protocol for a systematic evidence map. *Environ Int* 130, 104851. [PubMed: 31284092]
- Place BJ, Field JA, 2012 Identification of novel fluorochemicals in aqueous film-forming foams used by the US military. *Environ Sci Technol* 46, 7120–7127. [PubMed: 22681548]
- Poothong S, Papadopoulou E, Padilla-Sanchez JA, Thomsen C, Haug LS, 2020 Multiple pathways of human exposure to poly- and perfluoroalkyl substances (PFASs): From external exposure to human blood. *Environ Int* 134, 105244. [PubMed: 31711019]
- Ritscher A, Wang Z, Scheringer M, Boucher JM, Ahrens L, Berger U, Bintein S, Bopp SK, Borg D, Buser AM, Cousins I, DeWitt J, Fletcher T, Green C, Herzke D, Higgins C, Huang J, Hung H, Knepper T, Lau CS, Leinala E, Lindstrom AB, Liu J, Miller M, Ohno K, Perkola N, Shi Y, Smastuen Haug L, Trier X, Valsecchi S, van der Jagt K, Vierke L, 2018 Zurich Statement on Future Actions on Per- and Polyfluoroalkyl Substances (PFASs). *Environ Health Perspect* 126, 84502. [PubMed: 30235423]
- Shaw DMJ, Munoz G, Bottos EM, Duy SV, Sauve S, Liu J, Van Hamme JD, 2019 Degradation and defluorination of 6:2 fluorotelomer sulfonamidoalkyl betaine and 6:2 fluorotelomer sulfonate by

- Gordonia sp. strain NB4–1Y under sulfur-limiting conditions. *Sci Total Environ* 647, 690–698. [PubMed: 30092525]
- Shoemaker J, Tetttenhorst D, 2018 Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Washington, DC https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=537290&Lab=NERL. Accessed on: January 15, 2020
- Silcock P, Karrman A, van Bavel B, 2020 Advancing Perfluorinated Compound Analysis Using Simultaneous Matrix Monitoring. *Waters*, <https://www.waters.com/webassets/cms/library/docs/720003162en.pdf>. Accessed on: September 17, 2019
- Spratlen MJ, Perera FP, Lederman SA, Robinson M, Kannan K, Herbstman J, Trasande L, 2020 The Association Between Perfluoroalkyl Substances and Lipids in Cord Blood. *J Clin Endocrinol Metab* 105.
- Spratlen MJ, Perera FP, Lederman SA, Robinson M, Kannan K, Trasande L, Herbstman J, 2019 Cord blood perfluoroalkyl substances in mothers exposed to the World Trade Center disaster during pregnancy. *Environ Pollut* 246, 482–490. [PubMed: 30583156]
- Stahl LL, Snyder BD, Olsen AR, Kincaid TM, Wathen JB, McCarty HB, 2014 Perfluorinated compounds in fish from U.S. urban rivers and the Great Lakes. *Sci Total Environ* 499, 185–195. [PubMed: 25190044]
- Stuchal L, Roberts SM, 2020 Development of Surface Water Screening Levels for PFOA and PFOS Based on the Protection of Human Health: Prepared for the District and Business Support Program Florida Department of Environmental Protection University of Florida, Gainesville, FL <https://floridadep.gov/sites/default/files/PFOA-PFOS-Human-Health-Surface-Water.pdf>. Accessed on: May 01, 2020
- Sunderland EM, Hu XC, Dassuncao C, Tokranov AK, Wagner CC, Allen JG, 2019 A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and present understanding of health effects. *J Expo Sci Environ Epidemiol* 29, 131–147. [PubMed: 30470793]
- Thomas A, 2019 ITC Fire Response Causes Toxic Contamination of Houston Ship Channel. Sierra Club, <https://www.sierraclub.org/press-releases/2019/09/itc-fire-response-causes-toxic-contamination-houston-ship-channel>. Accessed on: January 28, 2020
- U.S. EPA, 2004 An Examination of EPA Risk Assessment Principles and Practices, Office of the Science Advisor Staff Paper, Washington, DC <http://www.epa.gov/osa/pdfs/ratf-final.pdf>. Accessed on: February 01, 2020
- U.S. EPA, 2016a Health Effects Support Document for Perfluorooctanoic Acid (PFOA). Office of Water, U.S. Environmental Protection Agency, Washington, DC Accessed on: February 01, 2020
- U.S. EPA, 2016b Third Unregulated Contaminant Monitoring Rule. Environmental Protection Agency, <https://www.epa.gov/dwucmr/third-unregulated-contaminant-monitoring-rule>. Accessed on: February 01, 2020
- U.S. EPA, 2018 Basic Information on PFAS. U.S. Environmental Protection Agency, Washington, DC, <https://www.epa.gov/pfas/basic-information-pfas>. Accessed on: February 01, 2020
- U.S. EPA, 2019 ITC Fire Response. Environmental Protection Agency, <https://epa.maps.arcgis.com/apps/Cascade/index.html?appid=f5eca85b79484cd69ea3a68cec886797>. Accessed on: February 01, 2020
- Wang N, Liu J, Buck RC, Korzeniowski SH, Wolstenholme BW, Folsom PW, Sulecki LM, 2011 6:2 fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants. *Chemosphere* 82, 853–858. [PubMed: 21112609]
- Wang Y, Arsenault G, Riddell N, McCrindle R, McAlees A, Martin JW, 2009 Perfluorooctane sulfonate (PFOS) precursors can be metabolized enantioselectively: principle for a new PFOS source tracking tool. *Environ Sci Technol* 43, 8283–8289. [PubMed: 19924957]
- Weiner B, Yeung LWY, Marchington EB, SD'Agostino LA, Mabury SA, 2013 Organic fluorine content in aqueous film forming foams (AFFFs) and biodegradation of the foam component 6 : 2 fluorotelomermercaptoalkylamido sulfonate (6 : 2 FTSAS). *Environ Chem* 10, 486–493.

- Woudneh MB, Chandramouli B, Hamilton C, Grace R, 2019 Effect of Sample Storage on the Quantitative Determination of 29 PFAS: Observation of Analyte Interconversions during Storage. *Environ Sci Technol* 53, 12576–12585. [PubMed: 31578061]
- Xu W, Wang X, Cai Z, 2013 Analytical chemistry of the persistent organic pollutants identified in the Stockholm Convention: A review. *Anal Chim Acta* 790, 1–13. [PubMed: 23870403]

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

Highlights

- ITC fire in the Houston area resulted in a major release of PFAS into adjacent estuaries
- This study aimed to address concerns about PFAS contamination in the surface water
- We evaluated surface water levels of PFAS over 6 months from March to August 2019
- Large-scale contamination was confirmed, temporal and spatial profiles were established
- Even though ITC fire led to a spike in PFAS in surface water, levels declined after 3 months

Figure 1.

Map of sampling locations in the Houston Ship Channel and Galveston Bay near the site of the ITC fire. Area of detail magnified in the map is indicated in the inset (top left panel). A series of surface water samples (orange dots) were collected between March 21 and August 2, 2019 from the shore or open water. GPS coordinates for each sampling location are listed in Table 1. Locations of open water sampling performed by the U.S. EPA (March 21, 2019) are indicated by the blue dots; these data are included in Supplemental Table 2. The site of the incident (ITC, $29^{\circ}43'45.8''\text{N}$ $95^{\circ}05'23.8''\text{W}$) is indicated and magnified in the inset (bottom left panel). Background map is from ESRI/OpenStreetMap. The lower left inset is from Google maps satellite layer.

Figure 2.

Temporal (March-July 2019) patterns in water concentrations of 6:2 FTS, PFOS, PFHxS, PFHxA, PFHpA, and PFPeA at the HSC/GB open water sampling locations. The site of the incident (ITC) is indicated (yellow-red diamond). Sampling locations are shown in the map inset, left (orange circles). Red box indicates the sampling location (SCWS2) that was closest to the site of the incident. Raw data and sampling location coordinates are provided in Supplemental Table 3. Background map was from ESRI/OpenStreetMap.

Figure 3.

Temporal (March–August 2019) patterns in water concentrations of 6:2 FTS, PFOS, PFHxS, PFHxA, PFHpA, and PFPeA at the HSC/GB shore-accessible sampling locations. The site of the incident (ITC) is indicated (yellow-red diamond). Sampling locations are shown in the map inset, left (orange circles). Raw data and sampling location coordinates are provided in Supplemental Table 3. Background map was from ESRI/OpenStreetMap.

Figure 4.

Interpolation of the spatial patterns in concentrations of PFOS (left panel) and 6:2 FTS (right panel) in HSC/GB for March, April and June 2019. The site of the incident (ITC) is indicated by a red symbol. RBF maps (see Methods) are shown for the HSC/GB estuary where sampling locations are indicated by the green dots and the estimated concentrations of PFOS and 6:2 FTS are visualized as a color gradient (see the heatmap legend for each substance) based on quintiles in the data range, please refer to Supplemental Tables 2–3 for raw data.

Figure 5. HSC/GB map showing the course of seven drogues (blue dots) at 60 min intervals, over the time period between March 17th, 2019 and April 30th, 2019. One drogue was released every day at midnight starting March 17th, 2019 and ending March 23rd, 2019. (A) The model that accounts for the water movement affected by tides based on the information in the Houston Ship Channel and Galveston Bay. (B) The model that includes both tide and wind forces. The location of the ITC incident is shown by the orange and red fire symbol. Orange circles show water sampling locations. The base maps are from ESRI/OpenMap.

Table 1.

Study sampling locations in Houston Ship Channel/Galveston Bay. Please refer to Figure 1 for the detailed map of sampling locations. Geographical coordinates for each sampling site are listed in Supplemental Table 3.

Sample Location ID	Latitude	Longitude	Distance from ITC (km)
<i>Open water (Ship Channel Water, SCW) samples</i>			
SCWS4	29.735627	-95.14041	-4
SCWS3	29.739474	-95.11276	-1.2
SCWS2	29.74442	-95.10216	0
SCWS1	29.754676	-95.09387	1.4
SCWS5	29.761123	-95.07675	3.4
<i>Shore-access samples</i>			
Santa Anna Marker	29.7249	-95.2128	-12.4
Lynchburg Ferry	29.764953	-95.07861	3.2
Baytown Nature Center	29.759842	-95.05636	5.3
River Terrace Park	29.7817	-95.101	5.3
Strang Road	29.7027	-95.0336	12.1
Bayland Park	29.710724	-94.99537	15.4
Morgan's Point	29.678439	-94.9825	18.3

Table 2.

Comparison of ITC sample concentrations and available U.S. water standards/guidance values for PFAS.

PFAS	Median and range during sampling month(s)			U.S. Water Standards/Guidance Values (2015–2020) ^[a]		
	March 2019	April 2019	June-August 2019	Fish Consumption	Drinking Water	Recreational ^[b]
PFOS	113.9 (<LOQ-302.1)	96 (49.3–167)	5.9 (2.7–26.3)	4–11	6.2–667	≥1,700
6:2 FTS	732.9 (<LOQ-1492.4)	1095.7 (632.7–1653.6)	42.6 (6.1–91.2)	NA	100–200 ^[c]	≥26,000
PFBS	141.6 (115.7–193.8)	74.8 (3.5–101.5)	16.4 (3.8–37.6)	NA	1,000–667,000	≥260,000
PFHxA	24.2 (<LOQ-78.4)	43.1 (29.4–87)	9.9 (5.1–18.5)	NA	93	≥24,000
PFHxS	21.5 (<LOQ-90.4)	21.3 (10.5–34)	1.8 (1–10.6)	NA	20–140	≥5,200
PFPeA	<LOQ (<LOQ-13.4)	26.5 (19.1–41.1)	13.1 (7.8–26.8)	NA	93	≥24,000
PFOA	<LOQ (<LOQ-13.7)	6.3 (4.8–8.7)	3 (1.7–7.2)	150–12,000	5.1–667	≥1,300
PFBA	<LOQ	17 (9.5–36.4)	7.1 (<LOQ-13.6)	NA	7,000–71,000	≥1,820,000
PFHpA	<LOQ	16.4 (8.1–37.2)	2.8 (1.6–11.3)	NA	20–560	≥5,200
PFNA	<LOQ	<LOQ	0.8 (0.3–2.3)	NA	9–290	≥2,300
PFDA	<LOQ	<LOQ	0.6 (<LOQ-3)	NA	20–370	≥5,200
PFDaA	<LOQ	<LOQ	<LOQ	NA	290 ^[d]	≥75,000
L-PFDaS	<LOQ	1.6 (<LOQ-3.1)	<LOQ	NA	290 ^[d]	≥75,000
PFTTrDA	<LOQ	<LOQ	<LOQ	NA	290 ^[d]	≥75,000
PFTeDA	<LOQ	<LOQ	<LOQ	NA	290 ^[d]	≥75,000
8:2 FTS	<LOQ	<LOQ	<LOQ (<LOQ-5.9)	NA	200 ^[c]	≥52,000

All concentrations are in ng/L. NA = Not available (neither U.S., nor international).

^[a] Values compiled by Interstate Technology and Regulatory Council (ITRC) as of 20-Feb-2020 [<https://pfas-1.itrcweb.org/fact-sheets/>].^[b] Adjustment of drinking water values to scenario involving incidental ingestion during swimming/wading (see text).^[c] No U.S. values available; therefore we used international values compiled by ITRC.^[d] Limit is for the sum of PFDS, PFUnA, PFDaA, PFTTrDA, PFTeDA