



## Increased levels of perfluorooctanesulfonic acid (PFOS) during Hurricane Dorian on the east coast of Florida

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### ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic chemicals commonly found in everyday consumer products and are an emerging concern due to their ubiquitous presence in ecosystems around the world. PFAS exposure, which often occurs through contaminated water, has been linked to several adverse health effects in humans and wildlife. PFAS can be transported in surface water and storm runoff in the nearshore environment. Episodic events, such as hurricanes, are projected to increase in frequency and intensity, and a critical unanswered question is: how do episodic events influence the concentrations and distributions of emerging contaminants, such as PFAS, in coastal systems? Here, we investigated the impact of the 2019 Hurricane Dorian on the Florida coast to assess how natural disasters, such as hurricanes, influence the fate and transport of PFAS in surface water. Water samples collected throughout the St. Augustine Intracoastal waterway before, during, and after the storm were analyzed and compared with baseline concentrations. Ultra-high-pressure liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS) was used in the detection and quantification of 23 and 17 PFAS, respectively. Perfluorooctane sulfonic acid (PFOS) was the compound with the highest concentration across all sampling sites. Mean PFOS levels showed the highest increase of 177% during the hurricane and returned to baseline levels after two days. Our findings highlight the need for continued research focused on understanding how large storms near all coastlines can impact the transport of environmental pollutants, such as PFOS, that can have adverse effects on human and environmental health. Further monitoring of PFAS in coastal systems is necessary to identify potential PFAS hotspots, investigate the impacts of episodic events on PFAS transport, develop mitigation practices capable of reducing the risk of PFAS exposure.

### 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of anthropogenic organic compounds with a fluorinated carbon chain and a variety of functional groups (Newman, 2009). PFAS have strong C–F bonds that are responsible for their high stability, inertness, and resistance to degradation (Kotthoff and Bücking, 2018). Due to these characteristics, they are often found in a wide variety of everyday consumer products,

such as fast-food packaging, pesticides, firefighting foams and stain resistant materials (Newman, 2009; Schaider et al., 2017). However, in recent years, PFAS have become an emerging concern due to their adverse health effects and ubiquitous presence in the environment.

The harmful health effects of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), the two most studied PFAS, have been observed in numerous animal models. These compounds have been linked to various health problems, such as weight loss and decreased

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cholesterol levels in rodents (Andersen et al., 2008) and suppression of immune functions in dolphins and sea turtles (Lau et al., 2009). PFOS and PFOA have also been shown to impact thyroid hormone levels and cause irregular menstrual cycles in humans (Zhou et al., 2017; Li et al., 2017). Studies conducted by the Center for Disease Control (USA) have detected and quantified multiple PFAS in the blood serum of thousands of Americans of different races, genders and age groups (U.S. Centers for Disease Control and Prevention, 2015) and found that PFOA and PFOS especially, were quantified at high concentrations. Geometric means of PFOS concentrations in the serum of U.S. citizens have been quantified as high as  $30.4 \text{ ng.L}^{-1}$  (95% CL: 27.1–33.9) (U.S. Centers for Disease Control and Prevention, 2015). Although health safety limits vary across different organizations and researchers, the Environmental Working Group (EWG) suggests that exposure to levels as low as  $1 \text{ ng.L}^{-1}$  of total PFAS in drinking water can be harmful to humans (Andrews, 2019). PFAS have also been detected in the tissues of fish, birds and marine mammals around the world, further highlighting their pervasiveness in the environment (Giesy and Kannan, 2001; Kannan et al., 2004; Zhou et al., 2014; Miller et al., 2015). In Australia, the National Health and Medical Research Council's guideline for PFOS and perfluorohexane sulfonic acid (PFHxS) combined in recreational water is  $2 \text{ ng.L}^{-1}$  (PFAS Guidance for Recreational Water FAQ's, n. d). Although the US Environmental Protection Agency (EPA) does not have a maximum contaminant level set, concern over PFAS has prompted the cessation of PFOS and PFOA production in the United States, although they are still produced internationally (U.S. EPA, 2016). Limited understanding of the toxicology of PFAS as well as their ubiquity and persistence in the environment call for increased research into possible routes of exposure and their character and nature in our environment.

PFAS have been detected in soils throughout the globe and can be retained in the vadose zone (i.e., unsaturated zone) over decadal time-scales. From there, they can leach to groundwater, or be transported in surface/storm water (Brusseau et al., 2020). Past research indicates that contaminated water is a major source of PFAS exposure (Vestergren and Cousins, 2009). It has also been suggested that PFAS can be transported through sorption to clouds and rain droplets (Moskeland, 2010; Arp and Goss, 2009; Goss and Arp, 2009). Due to their strong affinities for surface waters and ability to travel through soil without retention, PFAS have long-range transport potential. Numerous papers have modeled the dispersion and transport of PFAS in the nearshore environment, and the numerical models of Hodgkins et al. (2019) indicated that PFAS could travel up to 31 km in two days during a storm with strong winds and waves (Hodgkins et al., 2019). Although mobilization of PFAS has been modeled before (Hodgkins et al., 2019), observational studies showing the impacts of hurricanes on PFAS transport and concentrations are scarce. Considering the critical role that episodic events may play in PFAS transport, and the predicted increase in storm frequency and intensity (Masson-Delmotte et al., 2018), further studies are needed to evaluate the distribution, mobilization, and transport of PFAS in the coastal zone.

Here, we investigated the distribution of PFAS across nine sites throughout the St. Augustine Intracoastal Waterway. This location was selected as it is within the Guana Tolomato Matanzas National Estuarine Research Reserve (Dix et al., 2008), which is a part of a nation-wide environmental monitoring network, and sites were selected to represent an urban-to-blackwater river gradient. The St. Augustine Intracoastal waterway is a system of various rivers and creeks surrounded by neighborhoods, development and agriculture; it is also frequently used for fishing, swimming, boating, and camping, all of which can serve as potential sources of PFAS contamination in the area. Florida is in a region of the world that experiences many hurricanes, and they can have widespread impacts on water quality of this region (Dix et al., 2008; Schafer et al., 2020). Recent work documented that Hurricane Irma caused a significant pulse of freshwater and dissolved organic matter, with concomitant increases in turbidity and decreases in salinity, dissolved oxygen, and chlorophyll-a (Schafer et al., 2020). Storm-driven

pulses of surface waters are also expected to impact the transport of PFAS from terrestrial to aquatic systems. Thus, the main goal of this study was to document changes in the concentrations and sources of PFAS during and after the passage of Hurricane Dorian, which skirted the Florida coast in fall 2019. More specifically, we aimed to detect and quantify PFAS using ultra-high-pressure liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS) at nine sites along the intracoastal waterway in St. Augustine, to better understand the impact of a hurricane event on PFAS levels in the coastal ocean. This work is part of a newly established collaborative study (iCOAST) within the Whitney Coastal Observatory, that will allow for further evaluation of PFAS transport and hotspots, and to develop mitigation practices to decrease the adverse effects of PFAS exposure to Florida coastal communities.

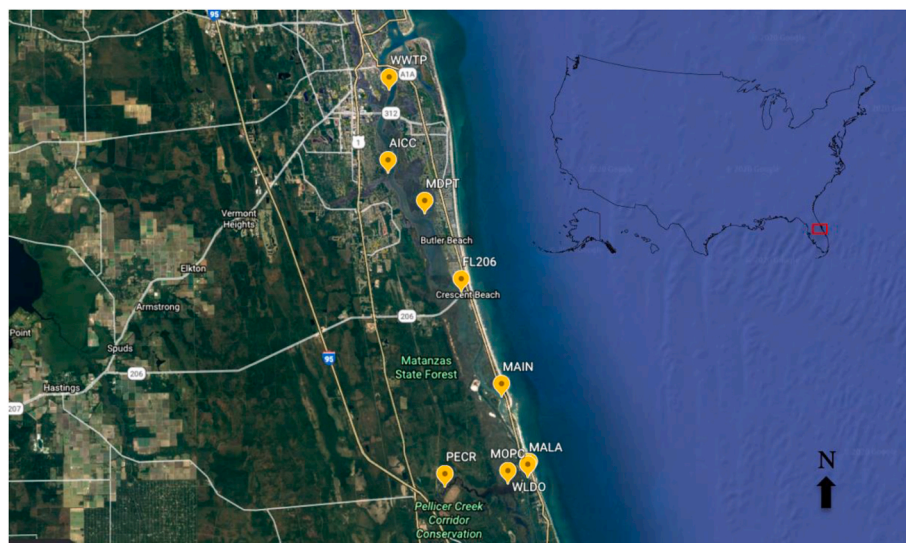
## 2. Materials and methods

### 2.1. Chemicals and reagents

Optima grade solvents and reagents (water, methanol, acetonitrile, ammonium acetate, ammonium hydroxide and acetic acid) were purchased from Fisher Scientific (Waltham, MA, USA) and were used in the preparation of analytical standard solutions and sample extractions prior to analysis by UHPLC-MS/MS. All 51 PFAS standards (mixture of PFAC-24PAR and individual standards) and 23 isotopic analogs (mixture of MPFAC-24ES and individual standards) used as internal standards were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Individual stock and internal standard (IS) solutions were prepared in methanol. Further details on PFAS abbreviations, as well as IS concentrations, can be found in the Supplementary Information (Table SI).

### 2.2. Site location and sample collection

The intracoastal waterway in the St. Augustine area is comprised of the Matanzas River, the St. Augustine and Matanzas inlets, and numerous tidal creeks draining saltmarshes, mangroves, and both developed and rural watersheds. These waterways fall within the boundary of the Guana, Tolomato, and Matanzas National Estuarine Research Reserve (GTMNERR) and also within the focus area of the UF Whitney Laboratory Coastal Observatory (WLCO). The GTMNERR maintains four long-term water quality monitoring stations (1 collocated with a sampling site in this study) and the WLCO has recently established six additional continuous water quality monitoring stations within this study area (three of which are collocated with sampling sites in this work). A strong municipal gradient exists from south to north with the southern component, the Pellicer Creek watershed, having little to no development and the City of St. Augustine, the northern component, having heavily urbanized watersheds. The area is impacted by various activities, such as heavy tourism, boating, and fishing activities with large influxes of seasonal visitors during the summer months. No past research has monitored PFAS levels in the Matanzas River or its tributaries. Surface waters were collected at nine sites along the Matanzas River and its tributary Pellicer Creek (Fig. 1), with over 6 collection events within one year (March 2019–March 2020). Further details of each site are described in Table SII. At each location, surface grab samples were collected in 500 mL high density polyethylene (HDPE) bottles. Each bottle was rinsed with the surface water three times prior to collection. Samples were kept on ice until they were transported to a  $-20 \text{ }^{\circ}\text{C}$  freezer, where they were stored until analysis. A total of six sample collections took place over the course of a year on March 8th, June 24th, August 30th (before the storm), September 4th (during the storm), September 6th of 2019 (after the storm) and March 2nd, 2020. A limitation of this study was that for the June 2019 collection, samples were not collected from the FL206 and MAIN site. Similarly, for the September 4th, 2019 collection, during the storm, surface water samples



**Fig. 1.** Geographic illustration of the nine sampling sites along the Intra Coastal waterway (Matanzas River) and its tributary, Pellicer Creek alongside an outline of the United States of America showing its geographical location. Sample site names and abbreviations can be found in Supplementary Information (Table SIII). (Google, 2020).

were not collected for the PECC, MAIN, and the MOPC sites.

### 2.3. PFAS extraction from surface water

Surface water samples were separated into six separate batches (of 12 each) and, prior to extraction, each bottle was allowed to reach room temperature and was subsequently mixed. Solid phase extraction (SPE) was performed, adapted from a procedure described by Robey et al., (2020) using Strata-X-AW cartridges (Polymeric Weak Anion Exchange, 500 mg, 100  $\mu\text{m}$ , 6 cc) purchased from Phenomenex (Torrance, CA, USA). Prior to extraction, each sample was pH-adjusted to 4 using glacial acetic acid and 25  $\mu\text{L}$  of the IS mixture were added into each sample. Samples were then centrifuged for 10 min at 2000 rpm. Prior to SPE, cartridges were conditioned with 4 mL of 0.3% ammonium hydroxide in methanol followed by 3 mL of methanol and 4 mL of ammonium acetate/acetic acid aqueous buffer solution (pH 4). Sample loading was performed using a flow of 1–2 drops per second. Cartridges were then washed with 4 mL of ammonium acetate/acetic acid aqueous buffer and were subsequently dried under vacuum for 5 min. Cartridges were eluted using 4 mL of methanol followed by 4 mL of 0.3% ammonium hydroxide in methanol into 15 mL falcon tubes. Samples were evaporated to complete dryness under a gentle nitrogen stream. The residue was immediately reconstituted with 150  $\mu\text{L}$  of methanol. Each sample bottle with surface water was gravimetrically weighed before and after water removal to obtain a total amount of water extracted (in g).

### 2.4. Ultra-high-performance liquid chromatography – tandem mass spectrometry analysis

PFAS measurements were carried out using a Thermo Scientific Vanquish UHPLC coupled to a TSQ Quantis triple quadrupole mass spectrometer. Briefly, chromatographic separation was achieved using a Gemini C18 column (100 mm  $\times$  2 mm; 3  $\mu\text{m}$  particle size) from Phenomenex (Torrance, CA, USA). The UHPLC was fitted with a Vanquish PFAS Replacement Kit, among which included an Acclaim 120 C18 (2.1  $\times$  50 mm, 5  $\mu\text{m}$ , 120  $\text{\AA}$ ) as a delay column and UHPLC PFAS-free plumbing and hardware to minimize PFAS background. Water [A] and methanol [B], both containing 5 mM ammonium acetate, were used as the mobile phases. The gradient elution was set as follows: 0–3 min 10% B, 3–4.5 min 10–35% B, 4.5–12.5 min 35–95% B, 12.5–12.51 min 95–99% B, 12.51–19 min 99% and then equilibrated back to initial

conditions in 30 min. The autosampler temperature was set to 4  $^{\circ}\text{C}$  and the flow rate and injection volume were 0.5  $\text{mL min}^{-1}$  and 10  $\mu\text{L}$ , respectively. Mass spectra were acquired in selected reaction monitoring mode (SRM) in negative polarity with the following parameters: ion spray voltage  $-1500\text{ V}$  and sheath and auxiliary gas set to 50 and 10 arb, respectively. Ion transfer tube temperature was set at 250  $^{\circ}\text{C}$  while the vaporizer temperature was set to 550  $^{\circ}\text{C}$ . Table SIII shows all PFAS transitions and additional parameters used for these experiments.

### 2.5. Quality assurance and quality control

The performance of the PFAS workflow was evaluated using quality control (QC) samples (extracted and processed alongside the surface water samples). QC samples were assessed by examining the experimentally derived concentration (and relative error) of Optima grade water spiked with a known concentration (Ck) of native PFAS and comparing the obtained concentration to the theoretical spiked concentration (Cs). IS were spiked into all samples prior to extraction to correct for losses during sample preparation.

Three different PFAS concentrations were performed in triplicate: low (0.35  $\text{ng L}^{-1}$ ), medium (1.7  $\text{ng L}^{-1}$ ) and high (3.5  $\text{ng L}^{-1}$ ) to ensure proper quantitation by mass spectrometry. Precision was determined by calculating the relative standard deviation (RSD) for the QC tests. Each extraction batch (of 12) contained at least one blank and one QC sample. The data used in this study consisted of PFAS that were quantified within the acceptable accuracy (relative error  $<20\%$ ). Method detection and quantification limits were defined as the minimum concentration which achieved a signal-to-noise ratio of 3 and 10, respectively, and the linearity was evaluated by linear regression without weighting. Calibration standards, QC samples, and blanks samples were measured randomly throughout the mass spectrometry sequence. Solvent blanks were included in the mass spectrometry sequence after each sample analyzed to check for any background and/or carryover. Quality assurance was performed by analyzing solvents blanks in triplicate before starting the batch to verify the conditions of the instrument prior to analysis.

Data acquisition and peak integration were performed using Xcalibur v.4.1 software (Thermo Fisher Scientific). SRM transitions were used to detect and quantify PFAS, with the most intense transition used to quantify the compounds while the second transition was used to confirm identification (if applicable). For those PFAS with no respective labeled standard, an alternative internal standard was chosen based on

structural and/or retention time similarity. A total sum of isomers is presented for PFHxS and PFOS (as  $\Sigma$ PFHxS and  $\Sigma$ PFOS, respectively), as these compounds were monitored as isomeric mixtures (Supplementary Information, Table SI).

### 3. Results and discussion

#### 3.1. QA/QC results

Quality assurance was performed prior to analysis to verify the ability of the instrument to measure the target compounds. Solvent blanks in triplicate were performed and after a clean background, the instrument was qualified to run the samples. A comprehensive overview of PFAS concentrations in each collected water sample can be found in the Supplementary Information (Table SIV). Table SV summarizes the accuracy (as relative errors (%)), precision (as relative standard

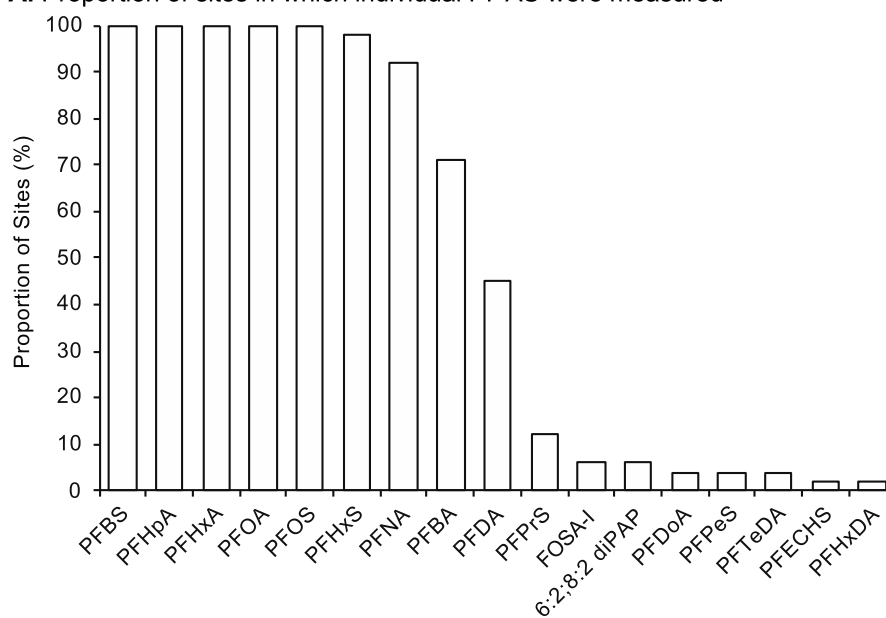
deviation, RSD (%)), limit of detection (LOD) and limit of quantification (LOQ) values of all observed analytes observed in all surface water samples. Linearity was greater than 0.99 for all PFAS measured.

#### 3.2. PFAS water concentrations

Among the 51 PFAS monitored, 23 were detected and 17 were quantified at least once across all forty-nine surface water samples collected (six were below our limits of quantitation). Perfluoroundecanoic acid (PFUnDA), perfluoroheptane sulfonic acid (PFHpS), perfluorodecane sulfonic acid (PFDS), N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA), 4:2 fluorotelomer sulfonate (4:2FTS) and 11-chloroeicosfluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS) were not quantified in any sample.

Perfluorooctane sulfonic acid (PFOS), one of the most discussed and studied PFAS, was expected to be detected across all sites due to its

#### A. Proportion of sites in which individual PFAS were measured



#### B. Mean concentrations of PFAS across all sampling sites

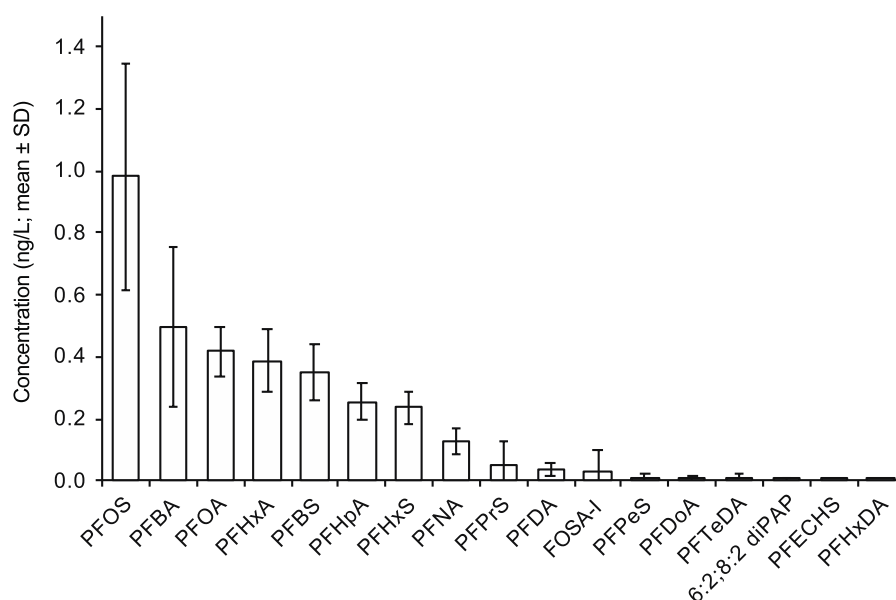


Fig. 2. A. Frequency of quantification of individual PFAS species across all sites, B. Mean concentrations for each quantified PFAS compound ( $\text{ng L}^{-1}$ ) across all surface water samples (mean  $\pm$  standard deviation).



ubiquitous nature (Ng et al., 2019; Elmoznino et al., 2018). The data showed that PFOS, perfluorobutane sulfonic acid (PFBS), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA) and PFOA were detected and quantified across all 49 collected surface water samples. Out of the five PFAS that were present in every single sample, PFOS was the most abundant at every site and day of sample collection. A reasonable explanation for this could be the use of PFOS and PFOA in a variety of products such as food packaging, metal plating, paints and much more that have been accumulating in the environment for decades (Schneider et al., 2017). Additionally, some PFAS have been shown to break down into PFOS and PFOA over time, which cannot be broken down any further (Xiao, 2017). Compounds, such as these, may contribute to the total PFOS and PFOA concentration and can possibly explain why PFOS has a higher concentration across all sample collections and sites. Various long-chain PFAS, specifically PFCAs, have also been shown to convert into short-chain PFAS over time, which may also be a contributing factor to PFAS levels within the area (Bentel et al., 2019). However, additional research is required to better understand the formation of PFOS and PFOA from their respective precursor compounds in the natural environment.

However, as shown in Fig. 2, the most frequently detected PFAS were not always the most abundant. For example, perfluorobutanoic acid (PFBA) was only quantified in 71% of the samples and was the analyte with the second highest concentration across all samples collected ( $0.50 \pm 0.52 \text{ ng L}^{-1}$ ). Additionally, PFNA was quantified in 92% of samples and had the eighth highest concentration across all samples collected ( $0.13 \pm 0.08 \text{ ng L}^{-1}$ ). Four out of the five analytes that were present in all samples, PFOA, PFHxA, PFBS and PFHpA, had the third, fourth, fifth and sixth highest total concentrations respectively across all samples.

Previous work in coastal Florida has found that hurricanes can cause elevated levels of turbidity and fluorescent dissolved organic matter as a result of high precipitation and elevated wind speeds (Schafer et al., 2020). It was predicted that PFAS levels would also increase during a hurricane, and that the northern (more populated) region of the Intra-coastal would have higher surface water PFAS levels in all sampling collections as compared with the southern (less anthropogenic) sites. Our data supports some of these observations, as two of the northern sites (AICC, WWTP) appeared to have higher PFAS levels as compared with southern sites (FL206, MALA), as shown in Fig. 3.

The AICC site had the highest concentration of PFAS per sample both with and without the storm samples included, while the southernmost sites had lower levels in comparison with the exception of the WLDO site, which had a mean concentration of ( $3.76 \pm 2.44 \text{ ng.L}^{-1}$ ) when storm samples were included. The AICC site had higher mean

concentrations of PFAS (total sums) than the MALA site by factors of 1.56 (exclusion of storm samples;  $p > 0.05$ ) and 1.41 (inclusion of storm samples,  $p > 0.05$ ). When comparing PFAS concentrations within sites, with and without the inclusion of storm samples, levels between all sites showed similar trends. However, when hurricane samples were omitted, the WLDO and FL206 sites both showed lower concentrations; these differences did not reach statistical significance (Fig. 3;  $p > 0.05$  for all). It is necessary to note that the changes in PFAS concentrations in FL206 and WLDO, when comparing the inclusion and exclusion of storm samples are mostly attributed to PFOS. Overall, these findings support previous findings on the impacts of urban development and increased population on environmental pollution observed on the Southeastern coast of Florida, where urban expansion has been a major contributor to algal blooms and pollution from farming byproducts (Finkl and Charlier, 2003).

The St. Johns County GIS Division used 2010 U.S. Census data and found that population density was 4–8 people per acre on the northernmost sites, WWTP, AICC and MDPT, and 0 to 0.5 people per acre in the Southernmost sites, MOPC, MALA, PECC, and WLDO (St. Johns County Government, 2013) The St. Johns County GIS Division also found that economic interests were mostly either residential or industrial around the northernmost sites and parks and conservation areas around the southernmost sites (St. Johns County Government, 2016) These differences in anthropogenic activities could be a possible explanation as to why some northernmost sites had higher PFAS levels compared to the southernmost sites. The southernmost sites may have experienced particularly substantial mixing of waters from the storm, as the Pellicer Creek, Matanzas River and the surrounding ocean all flow into these southern sites from different directions. This pattern of enhanced mixing and transport of waters likely explains the lower levels of PFAS – via export through the Intracoastal canal to coastal waters.

Perfluoroalkyl carboxylic acids and sulfonic acids had the highest mean concentrations across all sites (Fig. S1). High levels of PFCA and PFSA compounds could be a result of the close proximity to local neighborhoods on the east and west sides of the Matanzas River, as well as the Anastasia Island Country Club – where pesticides are likely used. Pesticides have been shown to contain PFAS and sometimes degrade into other PFAS, such as PFOS, and can act as possible sources for PFAS exposure at the AICC site (Nascimento et al., 2018). Pesticides have also been observed in wastewater treatment plant effluent which could explain the high levels of PFAS in the sites in close proximity of the St. Augustine Wastewater Treatment Plant (Ng et al., 2019). PFOS was the greatest contributor to the high levels of PFSA across the intracoastal area sites and may arise from the pesticides and wastewater effluent

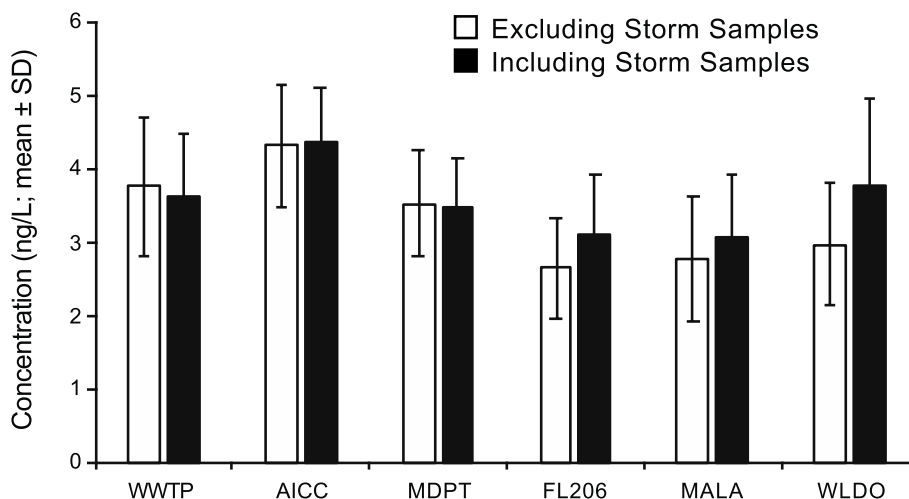


Fig. 3. Mean  $\pm$  standard deviation concentration of PFAS ( $\text{ng.L}^{-1}$ ) at each sampling site from the most northern to the southern sampling site. Samples were not collected from the MAIN, MOPC and PECC sites during the storm and were thus excluded from this figure.

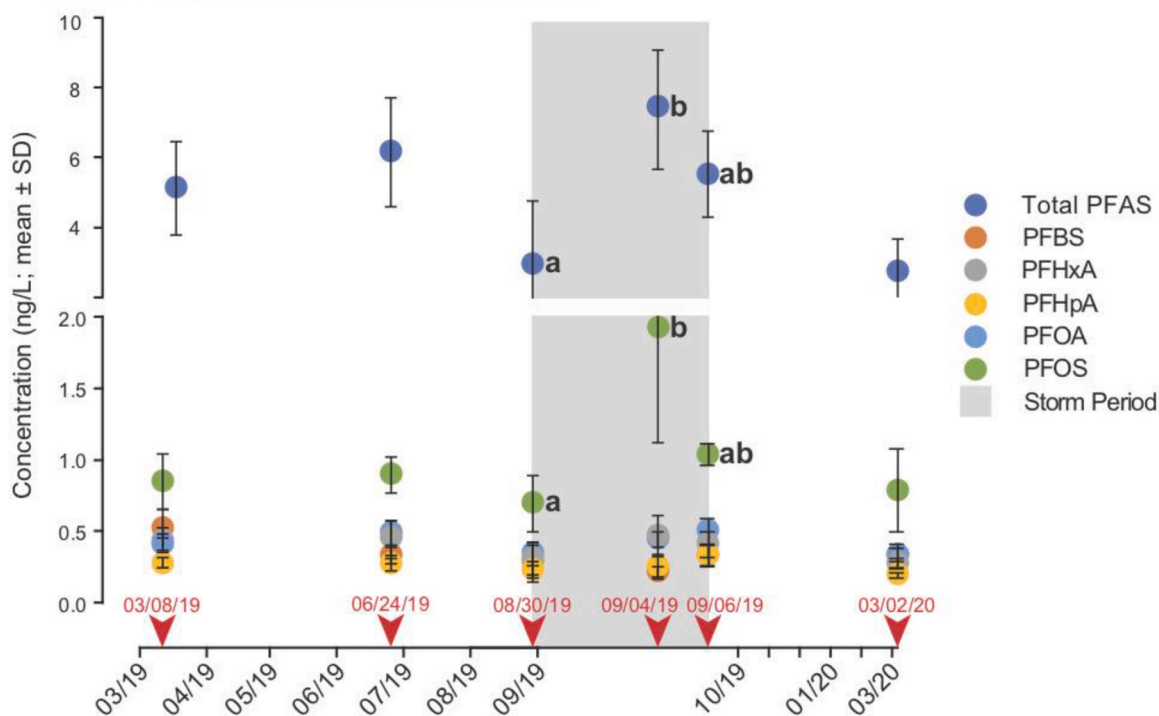
used throughout the intracoastal area.

PAP compounds were found in low concentrations in the northernmost sites (WWTP, AICC, MDPT), while sulfonamides and “other” compounds, which accounted for less than 1% of PFAS across all samples, were measured in both northern (WWTP, AICC) and southern (PECR) sites. One PAP compound (6:2 fluorotelomer phosphate diester (6:2diPAP)) and one FTS compound (6:2 fluorotelomer sulfonate (6:2FTS)) were quantified in some of the sites (Supplementary Table SIV). However, due to low accuracy in the measurement of these

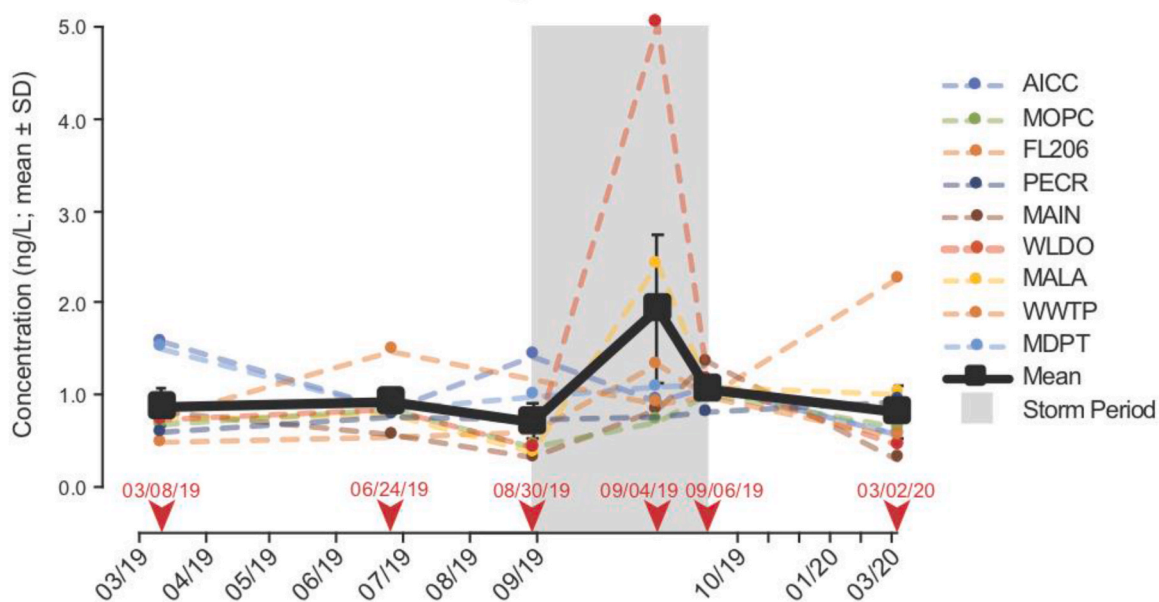
two compounds, they were excluded from the results displayed here.

While PFAS levels showed high variability between sampling sites, mean PFAS concentrations (composite of all sites) changed considerably from before to during the storm. Statistically significant differences were observed between the sums of total PFAS concentrations before and during the storm (Fig. 4A). Levels peaked from the August 30th, 2019 sampling date (before storm;  $2.47 \pm 1.82 \text{ ng.L}^{-1}$ ) with an 89% increase for the September 4th, 2019 collection date (during the storm;  $4.69 \pm 1.70 \text{ p} < 0.05$ ). Mean PFAS concentration levels on September 6th, 2019,

**A. Concentrations of total PFAS and selected compounds across all sampling sites before, during and after Hurricane Dorian**



**B. PFOS levels at individual sites throughout Hurricane Dorian**



**Fig. 4.** A. Mean concentration of total PFAS as well as selected species over the six collection dates. B. PFOS levels at individual sites (single sample replicates) and overall PFOS mean throughout the storm. Different letters (in panel A) indicate statistically significant differences following one-way analysis of variance with Tukey HSD post-hoc test, statistical significance was inferred at  $p < 0.05$ .

two days after the storm, had decreased by 19% ( $3.76 \pm 1.23 \text{ ng.L}^{-1}$ ,  $p > 0.05$ ). On the final collection in March 2020, mean PFAS concentrations ( $2.36 \pm 0.96 \text{ ng.L}^{-1}$ ) were lower than the levels found a year prior in March of 2019 ( $3.56 \pm 1.33 \text{ ng.L}^{-1}$ ). Similar trends were observed throughout the storm for PFOS as what was observed for total PFAS concentrations (PFOS was the main driver for total PFAS increases). More specifically, PFOS concentrations increased significantly during the storm (+176%,  $p < 0.05$ ) and decreased after the storm (-46%); however, this decrease was not statistically significant. Differences in the levels of PFBS, PFHxA, PFHpA and PFOA before, during and after the storm did not reach statistical significance ( $p > 0.05$  for all).

Marked differences in PFAS concentrations were found when comparing the total PFAS levels before and during the storm. This shows that the storm had a significant impact on PFAS concentration levels, that were largely driven by PFOS, and increased the concentration of PFAS in the surface water between these two sets of dates. However, the National Estuarine Research Reserve System measured precipitation levels on August 30th, the sample collection date before the storm and on September 6th, the sample collection after the storm, and found that it had rained 46.0 mm before the storm and 10.7 mm after (Natural Estuarine Research Reserve System, n.d.). The high level of rain before the storm likely diluted surface waters, which may explain the lower PFAS levels compared to after the storm (Fig. 4). Other possible explanations could be associated from the export of PFAS in mixed waters during high conditions in the storm. The strong affinities of PFAS for water allows for a broad spectrum of hydrological pathway mechanisms, such as fluvial transport to street runoff. PFAS can also be transported through sorption via clouds and rain droplets (Moskeland, 2010; Arp and Goss, 2009; Goss and Arp, 2009). All these factors, particularly during high wind and rainfall perturbation events like hurricanes, likely contributed to import and export patterns observed in PFAS concentrations during Hurricane Dorian. While PFAS are particle reactive, much of the organic matter being transferred was likely dominated by dissolved organic matter (high in humic materials and colloids), since much of this region is fed by black water streams (Schafer et al., 2020). This may have also impacted the partitioning coefficients of PFAS between particle and dissolved phase since the fate of contaminants have long been known to impact partitioning coefficients (Kogel-Knabner and Totsche, 1998). Although these factors may influence most PFAS, the observed influx of PFOS specifically in this intracoastal area may be due to the fact that there are typically higher concentrations of PFOS compared to any other compound in this area. Although this significant difference was found between these two sets of dates, it is evident that there are many factors that may influence changes in PFAS concentrations in the St. Augustine Intracoastal Waterway and more research on storm events (with a higher frequency of sample collections during the storm) must be conducted to better understand the impact that storm events have on coastal areas.

PFOS was the dominant contributor to the increase of PFAS concentrations during the storm on the September 4th, 2019 collection. Across multiple sites, these compounds showed a large increase from the August 2019 collection, before the storm, to the September 4th, 2019 collection, during the storm, particularly in the WLDO and MALA sites. Possible explanations could be the disruption of water by heavy winds and rain that transport contaminants to the area, as mobilization of organic matter from soils and wetlands in this region is significant during storm events (Schafer et al., 2020). On the other hand, due to the high levels of rain that took place before the storm, PFAS contaminant levels may have been diluted and then become more concentrated as the rainwater dried up in the soil or moved to other areas, leaving behind high concentrations during the storm (Natural Estuarine Research Reserve System, n.d.). During the storm, PFAS can be easily transported into the closest surface water. However, when natural conditions were reestablished, it was observed that PFAS concentrations decreased by 19%. Reasonable explanations could also be related to PFAS that comes from population, industry, and tourism that may take longer to reach the

surface water than they would without the movement of the storm. PFAS can remain on streets and could be introduced into surface water gradually. Another possible explanation is that, during the storm, the ocean surge increases and then decreases, after the storm. This can reduce PFAS concentrations as the surge goes down and transports PFAS contaminants back into the ocean and away from the rivers and creeks observed in this study. However, similar trends were observed in the sum of total PFAS throughout the storm period even when these compounds were included (Supplementary Fig. SIII). All other PFAS species that were detected in at least 70% of all sites (PFBA, PFBS, PFHxA, PFHxS, PFHpA, PFOA and PFNA) were also examined individually at each site throughout the storm (Supplementary Fig. SIII). PFNA was the only other compound that, in addition to PFOS, showed a spike at the WLDO and MALA sites during the storm. Additionally, due to increased populations in the summer months, it was expected that PFAS levels would be higher in the June (2019) sample collection as compared with the other sample collections in other times of the year which was reflected in the data as the June sample collection had the second highest total PFAS level of any day of sample collection (Fig. SIII).

#### 4. Conclusions

This study provides the first analysis on the distribution of various PFAS throughout the St. Augustine Intracoastal along with observations of PFAS levels before, during and after a hurricane. This study observed a considerable increase of PFOS during the 2019 Hurricane Dorian while other PFAS had little to no changes in concentration in comparison. Higher levels of PFAS were observed on the more densely populated northern region of the intracoastal waterway, while lower concentrations were observed on the less-populated southern sites. The higher PFAS levels in the northern sites can be mostly attributed to the higher concentrations of PFOS. Throughout the six sampling dates, PFAS concentrations showed a large increase during Hurricane Dorian and returned back to their baseline levels two days after the storm. Statistically significant differences were only found between the PFAS concentrations before and during the storm. PFOS was the largest contributor to the increase in mean PFAS levels during the storm as compared with the other analytes; these showed little changes in concentration throughout all six sampling collections. Our findings suggest that more work is necessary to further our understanding of the impact of storm events on PFAS mobilization, specifically for PFOS. Previous work has suggested that soils and sediments may serve as a reservoir and long-term source for PFAS. Here, we posit that high concentrations of PFAS during the storm may have been exported from adjacent terrestrial systems, highlighting the need to further investigate relationships between PFAS mobilization driven by precipitation from episodic events, resulting in runoff from terrestrial to aquatic systems.

The St. Augustine Intracoastal is home to many people and ecosystems that depend on the area to maintain their way of life. However, the threat of PFAS exposure puts many at risk due to the adverse effects of these ubiquitous compounds. Continued monitoring and modeling of the impact of large (episodic) weather events, at sites like St. Augustine, will help inform the impact of these events along other coastal communities. Further investigations into monitoring changes in PFAS levels over time, coupled with in-depth investigations into specific sources (e.g., anthropogenic gradients), will help develop a better understanding of PFAS hotspots, mobilization, and transport in coastal systems. The movement and behavior of PFAS in coastal areas in normal and storm conditions is an important topic for all coastal communities. PFOS, in particular, requires continued attention to determine if the same influx is observed during other storm events in other intracoastal areas and specifically, if there is something about its chemical/physical properties that may promote this behavior. As more is understood about the impact episodic weather events have on coastlines, from both a monitoring and human/environmental health standpoint, more optimal preventative or post-clean actions can be developed. From this, as more is understood of

the behavior of PFAS in different conditions and more is discovered of the specific risks of PFAS exposure, we aim to create preventative actions to mitigate its exposure and impact on coastal communities.

### Credit author statement

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### Declaration of competing interest

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

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### Appendix A. Supplementary data

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