PFASs pollution in Galveston Bay surface waters and biota (shellfish and fish) following AFFFs use during the ITC fire at Deer Park (March 17th-20th 2019), Houston, TX

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Abstract

The use of aqueous film forming foams (AFFFs) as fire retardants is an critical point-source for per- and polyfluoroalkyl substances (PFASs) pollution into the aquatic environment. This study investigated PFASs pollution in the surface waters and biota (shellfish and fish) of Galveston Bay, following AFFFs use to extinguish a petrochemical fire (March 17th to 20th, 2019) of oil storage tanks at the International Terminals Company (ITC) in Deer Park (Houston, TX). The levels of up to twelve EPA priority PFASs were measured in surface waters and biota from March - November 2019. PFASs levels in surface waters showed mean total levels in March and April 2019 to be from 4x - ~300x higher than those measured in the following months. PFOS (perfluorooctanesulfonic acid) was the most abundant homolog measured at $\geq$66% of total PFASs. Maximal PFOS levels exceeded the State of Texas' water regulatory limit of 0.6 µg L^{-1} in 3% of the samples analyzed in March and April 2019. PFOS was also the most prominent homolog ($\geq$66% of total PFASs) measured in eastern oysters (*Crassostrea virginica*), red drum (*Sciaenops ocellatus*), gafftopsail catfish (*Bagre marinus*), and spotted seatrout (*Cynoscion nebulosus*). A statistically significant elevation of PFOS body-burdens was measured in oysters and spotted seatrout in April and May 2019, respectively. A Hazard Ratio calculation for seafood safety suggests an advisory of 1-2 meals per week for gafftopsail catfish and red drum, and 2 meals per week for spotted seatrout to be protective for human exposure to PFOS. The levels in oysters indicated no immediate concerns for the dietary exposure of humans. Our results highlight a need for continual monitoring to assess the long-term fate and seafood advisories for PFASs.

Keywords: PFOS, fire retardants, fish, oysters, body-burdens, seafood safety

Highlights

- PFASs were quantified in Galveston Bay waters and biota following the use of AFFFs.
- AFFFs were used to extinguish a petrochemical fire at Deer Park in Houston, TX.
- Highest PFASs levels were measured in water up to 2 months following AFFFs use.
- Elevated body-burdens in oysters and fish was also measured.
- Risk assessment suggested a protective seafood consumption advisory.

1. Introduction

Per- and polyfluoroalkyl substances, or PFASs, are a group of anthropogenic ‘emerging’ pollutants that comprise ~3000 structurally related chemicals (Buck et al., 2011; Key et al., 1997; Wang et al., 2017). These highly fluorinated aliphatic chemicals contain one or more carbon atoms covalently linked to fluorine atoms and are represented by the general formula $C_nF_{2n+1} - R$, where C_nF_{2n+1} refers to the fluoroalkyl ‘tail’ (containing 3 to 14 carbons) and R denotes an attached functional ‘head’ group (carboxylic acid or sulfonic acid moiety) (Buck et al., 2011; Muller and Yingling, 2020; Wang et al., 2017). The extremely strong carbon-fluorine covalent bonds shield the carbon backbone of PFASs, conferring hydrophobicity, high stability, and resistance to degradation. Whereas the presence of a charged carboxylic acid or sulfonic acid moiety as the functional group confers hydrophilic properties (Buck et al., 2011; Ding and Peijnenburg, 2013). The resulting amphiphilic nature of PFASs (i.e., both hydrophobic and hydrophilic properties) has enabled their widespread use in industrial and commercial applications as surfactants, stain repellents, grease-proof contact paper, coatings, production of plastics and rubber, and in aqueous film forming foams (or AFFFs) (Buck et al., 2011; Glüge et al., 2020).

Such a wide range of uses for PFASs contributes to their near continuous release and ubiquitous presence in the environment, resulting in the inadvertent exposure of wildlife and humans (Giesy and Kannan, 2001; Hansen et al., 2001). The structural stability and poor biodegradation of PFASs also enables their bioaccumulation in exposed organisms and biomagnification across food webs (Ahrens and Bundschuh, 2014; Houde et al., 2006; Kelly et al., 2009). Therefore, the environmental persistence of these compounds and concerns for associated toxicity in exposed taxa has led to the characterization of some PFASs as persistent organic pollutants (POPs) (Ankley et al., 2020; UNEP, 2017).

While a large proportion of PFASs pollution in the aquatic environment can be attributed to their release from municipal waste water treatment plants (Abunada et al., 2020; Coggan et al., 2019), the use of AFFFs as fire retardants has been shown to be a critical point-source release responsible for elevated PFASs levels in the aquatic environment. Importantly, monitoring studies show elevated PFASs release due to AFFFs use to be correlated with the increased body-burdens in exposed biota (such as fish) (Lanza et al., 2017), and increased human exposure from the consumption of such tainted fish (Hansen et al., 2016). Studies also reveal that aquatic exposure to PFASs plays a more prominent role in influencing elevated body-burdens in fish vs. exposure through diet (Martin et al., 2003a; Martin et al., 2003b). Therefore, the point-source release of elevated PFASs during AFFFs spills are likely to contribute significantly to the exposure and bioconcentration of these pollutants in resident biota.

In this study we investigated the environmental fate of PFASs in the surface waters and resident biota (shellfish and fish) of Galveston Bay, following the use of AFFFs to extinguish a petrochemical fire (March 17th to 20th, 2019) of oil storage tanks at the International Terminals Company (ITC) in Deer Park (Houston, TX). The fire at Deer Park is estimated to have released ~2.64 million liters of oil-contaminated water and used ~5.7-18.9 million liters of AFFFs to extinguish the petrochemical fire, much of which is anticipated to have flowed into the surface waters of Galveston Bay (Aly et al., 2020; Rice, 2019). The large magnitude of this disturbance impacted the local and national economy due to a partial closure of adjacent waterways of the

Houston Ship Channel (HSC), with an estimated economic impact of \$0.5 – \$1 billion (Leinfelder and Blum, 2019). The ecological impact of the fire is still not fully known. In the aftermath of the fire (March 23rd, 2019), the Texas Commission on Environmental Quality (TCEQ) released a water quality report of their chemical analysis of surface waters in the immediate vicinity of the fire. The report found oil-derived hydrocarbon levels to far-exceed their regulatory mandated health-protective concentrations (TCEQ, 2019). Initial public concerns were mainly over the release of volatile organic compounds, such as benzene (a known human carcinogen) (Loomis et al., 2017). However, subsequent analytical chemical analysis showed the absence of volatile organics (including benzene) in water samples taken from the vicinity of the fire (ELI, 2019). Concerns for human exposure due to the consumption of contaminated fish and shellfish from the HSC also led to the issuance of a temporary sea food consumption advisory (DSHS, 2019).

Despite the initial concerns pertaining to hydrocarbon and volatile organics release, no attention was given to the runoff of AFFFs into the surrounding waterways of the HSC and Galveston Bay. Aly et al., (2020) were the first to study the release of AFFFs into the HSC and upper Galveston Bay by monitoring the levels of various PFASs homologs immediately after, and up to several months following the ITC fire at Deer Park. As a result, these authors provided a first-glimpse into the temporal (and spatial) trends of PFASs release and distribution in the HSC area (Aly et al., 2020). However, lacking from this invaluable contribution was information of PFASs distribution across Galveston Bay surface waters and the exposure of resident biota. Specifically, the fate of PFASs in shellfish and fish following AFFFs use (i.e., up to several months), was not known. Such knowledge can provide invaluable information on the fate of PFASs in biota and can guide regulatory sea food consumption advisories.

This study measured the levels of up to twelve EPA priority PFASs (EPA 533, 2019) in the surface waters of the HSC and Galveston Bay (**Fig. 1**) immediately following the ITC fire at Deer Park (first water samples collected on March 23rd, 2019), and then up to several months following the fire (final water samples collected on November 16th, 2019). The central hypothesis of this study was that the acute release of PFASs into Galveston Bay will result in elevated PFASs body-burdens in the resident biota of the bay. Surface waters from Galveston Bay were sampled along a transect from the entrance to the HSC (Morgan's Point; stations 1-7), and then to the northern Gulf of Mexico (just off Pelican Island; station 14). Alongside water sampling, shellfish and fish samples were also opportunistically collected from various randomized sites across Galveston Bay (on April, May, June, October, and November 2019). The species selected for analysis support valuable commercial and recreational fisheries in the bay. Analysis of PFASs body-burdens included the commercially important fish and shellfish species: red drum (*Sciaenops ocellatus*), gafftopsail catfish (*Bagre marinus*), spotted seatrout (*Cynoscion nebulosus*), and the eastern oyster (*Crassostrea virginica*). PFASs body-burden was quantified in the skin-free muscle (edible portion) and liver of fish, or mantle/gill tissue of oysters. The measured body-burdens of select PFASs in shellfish and fish allowed comparison with regulatory limits and enabled the putative assessment of likely human exposures given the consumption of seafood from the bay.

2. Materials and methods

2.1 Water sample collection and PFASs extraction

Surface water (1 liter) was collected in the HSC near the site of the ITC fire at Deer Park, and along a transect of Galveston Bay from the entrance to HSC at Morgan's Point to just off Pelican Island (**Fig. 1**). Please see **Supplemental 1** for a full list of the numbers of samples collected (and their respective latitude and longitude coordinates). Water samples were collected in 1 Liter amber glass bottles, immediately acidified to pH 1 using hydrochloric acid, and stored at -20ºC. Water samples were thawed overnight at 4ºC prior to analysis, and a 500 mL aliquot of each sample was spiked with internal standard (13C8-PFOA, 20 ng mL^{-1} final concentration). Solid phase extraction (SPE) was performed using Agilent SampliQ WAX polymer 6 mL/150mg SPE cartridges (Agilent, Cat.# 5982-3667). Each SPE cartridge was conditioned with 5 mL of 5% ammonium hydroxide (NH_4OH) in 60:40 acetonitrile:methanol (ACN:MeOH), washed with 5 mL 1% acetic acid, and another 1mL of 1% acetic acid was loaded onto each cartridge to keep the sorbent bed solvated. Samples were then extracted through the SPE cartridges under vacuum (10-15 mmHg) and not exceeding ~1 mL min^{-1} flow-through rate. The cartridges were subsequently dried under vacuum for 5 min, and then eluted with 4 mL of 5% NH_4OH in 60:40 ACN/MeOH. The collected eluate was dried in a speedvac (55ºC for ~1 hour) and the resulting residue was adjusted to 1mL in methanol for liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis.

2.2 Biota sample collection and PFASs extraction

Shellfish and fish were opportunistically sampled as part of annual stock assessments by the Texas Parks and Wildlife Department (TPWD), Dickinson Marine Labs (Dickinson, TX). The biota sampled included: eastern oyster, red drum, gafftopsail catfish, and spotted seatrout

(**Supplemental 1**). Specifically, a random stratified sampling design was employed to select sites across the Galveston Bay ecosystem. Shoreline sites were sampled using 18.3 meter bag seines, and open water sites were sampled using 6.1 meter bay trawls. The sizes of all biota sampled were above the minimum regulatory length limits set by TPWD for recreational and commercial fishing or harvesting for eastern oysters (5-8 inches), gafftopsail catfish (≥14 inches), red drum (≥20 inches), and spotted seatrout (≥15 inches) (TPWD, 2021). Once collected, all biota samples (i.e. whole organisms) were maintained on ice and stored at -20ºC upon return to the laboratory facilities at Dickinson Marine Labs. Subsequently, samples were moved to -20ºC storage facilities at A&M Galveston and thawed on ice prior to excising a few grams (~5-10 grams) of muscle (skin-free fillet) or liver tissue from fish, and ~1-2 gram of mantle plus gill (or mantle/gill) tissue from oysters. The excised samples were stored separately at -20ºC until needed for analysis.

Previously developed protocols by Hansen et al., (2001) and Bossi et al., (2005) were adapted for PFASs extraction from tissue samples. For brevity, an approximately 0.5 gram of muscle or liver (fish), and ~1 gram of mantle/gill (oysters) was homogenized in 7 mL polypropylene tubes containing ceramic beads (Fisher Scientific, Cat.# 15-340-157), and containing 4 mL of MilliQ water. All tissues were homogenized in a Fisherbrand Bead Mill 4 Homogenizer (Fisher Scientific) at a processing power of 150 g for 2 minutes. The resulting homogenate was spiked with the internal standards 13C4-perfluorooctanesulfonate (13C4-MPFOS) and 13C8-Perfluorooctanoic acid (3C8-PFOA) (50 ng mL^{-1} final concentration for each), and liquid:liquid extracted into methyl-tert-butyl-ether (MTBE) containing 0.5 M tetra-butyl-ammonium hydrogen sulphate (TBA) solution (pH 10), 0.25 M sodium carbonate and

0.25 M sodium bicarbonate buffer (Bossi et al., 2005; EPA Method 533, 2019; Hansen et al., 2001). The liquid:liquid extraction was performed twice, and the solvent supernatants were pooled together, and dried under a gentle stream of nitrogen. The resulting residue was reconstituted to 1 mL with acetonitrile containing 1% formic acid. In order to remove lipid or other particulate residue, samples were frozen for 1 hour and an 0.8 mL aliquot was removed and filtered through an Agilent Captiva EMR-Lipid removal cartridge (1 mL, 40 mg) (Agilent, Cat.# 5190-1002). The recovered solvent was then dried and concentrated to 0.04 mL in methanol and stored at -20ºC prior to LC-MS/MS analysis.

2.3 LC-MS/MS analysis of PFASs

The liquid chromatography and tandem mass spectrometry (LC-MS/MS) system comprised an Agilent 1260 UHPLC system with triple-quad 6420 mass detector (Agilent, Santa Clara, CA). A 12-point standard curve was constructed for each of the following Environmental Protection Agency's (EPAs) priority PFASs: PFBS (perfluorobutanesulfonic acid), PFHxA (perfluorohexanoic acid), PFHpA (perfluoroheptanoic acid), PFHxS (perfluorohexane sulfonate), PFOA (perfluorooctanoic acid), PFNA (perfluorononanoic acid), PFOS (perfluorooctanesulfonic acid), PFDA (perfluorodecanoic acid), PFUnA (perfluoroundecanoic acid), PFDoA (perfluorododecanoic acid), PFTrDA (perfluorotridecanoic acid), PFTA (perfluorotetradecanoic acid). All PFASs standards were purchased from Sigma-Aldrich. Each standard curve was run between 0.098 ng mL^{-1} and 200 ng mL^{-1}, using 13C4-perfluorooctanesulfonate (13C4-MPFOS, Wellington Labs) and 13C8-perfluorooctanoic acid (13C8-PFOA, Cambridge Isotope Labs, Cat.# CLM-8005-S) as internal standards at 50 ng mL^{-1} final concentration (**Supplemental 2**). Chromatographic separation was performed at a flow rate of 0.4 mL $minute^{-1}$ on an Agilent

ZORBAX Eclipse Plus C18 RRHD column (3.0 x 50 mm, 1.8 µm) (Agilent, Cat.# 959757-302). The liquid mobile phase comprised: Milli-Q water (A) and methanol (B), and with each containing 5 mM ammonium acetate. The mobile phase gradient started at 10% (B) (held for 0.5 min), then transitioned linearly from 10% (B) to 30% (B) over 2 minutes, and then to 95% (B) in 12 minutes, and back to the initial condition of 10% (B) over 1 minute. The total run-time was 15.5 minutes. All analytes were detected in negative electrospray ionization (ESI-) mode with nitrogen used as the desolvation gas (heated to 230ºC and flow rate of 4 L/minute). Multiple reaction monitoring (MRM) was used to detect precursor>product ions at a capillary voltage of 2.5 kV. The specific mass spectrometer settings and precursor>product ions for each PFASs homolog are reported in **Supplemental 2**. The instrument limit of detection (LOD) was set to the lowest calibration point that gave an accuracy $\geq$70%, and a precision $\leq$20%. The subsequent methodological limit of detection was set to the instrument LOD value corrected to the water or tissue concentration factor (**Supplemental 2**).

2.4 Quality assurance and control

Sample quality assurance and quality control measures were conducted by optimizing PFASs extractions from water and matrix-matched tissue samples. For the optimization of extraction efficiency from water, Milli-Q water samples in glass bottles (n=2) were spiked (as a standard addition) with a representative mixed standard comprising representative short and long chain PFASs, with percent recovery was quantified for PFHxA (89% recovery, $\pm$1% s.e.m or standard error of mean), PFOA (77$\pm$7%), PFOS (40$\pm$5%), and PFDoA (20$\pm$2%). Similarly for biota samples, matrix-matched standard addition spikes were conducted into liver samples from fish (n=3). The percent recovery was quantified for PFHxA (78$\pm$0.1%), PFOA (121$\pm$2%), PFOS

(82±4%), and PFDoA (26±1%). For continued quality assurance, recoveries of the select PFASs in standard addition samples (using fish liver as a representative matrix) was routinely tested every 10 biota samples analyzed. Compound recoveries remained relatively consistent throughout the project duration for PFHxA (101±12%), PFOA (103±12%), PFOS (89±15%), and PFDoA (58±9%) (n=21 samples). The PFASs concentrations analyzed in surface waters and biota samples from Galveston Bay were not corrected for the percent recoveries established during standard addition trials, as the method recoveries were considered adequate for the purpose of quantification.

2.5 PFOS risk assessment for seafood consumption

Given regulatory oversight to mitigate the dietary exposure of humans to PFOS (EPA, 2016), a risk assessment for seafood consumption was also conducted. Using the risk assessment approach detailed in Fair et al., (2019), a hazard ratio (HR) was calculated to estimate the potential risk for human exposure from the consumption of oysters and fish from Galveston Bay. First, a daily intake (DI) rate of seafood in gram/kg human body weight/day was calculated ($Eq. 1$) by dividing the estimated daily consumption ($DC_{shellfish/fish}$) of shellfish or fish (gram per day) per unit body weight (BW) of an adult human (kg). The Texas Department of State Health Services' (DSHS) Seafood and Aquatic Life Group's (SALG) criteria of assuming a standard adult weight of 70 kg and consumption of 30 grams of shellfish or fish per day was used to calculate the DI (DSHS, 2011). Second, an average daily intake (ADI) rate of PFOS exposure (in ng/kg human body weight/day) was calculated by multiplying the average PFOS concentration in muscle (fish) or mantle/gill (oysters) in ng gram^{-1} wet weight (C_{PFOS}) by the DI ($Eq. 2$). Third, a hazard ratio (HR) was calculated ($Eq. 3$) by taking the ratio of the ADI to the

EPA reference dose for PFOS (RfD_{PFOS}) of 0.000025 mg/kg human body weight/day (or 25 ng/kg human body weight/day) (EPA, 2016). With a calculated HR>1 indicating a potential risk of human exposure and adverse effects from the consumption of PFOS contaminated seafood (Fair et al., 2019).

$Eq. 1$: $DI = DC_{shellfish\ or\ fish}/BW$

$Eq. 2$: $ADI = C_{PFOS} * DI$

$Eq. 3$: $HR = ADI/RfD_{PFOS}$

In addition to the calculation of a HR for the consumption of oysters and fish, a seafood 'meal frequency' was also estimated based on the thresholds set by the Great Lakes consortium for PFOS levels in fish. The estimated meal frequency was compared against the PFOS body-burdens in fish (Minnesota Department of Health, 2019).

2.6 Statistical analysis

All statistical analyses were performed using the Python programing language (v3.7.4), along with associated data handling (pandas), visualization (matplotlib), and statistical analysis (scipy, scikit) libraries. The normal distribution of datasets was tested using the Shapiro-Wilk test, with homogeneity of variance tested using the Levene test. Parametric testing was done either using a student's t-test (comparing two groups), or one-way analysis of variance (ANOVA) followed by Tukey's posthoc test to compare for differences (when comparing multiple groups). Non-parametric testing was done using the Mann-Whitney U-test (comparing two groups), whereas a Kruskal-Wallis test followed by the Dunn's posthoc test was used to compare for differences across multiple groups. The standard error of mean (s.e.m) was calculated for replicates and significance for all tests was established at $\alpha = 0.05$.

3. Results

3.1 PFASs in surface waters of Galveston Bay following AFFFs use

The monthly analysis of total PFASs showed elevated levels immediately following the ITC fire in March and April 2019 (**Fig. 2**, **Supplemental 3**). Surface water samples were not collected in May or December 2019. The total PFASs levels measured in April were ~2x higher than those measured in March. However, the mean total PFASs levels measured in March and April were 4x to ~300x higher than total levels measured in the months thereafter (i.e., until November 2019) (**Fig. 2(a)**). Changes in total PFASs levels along the sampling transect, i.e., starting from the HSC/Morgan's Point, progressing along Galveston Bay, to Pelican Island (the Gulf of Mexico), was also assessed (**Fig. 2(b)**). The total PFASs levels per sampling point showed that the highest levels were measured around the sampling locations in close proximity to the site of the chemical fire (i.e., HSC/Morgan's Point) (**Fig. 1**). PFASs levels fell precipitously along Galveston Bay to Pelican Island (**Fig. 2(b)**). The overall decreasing levels of total PFASs along the sampling transect is attributable to the dilution of the nearly freshwater input (1-5 parts per thousand or ppt) from the HSC where the two major inflowing rivers (San Jacinto and Trinity) intersect with sea water from the Gulf of Mexico (>30 ppt) (TCEQ, 2009). In the subsequently sampled months (i.e., June and onwards), PFASs levels were $\leq$6% of the maximal levels measured in April. An exception however was seen in August, where elevated PFASs levels were measured at the final sampling location just off Pelican Island, with levels

67% that of the maximal level measured in April at the HSC/Morgan's Point sampling location (**Fig. 2(b)**).

The overall analysis of individual PFASs homologs as normalized to the total measured at each monthly time point showed the predominant detection of mainly short-chain PFASs (**Fig. 3**). Namely, those containing a carboxylate hydrophilic group with $n < 7$ perfluorinated carbons, such as PFHxA (5 perfluorinated carbons) and PFHpA (6 perfluorinated carbons); and those with a sulfonate hydrophilic group with $n \leq 6$ perfluorinated carbons, such as PFBS (4 perfluorinated carbons) and PFHxS (6 perfluorinated carbons). The only long-chain PFASs most prominently detected included PFOA (carboxylate with 7 perfluorinated carbons) and PFOS (sulfonate with 8 perfluorinated carbons). The remainder of long-chain PFASs also detected included PFTrDA and PFTA (carboxylates containing 12 and 13 perfluorinated carbons respectively) (**Fig. 3**).

Of all PFASs homologs, PFOS was the most abundantly detected in surface waters following the ITC fire at Deer Park, constituting some 66% and 68% of total PFASs detected in March and April (2019) respectively (**Fig. 3**). The levels of PFOS thereafter were <50% of total PFASs, with exception of elevated levels detected in October at 71% (although total PFASs levels in ng/L in October were only 14% of the peak levels measured in April, **Fig. 2(a)**). Concomitantly, PFHxS levels were also elevated in March and April, albeit at a lower proportion to total at 12% and 16% respectively. Juxtaposed with successively decreasing PFOS and PFHxS levels in Galveston Bay following the ITC fire at Deer Park, PFBS, PFHxA, PFHpA, and PFOA levels showed a slight initial increase in the subsequent months following the fire, but overall declined near the end of the year (**Fig. 3**). For example, the highest levels of PFBS and PFHpA were recorded in September and November (2019) at 31% and 47% of total PFASs measured at each month respectively. PFHxA and PFOA concomitantly exhibited their highest levels in July at 15% and 13% respectively. Finally, PFTrDA and PFTA showed marginally elevated levels in November only at 14% and 4% respectively (**Fig. 3**).

3.2 PFASs body-burdens in biota (shellfish and fish) of Galveston Bay

PFASs levels in muscle and liver tissue of fish, and mantle/gill tissue of oysters are reported as ng $gram^{-1}$ tissue wet weight in **Supplemental 4**. The analysis of mean total PFASs body-burdens indicated the highest levels in liver versus muscle of fish (**Fig. 4**). The total PFASs levels in muscle was 9%, 14%, and 16% of levels in the livers of gafftopsail catfish, spotted seatrout, and red drum respectively (**Fig. 4**). Comparison of levels in muscle indicated statistically significantly higher levels in fish vs. oyster (Kruskal-Wallis test, $p \leq 0.05$) (**Fig. 4**). Whereas gafftopsail catfish exhibited the highest hepatic levels of PFASs in fish, with levels 5x and 3x higher than in spotted seatrout and red drum respectively (Kruskal-Wallis test, $p \leq 0.05$) (**Fig. 4**).

The subsequent analysis of PFASs homolog composition in muscle and liver tissue (normalized to total PFASs levels) indicated PFOS to dominate in both tissues. The analysis of muscle tissue in fish and mantle/gill from oysters, showed PFOS to constitute $\geq$66% of total PFASs (**Fig. 5(a)**). The only other homolog comprising noticeably high levels was PFHxS, contributing 5 - 8% of total PFASs in all taxa. As an exception, PFHxA was highest in oysters only, comprising 10% of total PFASs. Whereas all other homologs were <10% of total (**Fig. 5(a)**). In contrast to muscle, the analysis of liver tissue in fish only clearly exhibited PFOS to be the most prominent homolog comprising $\geq$92% of total, with the remainder of homologs comprising $\leq$3% of total PFASs (**Fig. 5(b)**).

Given the predominance of PFOS in biota, it was henceforth used as a 'tracer' to further study sex-specific differences of body-burdens in male versus female fish. The spotted seatrout was the only fish species to exhibit a statistically significant difference for PFOS levels in muscle or liver tissue between male versus female fish (Mann-Whitney U-test, $p \leq 0.05$) (**Supplement 5**). PFOS levels in the muscle and liver tissue of male spotted seatrout were 4x and 3x higher than in female fish respectively (**Supplement 5**).

Finally, changes in PFOS body-burdens in oysters and fish was assessed over time (months) following the ITC fire at Deer Park. Elevated trends in PFOS body-burdens were evident in all biota species (**Fig. 6**). Specifically, for oysters a statistically significant elevation in PFOS body-burden was evident one month (April) following the ITC fire (Kruskal-Wallis test, $p \leq 0.05$). Whereas for fish, spotted seatrout exhibited significantly elevated levels in May (2019) relative to subsequent months (Kruskal-Wallis test, $p \leq 0.05$). While there were no statistically significant differences in PFOS levels over time for the gafftopsail catfish and red drum, an overall elevated trend of PFOS body-burdens appears evident for these fish in the months immediately following the ITC fire (**Fig. 6**).

3.3 Human seafood exposure risk assessment

While the mean hazard ratios (HRs) for all species was below the EPA reference dose (RfD), i.e., $HR < 1$, the maximal ratio was within range of potential risk to human health (i.e.,

$HR \geq 1$) (**Table 1**). Specifically, the max HR for gafftopsail catfish and red drum exceeded (2x higher) the expected safe $HR < 1$. In addition, the max HR for spotted seatrout was equivalent to the EPA determined RfD (i.e., $HR = 1$). Only the max HR for eastern oysters was below the EPAs RfD (i.e., $HR < 1$) (**Table 1**). Furthermore, the comparison of PFOS levels in muscle (fish) or gill/mantle tissue (oysters) with the meal frequency estimates of the Minnesota Department of Health (2019) advisory, identified gafftopsail catfish and red drum to be within the 2 meals per week seafood consumption advisory (**Fig. 7**).

4. Discussion

4.1 PFASs in the surface waters of Galveston Bay following AFFFs use

In this study, select PFASs homologs were detected at elevated levels in the surface waters of Galveston Bay following the ITC fire at Deer Park in March 2019 (Houston, TX). This detection of elevated PFASs levels is consistent with the anticipated runoff of AFFFs, used to quench the ITC fire at Deer Park, into the HSC and Galveston Bay (Aly et al., 2020). The most prominently detected PFASs homologs measured in our study were PFOS > PFBS > PFHpA > PFOA > PFHxA > PFHxS > PFTrDA > PFTA. The overall abundance of these homologs agrees with those quantified by Aly et al., (2020), whom also quantified PFASs in the surface waters of the HSC following the ITC fire at Deer Park, finding the two most abundant homologs to be 6:2 fluorotelomer sulfonic acid (or 6:2 FTS) and PFOS. While 6:2 FTS was not measured in our study, there is good agreement for the PFOS levels measured between the two studies, with a median PFOS concentration of 114 ng/L measured by Aly et al., (2020) in March 2019 (maximum level of 302 ng/L), and an average concentration of 173 ± 120.5 ng/L (± s.e.m) measured in our study in March 2019 (**Supplemental 3**).

Aly et al., (2020) intensively sampled along the HSC and upper Galveston Bay (Morgan's Point). These sampling locations are near the site of the fire and AFFFs use (**Fig. 1**). By contrast in our study, a wider sampling transect was used that included the HSC and entire length of Galveston Bay (**Fig. 1**). The large amounts of AFFFs released (~≤19 million liters) into the surface waters of the HSC and upper Galveston Bay acted as a point-source for PFASs pollution (Aly et al., 2020; Rice, 2019). Therefore, the sampling points closest to the ITC fire occurrence in time (i.e., March and April 2019), and location (i.e., HSC/Morgan's Point) exhibited the most elevated PFASs levels (**Fig. 2(b)**). Furthermore, the prevalence of elevated PFASs levels ~2 months after fire (i.e., in March and April 2019) agrees with the hydrodynamics of the bay, with estimates of water residence time of ~1.5 months (Rayson et al., 2016), and pollution retention time of ≤3 months (Du et al., 2020). This also agrees with Aly et al.'s, (2020) observations of 6:2 FTS and PFOS dissipation from the HSC within ≤4 months following the ITC fire at Deer Park.

While the use of AFFFs at Deer Park resulted in total PFASs levels in March and April (2019) that were up to two orders of magnitude greater than those detected in subsequent months (**Fig. 2(a)**), varying levels of PFASs homologs were continuously detectable in the surface waters of Galveston Bay (**Supplemental 3**). Case in point was the detection of all measured PFASs homologs at the sampling location off Pelican Island in August (2019) (**Supplemental 3** and **Fig. 2(b)**). The total PFASs measured in August was ~20% of the highest levels measured in April following the ITC fire, and 3x to 85x higher than those measured in the preceding (July) and proceeding (September) month respectively (**Fig. 2(a)**). This result indicates another likely point source release of PFASs, either associated with AFFFs use or some other industrial activity. The Galveston Bay estuary houses 30-50% of the US capacity of oil refineries and chemical industries (Rowe et al., 2021). Almost a year after the ITC fire, there was a smaller petrochemical fire at the Pelican Island Storage Terminal facility near Galveston, TX (on May 19th, 2020). While largely contained, AFFFs were once again used to quench this fire (Ferguson et al., 2020; Napoli, 2020). Therefore, it appears that Galveston Bay may be a major sink for industrial (or AFFF related) discharges of PFASs pollutants, potentially explaining continued detections (and at times at elevated levels) of PFASs in the bay.

From a regulatory perspective at present there are no enforceable maximum contaminant levels (MCLs) for PFASs under the US EPAs Safe Drinking Water Act (SDWA). However, under the EPAs Third Unregulated Contaminant Monitoring Rule (UCMR3), six PFASs have been included for monitoring in drinking water, which include: PFOS, PFOA, PFNA, PFHxS, PFHpA, and PFBS (EPA, 2021). As a result of this requirement, various states have established their own guidelines for PFOA and PFOS MCLs in drinking water and groundwater. For PFOA, state specific guidelines range from 0.02 – 2 μg L^{-1} (0.3 μg L^{-1} for Texas), whereas for PFOS they range from 0.01 – 0.6 μg L^{-1} (0.6 μg L^{-1} for Texas) (EPA, 2017). In our study, the maximum PFOA level measured was 0.02 μg L^{-1} as detected in August 2019, in the sampling point off Pelican Island. Whereas the maximum PFOS level measured was 0.76 μg L^{-1} as detected in the HSC in March 2019. Overall, only PFOS levels exceeded the State of Texas' MCL in only 3% of the total samples analyzed, with the elevated levels above MCL (i.e., >0.6 μg L^{-1}) only detected in March and April 2019 (i.e., immediately following the fire).

Finally, given the PFASs pollution of the surface waters of Galveston Bay, we next investigated whether there was concomitant elevated exposure of select biota in the bay.

4.2 PFASs body-burdens in biota of Galveston Bay

The analysis of PFASs body-burdens in the resident biota (shellfish and fish) from Galveston Bay showed significant differences between invertebrate (eastern oysters) versus vertebrate taxa (fish). The comparison of PFASs levels in the gill/mantle in oysters vs. muscle in fish showed levels in fish to be $\geq$4x higher than in oysters (**Fig. 4**). Overall, total PFASs levels were $\geq$6x higher in liver tissue versus muscle from fish, reflecting their preferential bioaccumulation in a tissue of high protein density (Lanza et al., 2017). The subsequent homolog analysis identified PFOS to be the predominant PFASs detected in all tissues (**Supplemental 4** and **Fig. 5**). This dominance of PFOS as the primary PFASs homolog in biota agrees with observations from other environmental monitoring studies (Lanza et al., 2017; Oakes et al., 2010; Taylor, 2019; Taylor and Johnson, 2016). PFOS dominance is likely attributed to its prominent use in consumer and industrial products (De Silva et al., 2021), and the high number of fluorinated carbon atoms (C=8) conferring greater hydrophobicity (Buck et al., 2011; Ding and Peijnenburg, 2013). As a result, PFOS acted as an appropriate 'tracer' for comparison and contrast with other studies measuring PFASs body-burdens.

The mean PFOS level measured in eastern oysters in this study ($\leq$2 ng gram^{-1} wet weight) was 0.2 – 3% of the levels (74 – 883 ng gram^{-1} dry weight) measured in eastern oysters from Galveston Bay by Kannan et al., (2002). More recent comparison of PFOS measurements with other studies shows agreement with the levels measured in this study. For example,

~1.3 ng gram^{-1} wet weight PFOS was measured in Pacific oysters (*Crassostrea gigas*) sampled in the coastal waters around Xiamen Island (Fujian Province, China) (Dai and Zeng, 2019); and 0.7 – 1.6 ng gram^{-1} wet weight was measured in Sydney Rock Oyster (*Saccostrea glomerata*) and Pacific Oyster (*C. gigas*) sampled from Port Stephens (New South Wales Australia) (O'Connor et al., 2018). The study by Kannan et al., (2002) measured PFOS in oysters from 77 locations around the Gulf of Mexico and Chesapeake Bay of the United States, and reported levels ranging from <42 - 1,225 ng gram^{-1} dry weight. The lower levels measured in oysters in this study may be a consequence of the EPAs 2006 stewardship program which invited leading companies responsible for PFASs production and use, to commit to a 95% reduction in their industrial and commercial applications. By the year 2015, this goal was met by all companies participating in the program (EPA, 2006). Therefore, a cessation in the widespread use of PFASs by its major producers and consumers may have contributed to overall lower levels in the environment.

Typical comparisons of PFOS body-burdens in shellfish (1 – 10 ng gram^{-1} whole body wet weight) versus fish (1 – 150 ng gram^{-1} liver wet weight) indicates at least a one to two orders of magnitude higher levels in vertebrates versus invertebrates (Ahrens and Bundschuh, 2014). In our study a direct comparison between levels of PFOS measured in oysters versus fish are confounded by the apparent increase in body-burdens (PFOS levels in muscle and liver) across the temporal sampling time frame from March to November 2019. These temporal differences in PFOS body-burdens appear highly indicative of the acute exposure to a point-source release of high levels of PFOS into Galveston Bay in March 2019. For example, in oysters PFOS levels significantly increased 3x in April versus March, with an apparent decline in PFOS levels by

May 2019 (**Fig. 6**). Spotted seatrout exhibited a 2x increase in PFOS body-burdens in May 2019, with a statistically significant decline in the months thereafter (i.e., October and November 2019) (**Fig. 6**). A concomitant increase in PFOS body-burdens in May and June 2019 was also evident for gafftopsail catfish (albeit a statistically non-significant increase), with subsequent levels decreasing in October and November 2019 (**Fig. 6**). Finally, red drum also showed a steady elevation in PFOS body-burdens with a peak level in October of 4x that in April (statistically non-significant), followed by a precipitous decline in body-burdens in November to levels near equivalent to those in April (**Fig. 6**). Therefore overall, there appears to be a trend of increasing PFOS body-burdens in the biota resident in Galveston Bay following the ITC fire in March 2019.

To our knowledge, this study is the first to measure PFOS body-burdens in fish from Galveston Bay, as a result precluding the comparison and contrast of PFOS levels to an existing or previously measured baseline. However, we can consider PFOS concentrations measured in spotted seatrout and red drum in April 2019 to be the most representative of a putative baseline levels, as these levels preceded the increase in PFOS body-burdens observed in subsequent months. The concentration of PFOS measured in the muscle (or fillet) of spotted seatrout (6.5 ± 1.5 ng gram^{-1} wet weight) and red drum (6.8 ± 3.3 ng gram^{-1} wet weight) (mean $\pm$ s.e.m), is in close approximation to the mean levels measured in the fillet of red drum (8.6 ng gram^{-1} wet weight) and spotted seatrout (9.3 ng gram^{-1} wet weight) sampled from Charleston Harbor, South Carolina, USA (Fair et al., 2019). It is unclear whether such agreement between PFOS body-burdens in spotted seatrout and red drum from Galveston Bay (this study) compared to those in Charleston Harbor (Fair et al., 2019), reflects a typical 'national average'. The continued monitoring of PFASs levels in biota from Galveston Bay should help to resolve typical baseline levels in this coastal ecosystem.

Regardless of a lack of complete knowledge of baseline PFOS levels in the biota of Galveston Bay, the overall increase in PFOS body-burdens observed in the 1-2 months following the ITC fire agrees with observations made following AFFFs release into the aquatic environment. Specifically, Lanza et al., (2017) demonstrated elevated PFOS body-burdens in fish one month following elevated levels in surface waters due to increased AFFFs runoff. Furthermore, the short water residence and pollution retention times (Du et al., 2020; Rayson et al., 2016), likely contributed to the continued exposure of resident biota in the bay following AFFFs release during the ITC fire in March 2019. The likely consequence of elevated PFOS bioaccumulation in shellfish and fish for human exposure through seafood consumption was explored in the conduct of a risk assessment, as described below.

4.3 Risk assessment of elevated PFOS body-burdens in shellfish and fish

Typical seafood advisories in Galveston Bay are issued subject to the monitoring of 'legacy' pollutants (i.e., persistent organic pollutants that are by-products of past and present industrial activities), such as dioxins, polychlorinated biphenyls (PCBs), etc. (DSHS, 2013). To our knowledge, this study is the first to report PFASs body-burdens in commercially important fish and shellfish species from Galveston Bay. While the calculated mean hazard ratios (HRs) for PFOS levels in oysters and fish were below the EPAs reference dose (RfD) threshold likely to cause toxicity (i.e., $HR < 1$) (EPA, 2016), consideration of the maximal range of HR values for gafftopsail catfish, spotted seatrout, and red drum included levels likely to cause toxicity (i.e.,

$HR \geq 1$) (**Table 1**). The toxicity effects anticipated at exposure to PFOS above the reference dose include immunotoxicity, endocrine effects, hepatoxicity, reproductive toxicity, and dyslipidemia (EPA, 2016). A closer examination of the percent fish that exhibited $HR \geq 1$ indicated inclusion of gafftopsail catfish (23% of the fish sampled), red drum (21%), and spotted seatrout (3%). All oysters sampled exhibited an $HR < 1$, indicating no immediate concerns for the dietary exposure of humans from the consumption of oysters. The interpretation of the calculated HR values to an actionable limit for seafood consumption is provided by the comparison of tissue burdens with the thresholds for meal advisories as proposed by the Minnesota Department of Health (2019) (**Fig. 7**). These meal advisory thresholds are also comparable with the fish consumption thresholds detailed in Fair et al., (2019). Therefore, a conservative estimate of 1-2 meals per week for gafftopsail catfish and red drum, and 2 meals per week for spotted seatrout is expected to be protective for minimizing human exposure to PFOS. Such an advisory is also sufficiently protective of the coastal communities along Galveston Bay, with 6% of survey respondents (as per a questionnaire survey of 525 persons) reporting the consumption of locally caught seafood multiple times a week, and 8% once per week (Ross et al., 2020).

While the calculation of HRs using the EPAs RfD for PFOS (25 ng/kg body weight/day) is relevant from a state regulatory risk assessment in the U.S., its comparison with the European Food Safety Authority's (EFSA) RfD for PFOS (2 ng/kg body weight/day) (EFSA, 2018) scales our calculated HRs by an order of magnitude. Using the previously calculated average daily intake (ADI) rates (**Table 1**), we find $HRs > 1$ for gafftopsail catfish ($HR = 4.1$), spotted seatrout ($HR = 1.9$), and red drum ($HR = 4.0$). Whereas, the oysters continue to remain below the threshold for concern ($HR = 0.4$). Therefore, comparison with the European RfD may trigger regulatory oversight of PFASs levels in biota from Galveston Bay. Future risk assessment may also consider PFASs burdens in skin-on fillets in order to comprehensively assess the sequestration of PFASs homologs in other edible compartments. Regardless, there is need for the continued and long-term monitoring of PFASs levels in biota from the bay as such efforts will help to establish a 'baseline' of PFASs contamination and likely delineate the impacts of disaster events (petrochemical fire and AFFFs use) versus routine input from municipal wastewater treatment works.

In addition to considering human exposure, PFOS levels measured in the surface waters and body-burdens of biota from Galveston Bay can also provide insights into likely toxicity effects in the exposed wildlife. A comprehensive survey of toxicity data by Beach et al., (2006) identifies a PFOS water concentration of ≤1.2 µg L^{-1} to be protective against adverse toxicity effects in exposed shellfish, fish, and amphibians (such as effects on survival, growth, embryo-larval hatching success). The authors also calculated a tissue-based toxicity reference value (TRV) for fish of ≤87 µg $gram^{-1}$ wet weight to be protective against toxicity effects. More recently, a study by Aquilina-Beck et al., (2020) identified ≤3 mg L^{-1} PFOS to be the lowest observed effect concentration (LOEC) for adverse immune effects in exposed eastern oysters. In our study, the maximum PFOS concentration measured in surface waters was 0.76 µg L^{-1} (detected in the HSC in March 2019). This levels is 63% of the 1.2 µg L^{-1} posited to be protective of aquatic organisms (Beach et al., 2006). Furthermore, the highest body-burden of PFOS (1.4 µg $gram^{-1}$ in liver of gafftopsail catfish, **Supplemental 4**), is only 2% of the TRV for fish of 87 µg $gram^{-1}$ (Beach et al., 2006). Therefore, we may not expect any overt toxicity effects (i.e., on fish survival, growth) in the Galveston Bay biota (shellfish and fish) exposed to PFOS following the ITC fire at Deer Park.

5. Conclusion

The use of AFFFs to quench the ITC petrochemical fire in March 2019 at Deer Park (Houston, TX) released elevated levels of PFASs into the aquatic environment of Galveston Bay. PFOS was the most prominent homolog measured in surface waters and biota samples collected in the bay. PFOS levels in surface waters initially exceeded the state of Texas' maximum contaminant levels in March and April 2019 (i.e., immediately following the fire), with levels declining in the months thereafter. Concomitant with elevated PFOS levels in the surface waters, significantly elevated body-burdens of PFOS was also quantified in eastern oysters (April 2019) and spotted seatrout (May 2019). The prevalence of elevated PFASs levels up to 2-3 months following AFFFs release is indicative of the hydrodynamics of the bay, with an average pollutant residence time of $\leq$3 months. A risk assessment of seafood safety indicated no restrictions for eastern oyster consumption. However, the risk assessment indicated a 1-2 meal/week limit for the consumption of gafftopsail catfish and red drum from the bay. In summary, our study reveals the fate of PFASs pollutants in the surface waters and biota of Galveston Bay following the use of AFFFs to quench a petrochemical fire. Despite the acute release of high PFASs concentrations immediately following AFFFs use, levels of PFASs were continuously detectable in the surface waters of Galveston Bay (albeit at lower levels). Our results highlight the need for continued monitoring of PFASs levels in surface waters and biota of the bay to establish a baseline of exposure in this industrialized estuarine/coastal ecosystem. Furthermore, there is also a need to build community awareness and interaction with these pollution monitoring efforts as research has shown frequent use of such information is associated with changes to individual consumption of seafood (Ross et al., 2020).

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7. References

Abunada Z, Alazaiza MYD, Bashir MJK. An Overview of Per- and Polyfluoroalkyl Substances (PFASs) in the Environment: Source, Fate, Risk and Regulations. Water 2020; 12: 3590.

Ahrens L, Bundschuh M. Fate and effects of poly- and perfluoroalkyl substances in the aquatic environment: a review. Environ Toxicol Chem 2014; 33: 1921-9.

Aly NA, Luo YS, Liu Y, Casillas G, McDonald TJ, Kaihatu JM, et al. Temporal and spatial analysis of per and polyfluoroalkyl substances in surface waters of Houston ship channel following a large-scale industrial fire incident. Environ Pollut 2020; 265: 12.

Ankley GT, Cureton P, Hoke RA, Houde M, Kumar A, Kurias J, et al. Assessing the Ecological Risks of Per- and Polyfluoroalkyl Substances: Current State-of-the Science and a Proposed Path Forward. 2020; n/a: 1-167.

Aquilina-Beck AA, Reiner JL, Chung KW, DeLise MJ, Key PB, DeLorenzo ME. Uptake and Biological Effects of Perfluorooctane Sulfonate Exposure in the Adult eastern Oyster Crassostrea virginica. Arch Environ Contam Toxicol 2020; 79: 333-342.

Beach S, Newsted J, Coady K. Ecotoxicological Evaluation of Perfluorooctanesulfonate (PFOS). Reviews of environmental contamination and toxicology 2006; 186: 133-74.

Bossi R, Riget FF, Dietz R, Sonne C, Fauser P, Dam M, et al. Preliminary screening of perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish, birds and marine mammals from Greenland and the Faroe Islands. Environ Pollut 2005; 136: 323-9.

Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, de Voogt P, et al. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. Integrated Environmental Assessment and Management 2011; 7: 513-541.

Coggan TL, Moodie D, Kolobaric A, Szabo D, Shimeta J, Crosbie ND, et al. An investigation into per- and polyfluoroalkyl substances (PFASs) in nineteen Australian wastewater treatment plants (WWTPs). Heliyon 2019; 5.

Dai Z, Zeng F. Distribution and Bioaccumulation of Perfluoroalkyl Acids in Xiamen Coastal Waters. Journal of Chemistry 2019; 2019: 2612853.

De Silva AO, Armitage JM, Bruton TA, Dassuncao C, Heiger-Bernays W, Hu XC, et al. PFASs Exposure Pathways for Humans and Wildlife: A Synthesis of Current Knowledge and Key Gaps in Understanding. Environmental Toxicology and Chemistry 2021; 40: 631-657.

Ding G, Peijnenburg WJGM. Physicochemical Properties and Aquatic Toxicity of Poly- and Perfluorinated Compounds. Critical Reviews in Environmental Science and Technology 2013; 43: 598-678.

DSHS. Characterization of potential adverse health effects associated with consuming fish from Sabine Lake. 2011: 1-42.

DSHS. Characterization of Potential Adverse Health Effects Associated with Consuming Fish from Galveston Bay. Department of State Health Services, 2013, pp. 1-68.

DSHS. Texas Department of State Helath Services (DSHS) fish and shellfish consumption advisory ADV-55, on-line: https://www.dshs.texas.gov/seafood/PDF2/Active/ADV-55_Modification_20190327.pdf (accessed on 4/27/2021). 2019.

Du J, Park K, Yu X, Zhang YJ, Ye F. Massive pollutants released to Galveston Bay during Hurricane Harvey: Understanding their retention and pathway using Lagrangian numerical simulations. Sci Total Environ 2020; 704: 21.

EFSA. Risk to human health related to the presence of perfluorooctane sulfonic acid and perfluorooctanoic acid in food,

DOI: https://doi.org/10.2903/j.efsa.2018.5194. EFSA Journal 2018: 1-284.

ELI. Envirodyne Laboratories Inc. City of Deer Park -ITC Water Check (published 29th March 2019), on-line: http://www.deerparktx.gov/DocumentCenter/View/7315/2019-03-27--Deerpark--ITC-Water-Check (accessed on 4/27/2021). 2019.

EPA 533. Determination of per- and polyfluoroalkyl substances in drinking water by isotope dilution anion exchange solid phase extraction and liquid chromatography/tandem mass spectrometry. Environmental Protection Agency 2019: 1-52.

EPA. PFOA Stewardship Program: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfas#pfoa (accessed on 6/11/2021). 2006.

EPA. Health effects support document for perfluorooctane sulfonate (PFOS), EPA 822-R-16-002, https://www.epa.gov/sites/production/files/2016-05/documents/pfos_hesd_final_508.pdf (Accessed 6/15/21). 2016: 1 - 245.

EPA. Technical Fact Sheet (EPA 505-F-17-001) - Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA). 2017: 1-8.

EPA. PFASs Laws and Regulations, https://www.epa.gov/pfas/pfas-laws-and-regulations (accessed on: 5/17/2021). 2021.

Fair PA, Wolf B, White ND, Arnott SA, Kannan K, Karthikraj R, et al. Perfluoroalkyl substances (PFASs) in edible fish species from Charleston Harbor and tributaries, South Carolina, United States: Exposure and risk assessment. Environmental Research 2019; 171: 266-277.

Ferguson JW, Elder L, LaCombe J. Explosion rocks Pelican Island tank farm, two injured; The Daily News on-line: https://www.galvnews.com/news/free/article_33e5f8c0-a045-5de5-a41d-693f7f3caae6.html (accessed on 5/12/2021). 2020.

Giesy JP, Kannan K. Global distribution of perfluorooctane sulfonate in wildlife. Environ Sci Technol 2001; 35: 1339-42.

Glüge J, Scheringer M, Cousins IT, DeWitt JC, Goldenman G, Herzke D, et al. An overview of the uses of per- and polyfluoroalkyl substances (PFASs). Environ Sci Process Impacts 2020; 22: 2345-2373.

Hansen KJ, Clemen LA, Ellefson ME, Johnson HO. Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. Environ Sci Technol 2001; 35: 766-70.

Hansen S, Vestergren R, Herzke D, Melhus M, Evenset A, Hanssen L, et al. Exposure to per- and polyfluoroalkyl substances through the consumption of fish from lakes affected by aqueous film-forming foam emissions - A combined epidemiological and exposure modeling approach. The SAMINOR 2 Clinical Study. Environ Int 2016; 94: 272-282.

Houde M, Martin JW, Letcher RJ, Solomon KR, Muir DCG. Biological Monitoring of Polyfluoroalkyl Substances: A Review. Environmental Science & Technology 2006; 40: 3463-3473.

Kannan K, Hansen KJ, Wade TL, Giesy JP. Perfluorooctane sulfonate in oysters, Crassostrea virginica, from the Gulf of Mexico and the Chesapeake Bay, USA. Arch Environ Contam Toxicol 2002; 42: 313-8.

Kelly BC, Ikonomou MG, Blair JD, Surridge B, Hoover D, Grace R, et al. Perfluoroalkyl Contaminants in an Arctic Marine Food Web: Trophic Magnification and Wildlife Exposure. Environmental Science & Technology 2009; 43: 4037-4043.

Key BD, Howell RD, Criddle CS. Fluorinated Organics in the Biosphere. Environmental Science & Technology 1997; 31: 2445-2454.

Lanza HA, Cochran RS, Mudge JF, Olson AD, Blackwell BR, Maul JD, et al. Temporal monitoring of perfluorooctane sulfonate accumulation in aquatic biota downstream of historical aqueous film forming foam use areas. Environ Toxicol Chem 2017; 36: 2022-2029.

Leinfelder A, Blum J. Houston Ship Channel closure could cost energy industry $1 billion, Houston Chronicle, on-line: https://www.houstonchronicle.com/business/energy/article/Houston-Ship-Channel-closure-could-cost-energy-13716058.php (accessed on 4/27/2021). 2019.

Loomis D, Guyton KZ, Grosse Y, El Ghissassi F, Bouvard V, Benbrahim-Tallaa L, et al. Carcinogenicity of benzene: Lancet Oncol. 2017 Dec;18(12):1574-1575. doi: 10.1016/S1470-2045(17)30832-X. Epub 2017 Oct 26., 2017.

Martin JW, Mabury SA, Solomon KR, Muir DC. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mykiss). Environ Toxicol Chem 2003a; 22: 196-204.

Martin JW, Mabury SA, Solomon KR, Muir DC. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (Oncorhynchus mykiss). Environ Toxicol Chem 2003b; 22: 189-95.

Minnesota Department of Health. Great Lakes consortium for fish consumption advisories - best practice for perfluorooctane sulfonate (PFOS) guidelines (url: https://www.health.state.mn.us/communities/environment/fish/docs/consortium/bestpracticepfos.pdf), 2019, pp. 1-22.

Muller R, Yingling V. Interstate Technology Regulatory Council (ITRC): Naming conventions and physical and chemcial propoerties of per- and polyfluoroalkyl substances (PFASs). ITRC PFASs Fact Sheet 2020: 1-15.

Napoli D. 2 workers injured in oil tank explosion in Galveston, Click2Houston on-line: https://www.click2houston.com/news/local/2020/05/19/developing-2-workers-injured-in-oil-tank-explosion-in-galveston/ (accessed on 5/12/2021). 2020.

O'Connor WA, Zammit A, Dove MC, Stevenson G, Taylor MD. First observations of perfluorooctane sulfonate occurrence and depuration from Sydney Rock Oysters, Saccostrea glomerata, in Port Stephens NSW Australia. Mar Pollut Bull 2018; 127: 207-210.

Oakes KD, Benskin JP, Martin JW, Ings JS, Heinrichs JY, Dixon DG, et al. Biomonitoring of perfluorochemicals and toxicity to the downstream fish community of Etobicoke Creek following deployment of aqueous film-forming foam. Aquatic Toxicology 2010; 98: 120-129.

Rayson MD, Gross ES, Hetland RD, Fringer OB. Time scales in Galveston Bay: An unsteady estuary. Journal of Geophysical Research: Oceans 2016; 121: 2268-2285.

Rice J. Texas A&M water researchers find waxy residue near Deer Park disaster. Houston Public Media: A Service of the University of Houston, on-line:

https://www.houstonpublicmedia.org/articles/news/2019/03/28/327062/texas-am-water-researchers-found-waxy-residue-near-deer-park-disaster/ (accessed on 4/7/2019). 2019.

Ross AD, Hotard A, Kamalanathan M, Nolen R, Hala D, Clay LA, et al. Awareness Is Not Enough: Frequent Use of Water Pollution Information and Changes to Risky Behavior. Sustainability 2020; 12: 8695.

Rowe GT, Fernando H, Elferink C, Ansari GAS, Sullivan J, Heathman T, et al. Polycyclic aromatic hydrocarbons (PAHs) cycling and fates in Galveston Bay, Texas, USA. PLoS ONE 2021; 15: e0243734.

Taylor MD. Survey design for quantifying perfluoroalkyl acid concentrations in fish, prawns and crabs to assess human health risks. Sci Total Environ 2019; 652: 59-65.

Taylor MD, Johnson DD. Preliminary investigation of perfluoroalkyl substances in exploited fishes of two contaminated estuaries. Mar Pollut Bull 2016; 111: 509-513.

TCEQ. Trinity - San Jacinto Basin and Bay Area Expert Science Team (BBEST): Technical support for the analysis of historical flow data from selected flow gauges in the Trinity, San Jacinto, and adjacent coastal basins. 2009: 1-53.

TCEQ. TCEQ analysis of ITC water quality sampling data, ITC Surface Water Sampling Data, posted 3/23/2019, on-line: https://www.tceq.texas.gov/response/itc-monitoring-water-quality/(accessed on 4/27/2021). 2019.

TPWD. Saltwater Bag and Length Limits: https://tpwd.texas.gov/regulations/outdoor-annual/fishing/saltwater-fishing/saltwater-bag-and-length-limits (accessed on 6/24/2021). 2021.

UNEP. The 16 New POPs: An introduction to the chemicals added to the Stockholm Convention as Persistent Organic Pollutants by the Conference of the Parties. Stockholm Convention on Persistent Organic Pollutants (POPs) 2017: 1-14.

Wang Z, DeWitt JC, Higgins CP, Cousins IT. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? Environmental Science & Technology 2017; 51: 2508-2518.

Figures and Table legends

Fig.1. Map of Galveston Bay (TX) showing the dates and sampling locations (numbered) of when and where surface water samples were collected for PFASs analysis. The flame symbol at Deer Park indicates the location of the ITC storage tanks which were the site of the petrochemical fire.

Fig. 2. Total PFASs levels (in ng L^{-1}) as measured during (a) monthly sampling, or (b) at sampling locations along Galveston Bay. Abbreviated sampling months include: Sept. = September, Oct. = October, and Nov. = November (shown as mean $\pm$ standard error of mean or s.e.m).

Fig. 3. The individual homolog profiles as normalized to total PFASs measured as measured in Galveston Bay surface waters at each sampling month. The profile of each homolog was averaged across all sampling locations on Galveston Bay (mean $\pm$ s.e.m).

Fig. 4. Mean total PFASs levels (ng $gram^{-1}$ tissue wet weight) in muscle and liver of fish, and mantle/gill of oysters from Galveston Bay. Levels sharing similar letters are not significantly different from one another, whereas dissimilar letters indicate significant differences ($p \leq 0.05$). Species with abbreviated names are: oyster = eastern oyster; gafftopCat = gafftopsail catfish.

Fig. 5. The profiles of individual PFASs homologs in the (a) muscle tissue of fish (mantle/gill for oysters), and (b) liver of fish sampled from Galveston Bay during select months following the ITC fire at Deer Park (March 2019) (shown as mean $\pm$ standard error of mean or s.e.m).

Fig. 6. The changes in PFOS body-burdens (mean $\pm$ s.e.m) for oysters and fish sampled from Galveston Bay following the ITC fire at Deer Park in Mach 2019. The shaded area between March and April encompasses the time span of the ITC fire and subsequent detection of elevated PFOS concentrations in Galveston Bay surface waters (as shown in **Fig. 2**). Concentrations sharing similar letters are not significantly different from one another, whereas dissimilar letters indicate significant differences ($p \leq 0.05$). *** indicates significance at $p \leq 0.001$.

Fig. 7. The comparison of PFOS body-burdens in the muscle tissue of fish and mantle/gill tissue of oysters with the seafood consumption advisory levels estimated by the Minnesota Department of Health (2019) (shown as horizontal dotted lines). Where a range of estimated seafood consumption advisory is given (i.e., >10-20 ng gram^{-1}), the mean value was taken to plot the advisory level (i.e., 15 ng gram^{-1}). Species with abbreviated names are: oyster = eastern oyster; gafftopCat = gafftopsail catfish.

Table 1. Summary of the average daily intake (ADI) and hazard ratio (HR) for the exposure of humans to PFOS in seafood (oysters and fish). The mean values are shown along with minimum and maximum (min – max) ranges. A $HR < 1$ is considered protective of PFOS exposure through the consumption of contaminated seafood (Fair et al., 2019). (0.0 = <LOD).