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## Per- and polyfluoroalkyl substances (PFAS) in sediments collected from the Pensacola Bay System watershed

Atiye Ahmadireskety<sup>a</sup>, Bianca F. Da Silva<sup>b</sup>, Jill A. Awkerman<sup>c</sup>, Joe Aufmuth<sup>d</sup>, Richard A. Yost<sup>a</sup>, John A. Bowden<sup>\*,a,b</sup>

<sup>a</sup>Chemistry Department, University of Florida, Gainesville, Florida, USA

<sup>b</sup>College of Veterinary Medicine, Department of Physiological Sciences, University of Florida, Gainesville, Florida, USA

<sup>c</sup>Gulf Ecosystem Measurement & Modeling Division, US Environmental Protection Agency, Gulf Breeze, Florida, USA

<sup>d</sup>George A. Smathers Libraries, University of Florida, Gainesville, Florida, USA

### Abstract

Sediment samples from 25 locations in the Pensacola Bay System (PBS) watershed were analyzed for the presence of 51 per- and polyfluoroalkyl substances (PFAS) using ultra high-performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) and selected reaction monitoring. Results revealed quantifiable concentrations of PFAS in all sampling locations. More specifically, perfluorobutanoic acid (PFBA) was present in every sediment sample with a minimum and maximum concentration of 0.04 to 0.48 ng g<sup>-1</sup> dry weight, respectively, across the 25 sites with an average of 0.1 ± 0.09 ng g<sup>-1</sup>. While PFOS, with an average of 0.11 ± 0.14 ng g<sup>-1</sup> (range: <LOQ – 0.52 ng g<sup>-1</sup>) was the most abundant by concentration. LOQ of PFBA and PFOS were 0.01 ng g<sup>-1</sup> and 0.1 ng g<sup>-1</sup>, respectively. PBS 22 site had the highest concentration of total (ΣPFAS) PFAS with 3.89 ng g<sup>-1</sup> and the third highest number of PFAS were detected in this location (23 out of 51 PFAS monitored). These results could be due to the proximity of this site to a paper manufacturing company. Site PBS 21, which is close to the Pensacola International Airport (PNS), had the second highest concentration of PFAS with 1.68 ng g<sup>-1</sup>. Comparison between the ΣPFAS concentration present in sediments collected in July 2020 and sediments collected from nine repeat sites after Hurricane Sally (HS, September 2020), showed values, on average, 47% lower. These results highlight that the PBS area require further environmental monitoring and management of PFAS.

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\*Corresponding author at: College of Veterinary Medicine, University of Florida, 1333 Center Drive, Gainesville, FL 32610, USA, john.bowden@ufl.edu (J.A. Bowden).

#### 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.

#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envadv.2021.100088.

## Keywords

Per- and polyfluoroalkyl substances (PFAS); Sediment; Pensacola Bay System; UHPLC-MS/MS; Storm events

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## 1. Introduction

The Pensacola Bay System (PBS: ~18,000 km<sup>2</sup>) is the fourth largest estuary in Florida, with approximately 34% of the watershed falling within northwest Florida and the remainder in Alabama. Pensacola Bay receives freshwater input from the Escambia (71%), Blackwater (4%), and Yellow (26%) rivers and comprises a series of interconnected estuaries including Blackwater Bay, East Bay, Escambia Bay, Pensacola Bay and Santa Rosa Sound (Thorpe et al., 1997; U. S. EPA, 2017). The state of Florida Department of Environmental Protection (FDEP) notes that the PBS is a widely used location for recreational and commercial activities, including fishing, industrial and port operations, and an active military presence (which includes, among other things, flight training) (U. S. EPA, 2004a). In addition, the estuarine area serves as an important habitat for wildlife such as fish, shellfish, and migratory birds (U. S. EPA, 2004a). Due to the proximity of the anthropogenic activity to the ecosystem, studies exploring the presence and distribution of ubiquitous chemicals, such as per- and polyfluoroalkyl substances (PFAS), need to be performed in a variety of biotic and abiotic media to investigate the potential impact of exposure in the system.

PFAS consist of hydrophobic C-F chain (the strongest single carbon bond) and hydrophilic functional head groups (Buck et al., 2011). Due to their exceptional physical and chemical properties, PFAS have been produced and utilized in vast quantities in consumer products and industrial applications since the 1950s (Cousins et al., 2016). In contrast to other organic pollutants, the sorptive behavior of PFAS to sediment is not only dependent on hydrophobicity but also governed by electrostatic interactions (Higgins and Luthy, 2007; Lampert, 2018).

Sediments are a crucial element of aquatic environments that have a vital role to the health of organisms and ecosystems. Throughout their lives, many organisms live in, ingest or frequently come into contact with sediments (Kennicutt, 2017). Moreover, sediments are sinks, which can be released back into the water during destructive events, like storms. Sediments exposed to anthropogenic contaminants have the potential to adversely affect the health of organisms and ecosystems. Sediment pollution and their role with environmental health are well-documented (Kimbrough et al., 2008; Lewis et al., 2016; Owens et al., 2005; Russell et al., 2017; U. S. EPA, 2004b). The first extensive study on sediment quality in the PBS area (Debusk and Box, 2002), was carried out for monitoring polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heavy metals, and pesticides. Mohrherr et al. have also reported the screening of the same pollutants (PAHs, PCBs, heavy metals, and pesticides) in sediment from Escambia Bay, Pensacola, Florida (Mohrherr et al., 2009). In another study, Lewis et al. (Lewis et al., 2016) reported the trace metals, PCBs, dioxins, chlorinated pesticides as well as PAHs in sediments collected from the PBS. The total concentration of PCBs and PAHs in the Lewis et al. study was reported to be higher

than the threshold effect level (TEL) guidelines (TEL guideline values were 21.6 ng g<sup>-1</sup> for PCB and 1684 ng g<sup>-1</sup> for PAH) (Lewis et al., 2016). Moreover, some of the contaminated sites in the Pensacola area previously manufactured treated wood, agrichemicals, oil products, or were disposal sites for waste and sludge and were assigned as Superfund sites by the U.S. EPA (U.S. EPA, 2004a; EPA, 1998). These anthropogenic chemicals have been reported to enter the PBS from a variety of sources including the atmosphere, groundwater, tributaries, municipal and industrial wastewaters, urban stormwater runoff, and residential use of pesticides and fertilizers (Debusk and Box, 2002; Lewis et al., 2016). There are also inputs of sediments and nutrients into Escambia Bay from upstream agricultural and forestry activities and unpaved surface roads (U. S. EPA, 2004b). History of high levels of anthropogenic pollution in the PBS is one reason to explore the levels of PFAS in this area.

Sediments have also been reported as reservoirs for other classes of anthropogenic pollutants such as PFAS (Bai and Son, 2021; Higgins et al., 2005; Lampert, 2018; Mussabek et al., 2019; Wang et al., 2019; Zhu et al., 2014). One primary source of PFAS release into the environment is through the use of aqueous film forming foams (AFFFs), which have been heavily used at airports and military bases (e.g., Naval Air Station in Pensacola) (Cui et al., 2020; Houtz et al., 2013; Mussabek et al., 2019). Other potential sources of PFAS include industrial and municipal discharges, wastewater treatment plants, agricultural runoff, and accidental spills (Kennicutt, 2017). Data from the Environmental Working Group (EWG)'s data base shows multiple military sites in the PBS that have PFAS contaminated ground water and drinking water (presumed to be from AFFF use) (EWG, 2021). The suspected source for many of these sites has been reported to be AFFF (EWG, 2021). A firefighting facility in Pensacola was the subject of a study which was focused on detecting perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (FDEP, 2020). In 2018, a news article also raised questions regarding the drinking water quality in Pensacola (Baucum, 2018), particularly the presence of PFOA and PFOS, which have previously been reported to be present above advisory levels in the Pensacola region's drinking (Baucum, 2018). Occurrence of PFOS, PFOA and perfluorooctane sulfonamide (FOSA) was investigated in 2001 in a variety of matrices, such as sediment, in a multi-city study, which included Pensacola, where a carpet manufacturer served as a source of fluorochemical products (3M, 2001). PFOA and FOSA were not detected in Pensacola sediment samples in this multi-city study; however, PFOS was measured ranging from not detected to 0.41 ng g<sup>-1</sup> (3M, 2001). Despite a history of PFAS burden in the PBS, there is limited information to date regarding PFAS levels and sites of concern (3M, 2001; Cui et al., 2020; FDEP, 2020). However, in response to growing concerns about PFAS contamination in Florida, the FDEP has recently released provisional Soil Cleanup Target Levels for direct human exposure pathway thresholds for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) of 1,300 ng g<sup>-1</sup> and 25,000 ng g<sup>-1</sup> for residential and commercial/ industrial applications, respectively, and a contamination of groundwater pathway threshold (leachability) of 2 ng g<sup>-1</sup> and 7 ng g<sup>-1</sup> for PFOA and PFOS, respectively (Stuchal and Roberts, 2019).

In this study, we performed a systematic evaluation of PFAS sediment burden within the PBS and surrounding areas. The main goal of this study was to provide baseline levels for a wide variety of PFAS over a wide geographic range within the PBS and to identify PFAS

hotspots in the region for more in-depth prospective studies. Moreover, we also present preliminary findings as to the potential impact of large episodic weather events on the fate and transport of PFAS in sediments within the PBS, both of which require more scientific attention. Sediment in this study were monitored for 51 PFAS, using the methodology described by Ahmadireskety et al. (Ahmadireskety et al., 2021), at three separate time periods, February 2020 (n= 8), July 2020 (n=17), and after Hurricane Sally (HS, September 2020) at nine overlapping sites (with July 2020).

## 2. Material and methods

### 2.1. Standards and reagents

Water, methanol, ammonium hydroxide, and ammonium acetate (all Optima grade), were purchased from Fisher Scientific (Waltham, MA, USA). Supelco ENVI-Carb (120–400 mesh) was purchased from Supelco (Sigma-Aldrich, Bellefonte, PA, USA). All PFAS standards, including the 51 non-labeled (native mixture of PFAC-24PAR and several individual standards) and 23 isotopically labeled analogs (internal standard (IS) mixture; MPFAC-24ES and several individual standards), were purchased from Wellington Laboratories Inc (Guelph, ON, Canada). Further details on the nomenclature of PFAS standards and their spiked concentrations in samples and calibration solutions can be found in the supplementary material Table S1 and Table S2, respectively.

### 2.2. Sediment samples

Sample sites were selected throughout Pensacola and Perdido Bays to include tributary input locations and potential sources of PFAS while covering a broad distribution of the estuaries. Thirty-four sediment samples were analyzed in this study. Eight (out of 34) of the sediment samples were collected in February 2020 using a mini-ponar dredge (PBS 8 and PBS 19–25), while 17 sediment samples were collected from additional coastal locations in July 2020 using a stainless steel scoop (PBS 1–7, PBS 9–18). After HS (September 2020), we resampled nine of the original July 2020 sites, denoted as PBS HS# throughout the manuscript (for more details about the sampling locations, see Table S3 and Fig. S1). Several sites visited in July were flooded post-hurricane, which precluded collection of a comparable sample without boat availability. This might have inadvertently biased post-hurricane collections to sites with better drainage. Samples were collected from adjacent riverine and estuarine areas including the East, Escambia, Pensacola, and Blackwater Bays (Fig. S1) in the PBS. High Density Polyethylene (HDPE) containers (1 L) were used for sediment collection and were stored on ice during transport to the laboratory, whereby they were stored at  $-20^{\circ}\text{C}$  until analysis. Before starting the extraction, sub- aliquots of the sediments were thawed at room temperature and air dried. Three analytical replicates for each sample were extracted for PFAS analysis.

Table S4 summarizes pH of the sediment samples which were measured based on EPA method 9045D (U.S. EPA, 2004b). The American Society for Testing and Materials (ASTM) method D2974 was used to find the moisture content and organic matter (Table S4) (ASTM, 2014).

### 2.3. Sample preparation and extraction workflow

Gravimetrically weighed ( $5.0 \pm 0.1$  g) dried sediments were placed into 50 mL polypropylene centrifuge tubes and spiked with a 40  $\mu$ L IS mixture of isotopically labeled PFAS (for details on concentration of each IS see Table S1). Samples were then extracted using Method 1B (methanolic ammonium hydroxide was used as the extraction solvent, and ENVI-Carb was used for cleanup) as described by Ahmadireskety et al. (Ahmadireskety et al., 2021). A weight of  $5.0 \pm 0.1$  g of the Standard Reference Material (SRM) 1944 (New York/New Jersey Waterway Sediment) from the National Institute of Standard and Technology (NIST), was also extracted with the same method noted above.

To evaluate the method performance,  $5.0 \pm 0.1$  g of air-dried sediments from each site were mixed to make a pooled sample in a PFAS free container and were manually mixed for 2 min. Pooled samples ( $n=3$ ) were extracted for matrix effects, recovery and accuracy studies.

### 2.4. Instrumental analysis

PFAS analysis was performed using a Thermo Scientific Vanquish ultra-high-performance liquid chromatograph coupled to a TSQ Quantis triple quadrupole mass spectrometer (UHPLC-MS/MS, Thermo Scientific, San Jose, CA, USA). Details on the instrumental analysis used in the present study are provided in the supporting information (SI)

### 2.5. Quality control (QC)

Three extraction (method) blanks were prepared (all extraction, cleanup, and reconstitution steps were conducted in empty centrifuge tubes) to investigate PFAS contamination or interferences during extraction. One solvent blank (methanol) was run on the UHPLC-MS/MS with every five samples to assess PFAS artifacts and/or carryover. Details on method accuracy, precision as well as extraction recovery and matrix effects are provided in the SI.

### 2.6. Data analysis

Data acquisition and peak integration were performed using Xcalibur v.4.1 software (Thermo Fisher Scientific). For targeted analysis of PFAS via UHPLC-MS/MS, two selected reaction monitoring transitions (if available) were employed for each PFAS, one for quantitation (most intense transition) and one for confirmation. The UHPLC-MS/MS method included 23 isotopically labeled PFAS and 51 non-labeled PFAS. For those native standards which did not have an isotopically labeled analog available, a labeled internal standard closely related by structure or retention time was used (Table S1). Calibration solutions were prepared by successive dilution from three primary stock solutions to generate a total of ten levels and quantitation was achieved via isotope dilution. Ten levels of the calibration curve were randomly run with the samples and were used to calculate the calibration equation for each compound. Table S2 in the supplementary material summarizes the respective concentrations at each level of the calibration curve for both the non-labeled and isotopically labeled PFAS. A linear regression model was used to build the calibration equation for each PFAS and the intercept, slope, and correlation coefficient  $R^2$  were calculated. The peak area of each PFAS was normalized to the peak area of each relevant internal standard and the final concentration of each PFAS was normalized to the

dry weight of each sediment sample extracted, thus providing results in units of ng of PFAS per g sediment. Background values in sediment samples correspond to the PFAS measured in the extraction blanks (as described in Section 2.5). PFBA, PFHpA, PFTeDA, and 6:2 FTS were present in the extraction blanks (n=3), although except for PFBA, the other three species were below the instrument's limit of quantification (LOQ). The average concentration of PFBA, in the extraction blanks ( $0.009 \text{ ng g}^{-1}$ ), was around 22% of the lowest concentration quantified in sediment sample ( $0.04 \text{ ng g}^{-1}$ ). For this compound, the final reported concentration in sediments was based on the subtraction of background values. Total sum of isomers is presented for perfluorohexane sulfonic acid (PFHxS) and PFOS (as  $\Sigma$ PFHxS and  $\Sigma$ PFOS, respectively), as these compounds were monitored as isomeric mixtures in the calibration. The instrumental limit of detection (LOD) was defined as the lowest concentration that would yield a visually detectable chromatographic peak with a signal-to-noise ratio  $S/N > 3$ , while the  $S/N > 10$  was used for LOQ. Details on compound specific instrumental LODs and LOQs are provided in the supplementary material (Table S5).

ArcGIS© v17 spatial software made by Environmental Systems Research Institute (ESRI) was used to visualize the sampling locations and PFAS concentration results.

## 2.7. Statistical analysis

One-way analysis of variance (ANOVA) with a Tukey's HSD post-hoc test was used to evaluate significant pairwise differences in PFAS concentrations between all sites. To explore Tukey's HSD post-hoc test PFAS with concentrations below LOQ were replaced by the limit of detection divided by two (LOD/2) (U.S. EPA, 2000). Weight-adjusted data were normalized by median and auto scaling (mean-centered and divided by the standard deviation of each variable). Principal component analysis (PCA) was also used to visually identify trends and to further examine similarities and differences between different sampling locations. All statistical analyses were completed using MetaboAnalyst (Chong et al., 2019). Paired Student's t-test was performed to check the similarity/differences between total PFAS concentrations in before and after storm (HS) samples.  $p$ -values  $< 0.05$  were considered statistically significant in this study.

## 3. Results and discussion

### 3.1. PFAS concentration in sediments collected in February and July 2020

The concentrations of each PFAS determined in the 25 different sites within and around PBS in February and July 2020, are summarized in Supplementary Material (Table S7-S9). The PBS area is in close proximity to many naval and military bases, airports, fire stations, and industrial complexes. AFFFs, as one of the suspected sources of PFAS, have been used in the U.S. military since 1963 (Place and Field, 2012), there are also reports on incorporation of AFFFs in fire training facilities in Pensacola (Cui et al., 2020), while wastewater treatment plants are another source of PFAS (Houde et al., 2006; Hu et al., 2016; Xiao et al., 2012). The sum concentration of PFAS at the individual PBS sites and their distributions are shown in Fig. 1. PBS 22, with a total PFAS ( $\Sigma$ PFAS) concentration of  $3.89 \text{ ng g}^{-1}$ , had approximately 29% of the total PFAS detected in all of the samples collected

from the PBS area, while PBS 21 and PBS 19 showed the second and third highest total PFAS concentration with 12.5% and 8.4%, respectively. PBS 22 is adjacent to Elevenmile creek which is an effluent conduit located near the Perdido River. Twenty-three (out of 51) PFAS were detected in Site PBS 22 (the second highest number of detected PFAS by number of species). N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA), the PFAS with the highest concentration in PBS 22 (33% of the  $\Sigma$ PFAS detected at this site), is commonly used in paper and textile manufacturing and has the potential to be degraded into PFOS (Wen et al., 2018). It should be noted that PBS 22 is in close proximity to paper company activities (Langberg et al., 2021). These findings are also in accordance with a previous study which revealed N-EtFOSAA strongly bind to sediments (Ahrens et al., 2009). PBS 21 is close to two potential sources of PFAS including the Pensacola Fire Department (station #2 and #6) and the Pensacola International Airport (PNS). PBS 21 had the second highest concentration of PFAS ( $1.68 \text{ ng g}^{-1}$ ) with 22 PFAS detected. PFOS was the dominant species at this site, accounting for 31% of total PFAS, which could be related to deployment of AFFF at the facilities close to this site.

A comparison between the distribution of PFAS with various chain lengths in the sediment from the 25 different sites, showed that short- chain PFCAs ( $C < 7$ ) were dominant in 68% of the sites (PBS 1, 2, 4–11, 13, 16–18, 23–25) while long-chain PFAAs (PFSA with  $C \geq 6$  and PFCA with  $C \geq 7$ ) were dominant in the other 32%, which could be explained by the recent shift in industry toward using shorter chain PFAS (Brendel et al., 2018). Perfluorobutanoic acid (PFBA) and PFOS were the two dominant species in the PBS. PFBA, the shortest chain PFAS quantified in this study, was the dominant species (by concentration) in almost 75% of the samples, while PFOS was dominant in the other 25%. Consistent presence of PFBA in sediment samples is remarkable since shorter chain PFAS (such as PFBA) tend to be present in water rather than sediment due to the sediment-water distribution coefficient (Kwadijk et al., 2010). However, previous studies have reported the occurrence of PFBA in Puget Sound, WA (Long et al., 2013), ranging from not detected to  $1.5 \text{ ng g}^{-1}$  and in Las Vegas, NV (Bai and Son, 2021), ranging from not detected to  $2.2 \text{ ng g}^{-1}$ .

Fig. 2 shows the spatial distribution of these two PFAS. Sites with the highest concentrations of PFOS include PBS 3, 20, 21, and 22. PFBA was found with high concentrations in PBS 11, 21, and 22. PBS 3 is close to the Hurlburt Field Air Force Base and PBS 11 is close to the Spencer Naval Outlying Field which is a military airport. Heavy usage of AFFF at these facilities could be the primary contributor of high PFOS and PFBA concentrations. High concentration of PFBA at PBS 22 could be attributed to the paper manufacturing company. The high concentration of PFOS, despite its voluntary phase out, demonstrates its persistence in the environment and that sediments are a sink for these compounds.

### 3.2. PFAS concentration in sediments collected in September after Hurricane Sally

In this study, we also carried out a preliminary investigation of sediment samples collected post Hurricane Sally (HS). The total concentration of PFAS in samples collected from nine sites after HS was  $1.06 \text{ ng g}^{-1}$  (Table S10), while this value for the same sites during the July sampling was  $1.96 \text{ ng g}^{-1}$ . The PFAS levels were 47% lower after the storm. In a study carried out by Martinez et al., during Hurricane Dorian on the east coast of Florida,

an 89% increase in total PFAS levels during the hurricane was reported in surface water (Martinez et al., unpublished results). Interestingly, a numerical model by Hodgkins et al. (2019) was developed to predict PFAS transportation in storm conditions (strong winds and waves), where it was reported that PFAS can travel up to 31 km (19.3 miles) in 48 hr (Hodgkins et al., 2019). Considering these findings, it is possible that sediment laden PFAS might be resuspended or re-introduced into the water column, from sediment, during large episodic storm events. Of the total PFAS quantified in sediments collected after HS, 62.4% PFCA, 37.2% PFSA, and 0.8% PFAA precursors were measured. PFOS was the compound with the highest concentration after HS samples with  $0.30 \text{ ng g}^{-1}$  (78% detection frequency) followed by PFBA ( $0.17 \text{ ng g}^{-1}$ , 100% detection frequency). Fig. 3 shows the spatial distribution bar graph of the total PFAS concentrations of the sediments collected in July 2020 (n=9) and after HS (September 2020, n=9). As can be observed in two (out of 9) sites, higher concentrations of PFAS were measured after HS (PBS 9 and PBS 16). The main contributor for this increase was PFOS. While in the other seven sites, the  $\Sigma$ PFAS decreased between before and after storm (HS) sediments ranging from approximately 9% (PBS 18) to 86% (PBS 11). Without fully established baselines for each sampling site, in combination with a lack of immediately preceding storm samples, the data herein is interesting yet also anecdotal. To have a more definitive answer, future studies need to be performed collecting sediments right before and after hurricane to investigate the explicit impact of large episodic weather events, such as hurricane, on the fate and transport of PFAS.

### 3.3. Statistical analysis of PFAS concentration

A Tukey's post hoc test was conducted using each replicate concentration (n=3) of individual quantified PFAS (n=28) and  $\Sigma$ PFAS at each site for all examined sites (n=25). The obtained results showed a significant difference between the concentration of all these substances, as well as  $\Sigma$ PFAS at different sampling locations ( $p$ -value < 0.05), which could be attributed to the presence of multiple sources in this area including deployment of AFFF at military bases, airports, and firefighting stations, as well as several industrial activities such as carpet and paper manufacturing. Using PCA (Fig. 4), samples from several locations formed distinct clusters, with principal components 1 and 2 accounting for 22.4% and 15.2% of the variance, respectively, suggesting the concentration of PFAS in these locations were significantly different. While some of these sites are close to military bases (PBS 3 and 20), some are adjacent to industrial facilities (PBS 12, 21 and 22). PBS 1, 5, and 15 are close to residential areas while PBS 19 is close to an effluent outflow. A paired t-test was also conducted on  $\Sigma$ PFAS of samples collected from the same locations in July and September 2020. The obtained result showed 6 pairs of samples collected from PBS 9, 11, and 13 to 16 that were significantly different ( $P$ -value < 0.05), which means in these sites, more PFAS re-distributed into the surrounding water columns.

### 3.4. PFAS concentration in SRM 1944

Thirty-six out of the 51 PFAS monitored were detected in SRM 1944 (Table S11), including all thirteen PFCA ( $C_4$ - $C_{14}$ ,  $C_{16}$ ,  $C_{18}$ ), five (out of nine) PFSA ( $C_4$ -  $C_8$ ,  $C_{10}$ ), and thirteen (out of 25) PFAA precursors. The total concentration of PFAS in SRM 1944 was  $11.8 \text{ ng g}^{-1}$ . N-EtFOSAA had the highest concentration in SRM 1944, followed by PFDS,



and diSamPAP. The total concentration of PFCA ( $\Sigma$ PFCA),  $\Sigma$ PFSA, and the total PFAS precursors were 3.26, 2.98, and 5.47 ng g<sup>-1</sup>, respectively.

Although there is no certified values for PFAS in SRM 1944, the measured PFAS concentration in this study were compared to that of an interlaboratory study carried out by NIST (Reiner et al., 2015). The Minnesota Department of Health was a participant in the NIST interlaboratory study and measured seven PFAS, where PFOS had the highest concentration in their SRM 1944 analysis (1.27 ng g<sup>-1</sup>). The Colorado School of Mines measured 16 PFAS in SRM 1944 with N-EtFOSAA as the predominant compound (4.49 ng g<sup>-1</sup>). Here, we detected 33 PFAS, where N-EtFOSAA with 2.99 ng g<sup>-1</sup> had the highest concentration, followed by perfluorodecane sulfonic acid (PFDS) with 1.2 ng g<sup>-1</sup>.

For short chain PFCA (PFBA, PFPeA), the results of this study were closer to the values reported by the Minnesota Department of Health with 0.25, and 0.10 ng g<sup>-1</sup> for PFBA and PFPeA, respectively, in this study versus 0.15, and 0.16 ng g<sup>-1</sup> for PFBA and PFPeA in their report. Although most of the longer chain PFCAs were not measured in the NIST study, PFOA values were very similar between our study (0.86 ng g<sup>-1</sup>) and the Minnesota Department of Health's report (0.84 ng g<sup>-1</sup>), while the measured concentration for PFOS in this study (0.79 ng g<sup>-1</sup>) was less than the value the other two lab reported (1.27, and 1.40 ng g<sup>-1</sup>).

The result of this study along with the NIST interlaboratory study shows the presence of different PFAS from several subclasses in SRM 1944 (Table S11). These findings will help the PFAS community harmonize measurements and improve QC for sediment-based studies.

### 3.5. Comparison of PFAS in sediments with published studies in other US areas

Various studies on the analysis of PFAS in sediments have differed in focus, for instance the main objective of the Higgins et al. study was to develop a method for the detection of anionic PFAS in sediments and sewage sludge (Higgins et al., 2005), while the objective of Long et al. (Long et al., 2013) was to establish a baseline for PFAS detection in Puget Sound sediment.

Twenty-three PFAS were quantified in at least one PBS site, which is comparatively higher than those in other U.S. coastal and urban areas such as Baltimore Harbor, San Francisco Bay (Higgins et al., 2005), and Charleston Harbor Estuary (White et al., 2015) (Table 1). Longer chain PFAS were usually the dominant PFAS and occurred more frequently in different sampling sites within the reported studies, while occurrence of short chain PFAS, such as PFBA, was reported in other studies (Bai and Son, 2021; Long et al., 2013). Compared with the present study, in which 28 PFAS were quantified, in sediment collected from Puget Sound, only 3 (out of 13 monitored) PFAS were present. PFOS was the species with the highest concentration in their study (mean 0.09 ng g<sup>-1</sup>), which according to the authors, could be the result of the proximity of the sampling sites to the Puget Sound Naval Shipyard and Naval Base Kitsap (Long et al., 2013). In sediments collected from estuarine areas of Charleston, SC, higher levels of PFAS were measured compared to other urban US cities. According to the authors, this observation could be the result of sampling close to multiple PFAS hot spots including Charleston Navy Base and several

chemical manufacturing companies. Further, the authors have also connected variation in PFAS concentration in different sampling locations to discharge from sewage treatment plants (White et al., 2015). The samples collected in the PBS area were in close proximity to the Pensacola Air Force Base, Naval Station, several industries such as paper and textile companies, firefighting stations, and wastewater treatment plants. All of these sources are suspected to contribute to the presence of PFAS in the environment (Langberg et al., 2021; Long et al., 2013).

#### 4. Conclusions

This study presented PFAS data in sediments from 25 sites in the Pensacola Bay area, Florida. The results attempted to fill the data gap on PFAS occurrence and distribution in a vulnerable environment which is in close proximity to a diverse combination of recreational, industrial, and military operations. Of the 51 PFAS monitored, 28 were detected in sediments, which included 13 PFCAs, 6 PFSAAs, and 7 precursors. The predominant PFAS detected in PBS sediment were PFOS and PFBA. One- way ANOVA showed significant difference between the quantified PFAS in all 25 different sites ( $p$ -value  $<0.05$ ). PCA analysis showed distinguishable clusters for several sites which could be due to the proximity of these sites to suspected PFAS sources such as, aviation bases, and several manufacturing companies. While different levels of PFAS were found in the PBS, it is not possible at this point to determine their specific sources. Potential sources of PFAS in this area may include, but are not limited to, the military bases, airports, carpet manufacturing, paper manufacturing, agricultural and forestry activities. Additional sampling after HS revealed a 47% lower PFAS concentration level in sediment collected post-storm, which could be the result of the reintroduction of PFAS into the water column under strong wind and wave conditions. Sediments, as a potential reservoir for PFAS, can provide helpful information about contamination history and long-term burden of exposure to PFAS. Moving forward, based on the critical locations found in this study, more sediments samples over longitudinal periods (factoring in episodic weather events) can be collected. Having more data points and studying the effect of seasonal variations and episodic events such as storms and hurricanes will help to better understand and interpret the fate and transport of PFAS. This information will allow monitoring and remediation of sites, that are potentially more hazardous, in order to efficiently allocate resources to minimize the risk.

#### Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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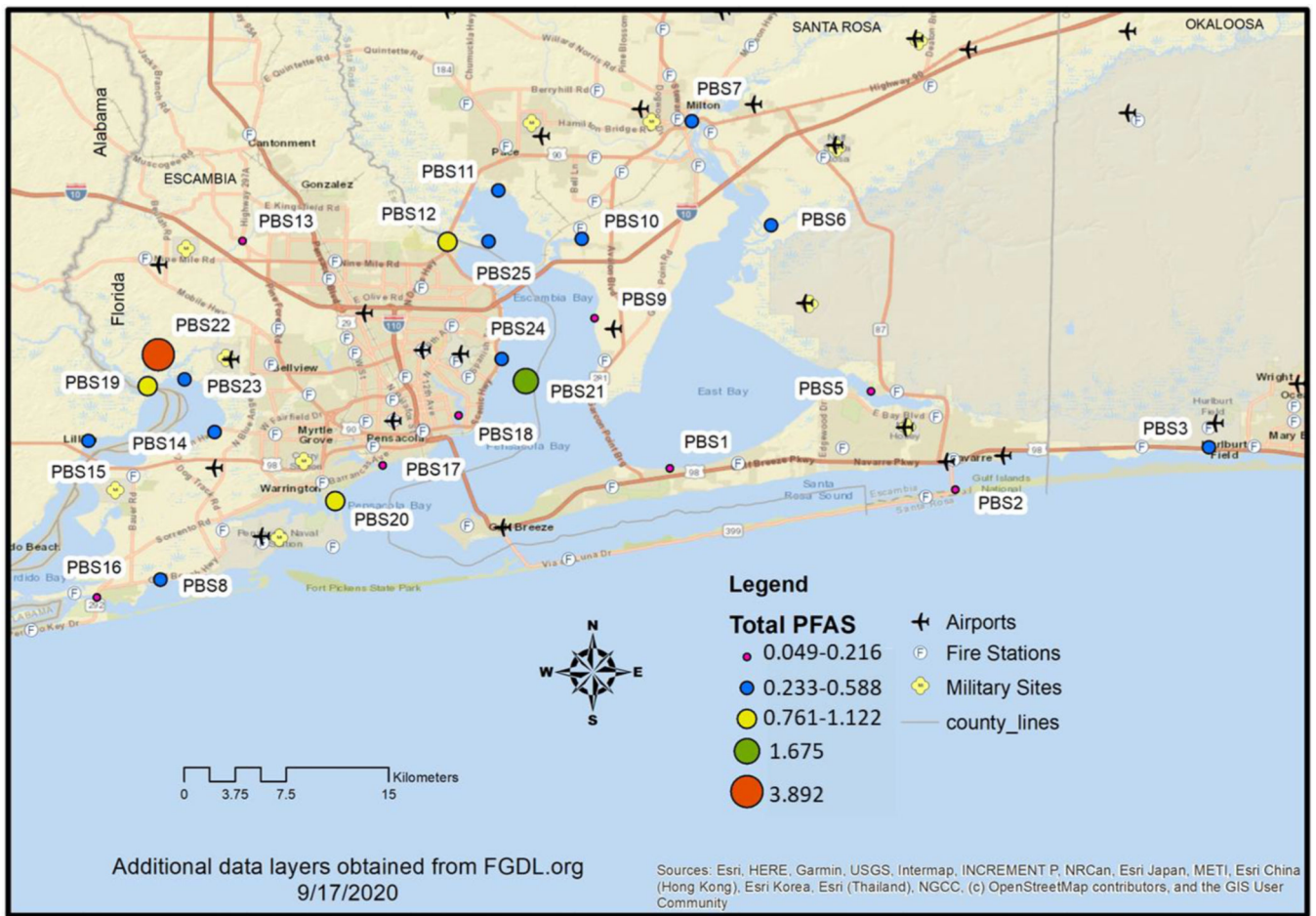
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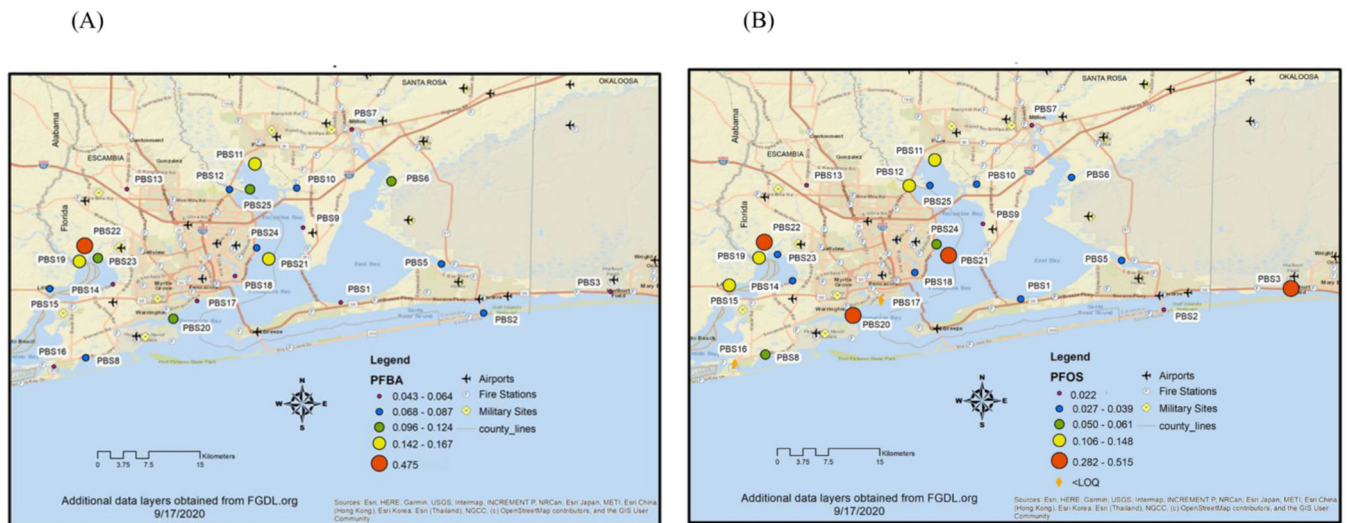
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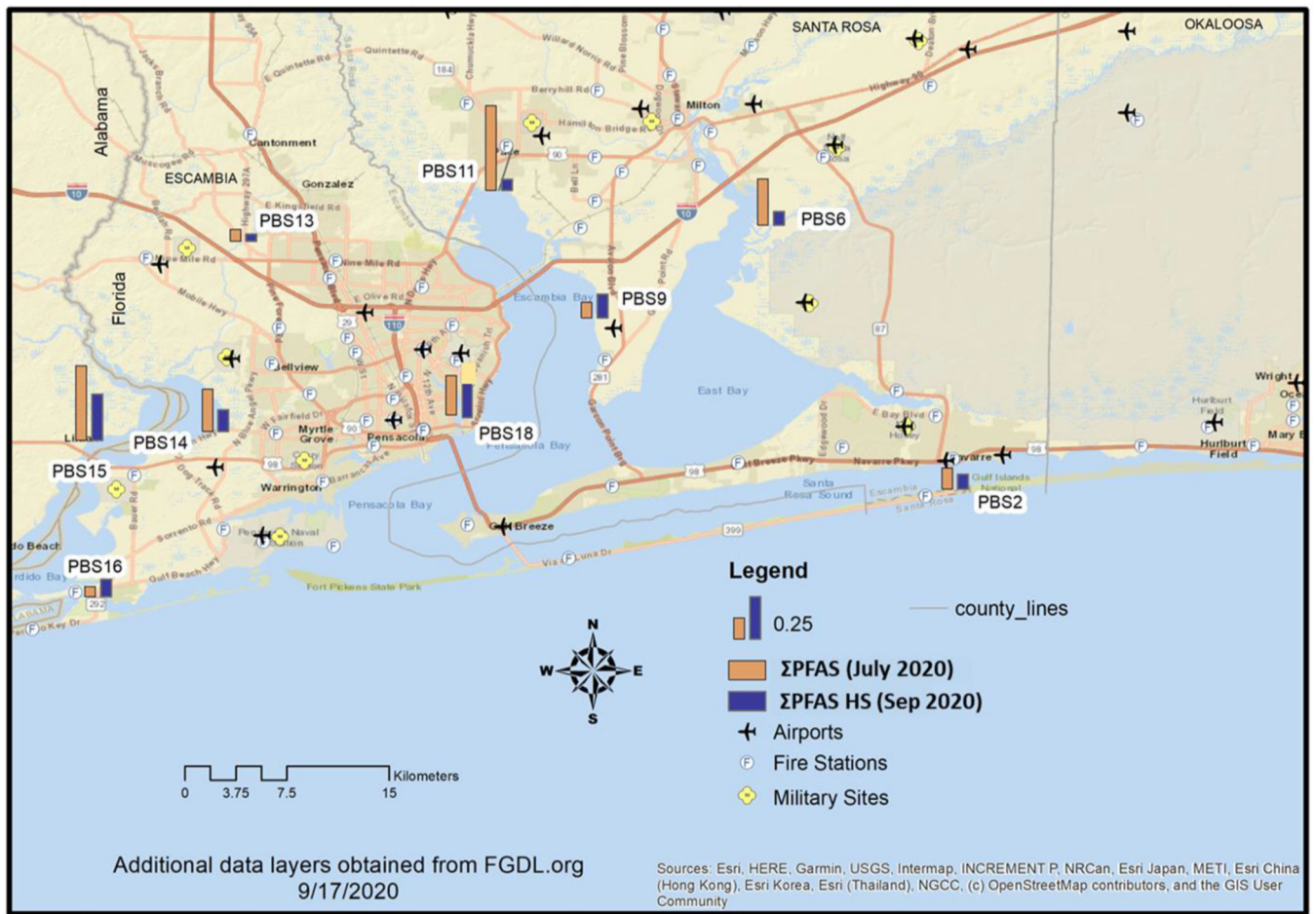


**Fig. 1.** Spatial distribution of total PFAS ( $\Sigma$ PFAS) concentrations ( $\text{ng g}^{-1}$ , dry weight) in sediment samples in the PBS; concentrations are the average of three analytical replicates from each sampling location (total number of twenty-five samples were collected in February and July 2020). ArcGIS v17 was used to create the map.



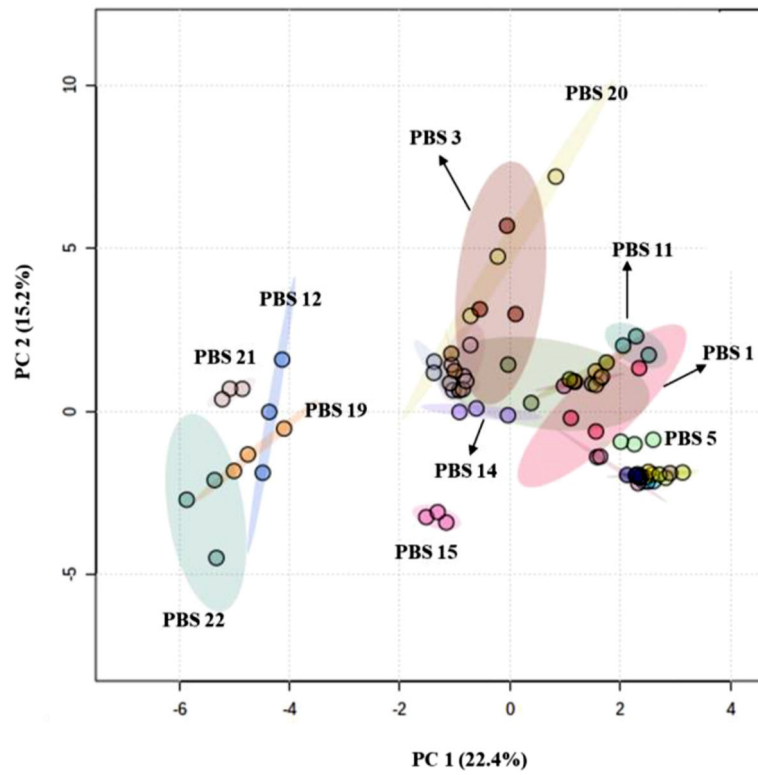


**Fig. 2.** Spatial distribution of two dominant PFAS in the PBS collected in February and July 2020 in the PBS (A) PFBA (DR=100%, and (B) PFOS (DR=92%); concentrations are the average of three analytical replicates from each sampling location. ArcGIS v17 was used to create the map.



**Fig. 3.** Spatial distribution bar graph of total PFAS concentration ( $\text{ng g}^{-1}$ ) in sediment samples collected in July 2020, and September 2020 after Hurricane Sally (HS) in the PBS.





**Fig. 4.** Principal component analysis (PCA) scores plot for concentration of all quantified PFAS (n=28) as well as  $\Sigma$ PFAS of each site in all sites (n=25); n=3 for each sampling location; values below LOQ were treated as LOD/2.

Table 1

Comparison of number of PFAS targeted, their concentrations, and occurrence in PBS sediments ( $\text{ng g}^{-1}$ ) with those reported in the literatures.

Location	# of sampling location	# of targeted PFAS	# of quantified PFAS in different sites	PFOS ( $\text{ng g}^{-1}$ )	PFBA ( $\text{ng g}^{-1}$ )	PFOA ( $\text{ng g}^{-1}$ )	Dominant PFAS	Most occurrence
San Francisco Bay, CA (Higgins et al., 2005)	13	12	1 – 11	ND– 3.07	NM	ND– 0.625	PFOS	PFOS
Baltimore Inner Harbor, MD (Higgins et al., 2005)	NA	12	11	ND– 0.846	NM	0.19 – 0.39	N-EFOSAA	NA
Puget Sound, WA (Long et al., 2013)	30	13	3	0.20 – 1.50	0.13 – 0.23	ND	PFOS	PFBA
Charleston, SC (White et al., 2015)	36	11	11	0.09 – 7.37	NM	0.101 – 2.51	PFOS, PFDA, PFOA	PFOS, PFDA, PFOA
Pensacola Bay system, FL (present study)	25 <sup>a</sup>	51	2 – 23	0.01 – 0.46	0.01 – 0.48	ND – 0.07	PFOS, PFBA	PFBA, PFOS

<sup>a</sup>total number of samples collected = 34 NM: not measured; ND: not detected.