

Spatial Distribution of Per- and Polyfluoroalkyl Substances (PFAS) in Waters from Central and South Florida.

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are notoriously persistent pollutants that are found ubiquitously present in aquatic environments. They pose a big threat to aquatic life and human health given the bioaccumulation feature and significant adverse health effects associated. In our previous study, PFAS were found in surface waters from Biscayne Bay and tap waters from the West coast of South Florida, at levels that arouse human health and ecological concerns. Considering that Florida supports millions population as well as treasured, sensitive coastal and wetland ecosystems, we have expanded the PFAS monitoring study on the occurrence, composition, spatial distribution, and potential sources encompassing tap waters from counties on the East coast of South Florida and Central Florida, and surface waters from Tampa Bay, Everglades National Park adjacent canals, Key West, including Biscayne Bay area. A total of 30 PFAS were analyzed based on solid-phase extraction (SPE) followed by liquid chromatography tandem mass spectrometry (LC-MS/MS). PFAS were detected in all tap water (N = 10) and surface water samples (N = 38) with total concentrations up to 169 ng L^{-1} . Higher PFAS concentrations ($> 60 \text{ ng L}^{-1}$) are mostly observed from polluted rivers or coastal estuaries in Biscayne Bay, and sites nearby potential points sources (military airbases, wastewater facilities, airports, etc.). Our findings on current PFAS contamination levels from diverse aquatic environments provide additional information for the development of more stringent screening levels that are protective of human health and the environmental resources of Florida, which is ultimately anticipated as scientific understanding of PFAS rapidly growing.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of notoriously persistent pollutants found worldwide. They have been manufactured for over 60 years and have wide applications in industrial and consumer products, such as non-stick cookware, waterproof fabrics, stain-resistant products, surfactants, protective coatings, cosmetics, firefighting foams, food packaging, wire manufacturing, paints, and more (Baran, 2001). PFAS possess incredible chemical and thermal stability due to their strong C-F bonds (Buck et al., 2011; Podder et al., 2021), and are consequently extremely persistent in the environment and can bioaccumulate through the food chain, which is often referred to as “forever chemicals” (Skutlarek et al., 2006). Even at low parts-per-billion level exposure, PFAS have proven to be associated with reproductive, developmental, hepatic, neurological, immunosuppressive, and endocrine disruptive toxicity (Grandjean & Clapp, 2015; Kato et al., 2018; Lopez-Espinosa et al., 2012; Vieira et al., 2013).

Generally, PFAS can be released into the environment through specific point sources areas: production and manufacturing facilities, facilities using Aqueous Fire Fighting Foams (AFFF) (Airport, military bases, firefighting training areas), landfills and wastewater treatment plants (WWTPs) (Cui et al., 2020). Nonpoint sources like atmospheric deposition and water runoffs (from industrial, wastewater, agriculture) can also introduce PFAS into the environment (Ahrens & Bundschuh, 2014). For example, PFAS-containing materials disposed into landfills will generate leachate, contributing to the discharge of PFAS to surface water, groundwater, and wastewater treatment plants (WWTPs) which are ineffective in

removing these compounds (Rahman et al., 2014). Using PFAS contaminated water as a source of tap water can recirculate PFAS in the water cycle (Winchell et al., 2021) and catalyze bioaccumulation in a plethora of biological organisms, which pose a huge concern to human health. The prevalence of PFAS in surface water also threatens the health condition of wildlife, such as aquatic animals, birds, especially the predators at the top of the food chain through bioaccumulation and biomagnification from contaminated waters and preys (Grønnestad et al., 2019; Quinete et al., 2011). PFAS have been observed in several aquatic animals in Florida, including alligators which hold a significant role in the food chain in the Florida Everglades (Bangma et al., 2017; Wood et al., 2021).

Higher PFAS levels are often associated with highly urbanized and industrialized areas having commercial and industrial complexes, ports and marinas, military bases, human waste facilities, etc. (Sardiña et al., 2019). Coastal estuarine environments make up the leading environment for PFAS pollution due to their proximity to urban and industrial centers (Yamashita et al., 2008). Recently, we have assessed a total of 30 PFAS for the first time in surface waters from Biscayne Bay and adjacent canals, which showed concentrations up to 106 ng L^{-1} of total PFAS, and in tap waters from populated counties in South Florida with levels up to 242 ng L^{-1} of total PFAS (Li et al., 2022). The PFAS levels found in these areas represent significant human health and ecological risks. Considering that Florida supports over 20 million people, as well as treasured, sensitive coastal and wetland ecosystems, it is vital to expand the PFAS monitoring study encompassing a broader area to provide needed information to the public and regional authorities addressing the issue.

In this study, we have expanded the study area to include tap waters from other major counties that are highly populated in Florida, and surface waters from important coastal and wetland ecosystems subject to anthropogenic activities that might be impacting the water quality. These areas include Tampa Bay and its adjacent area on the West coast of South Florida, Biscayne Bay and its adjacent area on the East coast of South Florida, the canals coming from preserved Everglades area- Everglades National Park (ENP), and coastal Key West. Therefore, our main goal was to evaluate the occurrence, levels, composition, and spatial distribution of PFAS along surface and tap waters in Central and South Florida. A total of 30 PFAS, including legacy long-chain and especially, emerging short-chain PFAS, were analyzed in this study to allow better coverage and understanding of the input and fate of PFAS in the environment.

2. Materials And Methodology

2.1 Chemicals and standards.

All the chemicals and solvents used in this study were Optima LC/MS grade and purchased from Fisher Scientific (Waltham, MA, USA), including methanol, water, hexane, acetone, methylene chloride, ammonium hydroxide, and ammonium formate. Strata-XL-AW 100 μm polymeric weak anion cartridges (500 mg/3 mL) were purchased from Phenomenex (Torrance, CA, USA), and used for the solid phase extraction (SPE) process.

30 PFAS native standards (PFAC30PAR), isotopically mass-labeled 19 PFAS standards (PFAC-24ES), and isotopically mass-labeled HFPO-DA (M3HFPO-DA), were purchased from Wellington Laboratories Inc (Guelph, Ontario, Canada). PFAC30PAR and PFAC-24ES were purchased as solutions of 1 mg L^{-1} in MeOH, and M3HFPO-DA was of 50 mg L^{-1} in MeOH. In addition, 24 PFAS native standard (PFC-24) was purchased from AccuStandard (New Haven, CT, USA) as solution of 2 mg L^{-1} in methanol: water (80:20) and used as a secondary standard for initial calibration verification (ICV) purpose. Working solutions of native standards (PFAC30PAR) were prepared at concentrations of $10 \text{ } \mu\text{g L}^{-1}$ and $1 \text{ } \mu\text{g L}^{-1}$ in water, while for the secondary standards PFC-24, a concentration of $1 \text{ } \mu\text{g L}^{-1}$ was prepared in water. For internal standards (IS), the working solution was prepared as a mixture of PFAC-24 ES and M3HFPO-DA at a concentration of $2.5 \text{ } \mu\text{g L}^{-1}$ in methanol. All the standards and working solutions were stored refrigerated at 4°C . The list of all the compounds presented in the native and internal standards used is shown in Table S1.

2.2 Study area and sample collection

Our study areas covered Biscayne Bay, Tampa Bay and their adjacent canals, canals coming from the ENP, and Key West. Surface water samples were collected from the nearshore and their adjacent rivers and canals. Biscayne Bay is a rectangular-shaped estuary located along the southeast coast of South Florida, which provides important habitat for a variety of wildlife as well as is a key part of the recreational, social, economic, and cultural life of South Florida. This study focused on the North region of the Biscayne Bay (North Bay), which is heavily populated (population: 2.5 million in Miami Dade), urbanized, and influenced by freshwater releases from rivers and canals such as Arch Creek, Biscayne Canal, Little River, Miami River (Caccia & Boyer, 2005). Similarly, Tampa Bay on the West coast of Florida also has its environmental significance as well as regional economic significance. It adjoins the highly urbanized land area with many industrial and agricultural cities surrounding Tampa Bay, such as Tampa city and St. Petersburg, with approximately 1.3 million population (Hillsborough and Pinellas County) (Yates et al., 2011). Key West is the southernmost tip of the Florida Keys and a popular vacation destination. It is occupied mostly by hotel businesses and single-family houses with a population of 24,649. In Key West, despite recent changes related to the wastewater collection and transmission system with some progress towards connecting some areas to municipal sewages sources, most of the single-family houses (especially trailer camps) and small businesses (e.g., hotels) are not served by modern sewage treatment plants. Instead, they rely on the use of onsite treatment systems, including septic tanks and shallow (90–120 feet) injection wells, which could lead to micropollutants leaching to groundwater and adjacent surface water (Yang et al., 2017). The ENP is the largest tropical wilderness in the United States and constitutes a preserved area due to its biodiversity and ecological importance. The samples were not collected inside the ENP but from its adjacent freshwater canals on the eastern boundaries, which are under the influence of subtropical agricultural lands and urban development areas (Quinete et al., 2013).

Surface water samples were collected using a swing arm sampler (Wooster, OH, US) with 500 mL pre-cleaned high-density polyethylene bottles (HDPE). Samples (N = 13) from Biscayne Bay (North Bay) were

collected in Aug 2021. Samples (N = 12) from ENP were collected in Feb 2020 and July 2021. Samples (N = 7) from Tampa Bay area were collected in May 2021. Samples (N = 6) from Key West were collected in July and Sep 2021. The map of collection sites is shown in Fig. 1. The corresponding coordinates, abbreviations, date of the sampling event, and salinity of the samples can be found in Table S2. Tap water samples were also collected in 500 mL pre-cleaned HDPE bottles from major municipalities in 9 counties in Florida (N = 10), including St. Lucie, Orange, Hillsborough, Pinellas, Manatee, Sarasota, Charlotte, Lee, and Collier, which covers major cities on the West coast of South Florida and Central Florida. The sampling event for tap water was conducted in May 2021.

2.3 SPE LC-MS method

A SPE method followed by liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis was used for PFAS extraction, preconcentration, and determination following the previously published procedure (Li et al., 2022). Briefly, 250 mL of the water sample was spiked with 100 μL of a 2.5 $\mu\text{g L}^{-1}$ IS and were passed through preconditioned Strata-XL AW cartridges on a semi-automated SPE system (12 samples per batch). Samples were eluted with 10 mL of 0.3% ammonium hydroxide in methanol, then evaporated to dryness using a nitrogen evaporator, and reconstituted to 1 mL with 90:10 (vol/vol) 5 mM ammonium formate /methanol for LC-MS/MS analysis. A volume of 100 μL was injected into the Agilent 1290 Infinity II LC interfaced to an Agilent 6470 triple-quadrupole LC-MS/MS system for PFAS identification and quantification. A Hypersil GOLD pentafluorophenyl (PFP) column (150 mm \times 2.1 mm, 3 μm) with a PFP guard column (Hypersil Gold PFP 5 μm drop-in guards) was used as the analytical column. The LC conditions, MS parameters, and MRM method can be found in Table S3, S4, and S5.

2.4 Quality control/quality assurance (QA/QC)

The methodology has been validated as described in our previous publication (Li et al., 2022). To ensure the quality of the obtained data, LC-MS Blanks (LC-MS water), procedural blanks (LC-MS water spiked with IS and processed through SPE), and field/trip blanks (LC-MS water carried through sampling events and processed through SPE) were also run with every batch of samples. Spiked blanks, which consisted of LC-MS water (250 mL) spiked with native standards at a final concentration of 10 ng L^{-1} and 100 ng L^{-1} and IS at a final concentration of 250 ng L^{-1} , were prepared and analyzed every 8–10 samples. An initial calibration verification (ICV) solution was prepared as secondary standards and run with every batch of samples after the calibration curve. An 11-point calibration curve was prepared in the concentration range of 2 to 1000 ng L^{-1} for quantitation purposes. The LC-MS system was modified with PFAS free tubing, and a delay column (Hypersil GOLD aQ C18, 20 \times 2.1 mm, 12 μm) to avoid potential contamination coming from the solvents. All bottles, vials, and tubing used in this study were cleaned with solvents, including methylene chloride, hexane, acetone, methanol, and water at least two times and airdried. The solvents used in this analysis were examined for potential PFAS contamination.

Concentrations found in blanks ranged from < MDL to 0.2 ng L^{-1} (for PFTTrDA) and were subtracted from results in the environmental waters.

2.5 Data analysis and statistics

PFAS quantitation was performed using Mass Hunter QQQ quantitation analysis software and the criteria of peak integration and quantitation follows the one reported in Li et al., 2022 for retention time matching (< 0.1 min of IS or native standards in the calibration curve), presence in the confirmation peak when available, signal to noise ratio (> 3), and above the method detected limits, otherwise reported as < MDL. Statistical tests and plots were conducted in the R software (version 3.5.0; R Team, 2019), with an alpha set at 0.05.

3. Results And Discussion

3.1 Occurrence, concentrations, and composition of PFAS in surface waters from Biscayne Bay, Tampa Bay, ENP, and Key West in Central and South Florida

PFAS were detected in samples from 33 sampling sites that cover 13 sites surrounding the Biscayne Bay area, 8 sites from the Tampa Bay area, 6 sites from the ENP adjacent canals, and 6 sites from Key West. The concentration of individual PFAS congeners and total PFAS concentrations (the sum of all the PFAS congeners detected for the same sites) are shown in Table S6. For the sampling sites collected multiple times (≥ 2), the average (Min, Max) concentrations were reported. The spatial distribution of total PFAS in the sampling sites along Central and South Florida is displayed in Fig. 2. Overall, total PFAS concentrations ranged from 6.50 ng L^{-1} (TWP, Key West) to 169 ng L^{-1} (HB, Miami) with 6 locations above 60 ng L^{-1} and 28 locations below 60 ng L^{-1} .

To better understand spatial variations in Biscayne Bay and canals, we have combined data from samples collected in Oct 2020 (N = 13), Jan 2021 (N = 14), which were previously analyzed and presented (Li et al., 2022), with recently collected samples in Aug 2021 (N = 13). As a result, a total of 40 samples were averaged from 3 sampling trips during 2020–2021, with the average of total PFAS concentrations ranging from 11.4 ng L^{-1} (MB17th) to 91.0 ng L^{-1} (LR2). Relatively higher concentrations were identified at two sites from Little River ($81.0, 91.0 \text{ ng L}^{-1}$), two sites from Miami River ($72.4, 72.1 \text{ ng L}^{-1}$), Little Arch Creek (54.5 ng L^{-1}), and Biscayne Bay canal C-8 (53.9 ng L^{-1}), whereas sites from Miami Beach (MB10th, MB14th, and MB17th) were all below 20 ng L^{-1} . The variability of the three sets of data is presented as error bars in Fig. 2. Results from multiple sampling events conducted during rainy and dry seasons suggested that PFAS concentration from the same location remains relatively stable with small variations throughout the whole period of study. Little River, Miami River, and Biscayne Bay canal BC-8 are identified as “hot spots”, where the highest levels were observed in this study and the previous one (Li et al., 2022).

From 10 samples collected at ENP adjacent canals in two sampling trips, the average of total PFAS concentrations ranged from 35.0 ng L^{-1} (C103) to 52.1 ng L^{-1} (C113), as shown in Fig. 2, Table S6. The surface water at site HB was also from canal C-103 closer to its east opening to Biscayne Bay passing Homestead Air Reserve Base. The sampling site HB is around 16 km away from site C103 adjacent to ENP and showed a total concentration of 169 ng L^{-1} , which was the highest total PFAS concentration

detected throughout this study. The 6 samples spreading along the coast of Key West presented total PFAS concentrations in the range of 6.50 ng L⁻¹ (TWP) to 19.1 ng L⁻¹ (EKP).

Total PFAS concentrations ranged from 17.4 (TC) to 60.6 ng L⁻¹ (TB) from the 7 samples collected from Tampa Bay and its adjacent area. Three sites from the North region of Tampa Bay (TB, CB, BPP) and two sites from central Tampa Bay (VP, CTB) falls into a range of 37.8–60.6 ng L⁻¹, whereas the surface water sample from Terra Ceia aquatic preserve located in South Tampa Bay (TC) had the lowest total PFAS concentration of 17.4 ng L⁻¹. Two samples collected along the west coast in Port Charlotte (PC) and Marco Island (MI) showed concentrations of 26.11, and 38.23 ng L⁻¹, respectively.

Overall, among 30 PFAS congeners covered in this study, all were detected in one or more sites. The PFAS composition in each location is presented in Fig. 3. It can be observed that compositions vary from location to location, however, predominant congeners of each defined area can be identified based on detection rates and mean concentrations.

In Biscayne Bay samples, among 28 PFAS congeners detected (Adona and PFONS were not detected), PFOS was the predominant PFAS, with concentrations ranging from 1.16 ng L⁻¹ to 24.1 ng L⁻¹ (mean: 10.1 ng L⁻¹), followed by PFPeA (1.50–12.5 ng L⁻¹; mean: 5.75 ng L⁻¹), PFHxA (1.15–10.9 ng L⁻¹; mean: 4.72 ng L⁻¹), 6 – 2 FTS (0.313–21.8 ng L⁻¹; mean: 4.32 ng L⁻¹), PFBA (1.15–10.2 ng L⁻¹; mean: 4.26 ng L⁻¹), PFBS (0.671–8.58 ng L⁻¹; mean: 3.46 ng L⁻¹), PFOA (0.660–6.90 ng L⁻¹; mean: 2.84 ng L⁻¹), PFHpA (0.766–5.01 ng L⁻¹; mean: 2.69 ng L⁻¹), and PFHxS (0.520–5.58 ng L⁻¹; mean: 2.43 ng L⁻¹). PFOS, PFPeA, PFHxA, PFBA, PFBS, PFOA, PFHpA PFHxS had detection rates of 100%, and 6 – 2 FTS had a detection rate of 92.5%.

In the ENP canal samples, 25 PFAS congeners were detected (6 – 2 FTS, Adona, FHxSA, PFTeDA, FOSA were not detected). Since HB is apart from the ENP adjacent canals, thus it was not included in the following composition analysis represented by ENP samples. PFBA (5.33–12.2 ng L⁻¹; mean: 9.98 ng L⁻¹; detection frequency- DF:100%), PFOS (3.42-13.0 ng L⁻¹; mean: 7.48 ng L⁻¹; DF: 100%), PFBS (2.01–5.54 ng L⁻¹; mean: 3.45 ng L⁻¹; DF:100%), PFPeA (1.85–3.56 ng L⁻¹; mean: 2.99 ng L⁻¹; DF:100%), PFHxA (1.14–2.62 ng L⁻¹; mean: 2.06 ng L⁻¹; DF:100%), PFOA (0.985-2.40 ng L⁻¹; mean: 1.74 ng L⁻¹; DF: 100%), and PFHpA (0.73–1.53 ng L⁻¹; mean: 1.23 ng L⁻¹; DF: 90%), were identified as the predominant congeners in the ENP canals. Different from Biscayne Bay samples, some long-chain PFAS such as PFOUDS, PFUdA, N-EtFOSAA, PFDOA, PFTTrDA were also predominantly present in the samples.

In Key West samples, 23 PFAS congeners were detected (8 – 2 FTS, PFNS, PFDS, FHxSA, PFUdA, PFTTrD, PFTeDA were not detected), whereas PFOS (0.675-3.70 ng L⁻¹; mean:1.98 ng L⁻¹), PFBA (1.18–2.15 ng L⁻¹; mean: 1.64 ng L⁻¹), PFHpA (0.568–2.62 ng L⁻¹ mean: 1.48 ng L⁻¹), and PFPeA (0.494–2.09 ng L⁻¹; mean: 1.23 ng L⁻¹) were identified as the predominant congeners at 100% detection rates.

In samples from Tampa Bay area, 19 PFAS were detected (4 - 2 FTS, GenX, Adona, PFONS, PFOUDS, FHxSA, N-MeFOSAA, N-EtFOSAA, PFDaA, PFTrDA, and PFTeDA were not detected), and PFOS was the predominant PFAS, with a concentration ranging from 2.40 ng L⁻¹ to 25.7 ng L⁻¹ (mean: 10.0 ng L⁻¹), followed by PFHpA (1.01–23.1 ng L⁻¹; mean: 8.36 ng L⁻¹), PFHxS (0.564–5.48 ng L⁻¹; mean: 2.83 ng L⁻¹), PFPeA (1.92–6.10 ng L⁻¹; mean: 3.72 ng L⁻¹), PFBS (1.19–4.49 ng L⁻¹; mean: 3.08 ng L⁻¹), PFBA (1.53–4.49 ng L⁻¹; mean: 3.08 ng L⁻¹), and PFHxA (1.33–4.38 ng L⁻¹; mean: 2.6 ng L⁻¹), with detection rates of 100% for all the congeners.

3.2 Occurrence, concentrations, and composition of PFAS in tap waters from West Coast and Central Florida

Tap water samples were collected along the West coast of Florida (Sarasota, Tampa City, St. Petersburg, Port Charlotte, Ft. Meyers, and Naples), as well as from cities in Central Florida, (Port St. Lucie, Fort Drum, St. Cloud, and Orlando). Total PFAS concentrations ranged from 1.61 ng L⁻¹ (Naples) to 45.2 ng L⁻¹ (Tampa City) in tap water as shown in Fig. 4, and Table S7. Most of the samples fell below 20 ng L⁻¹ with the exception of Tampa City, where was found a concentration of 45.2 ng L⁻¹. Tap waters from Naples, Ft Meyers, Sarasota, Orlando, St. Cloud showed total PFAS concentrations below 6 ng L⁻¹.

Among 30 PFAS, 17 compounds were detected in one or more samples, with FHxSA, PFONS, FOSA, PFNS, PFDS, PFUdA, PFTeDA, 4 - 2 FTS, 6 - 2 FTS, N-EtFOSAA, PFONDS, GenX, and Adona not being detected. The predominant congeners were PFHpA (< MDL-8.57 ng L⁻¹; mean: 2.45 ng L⁻¹), PFPeA (< MDL-8.76 ng L⁻¹; mean: 1.95 ng L⁻¹), PFOS (< MDL-6.50 ng L⁻¹; mean: 1.63 ng L⁻¹), PFHxA (< MDL-3.70 ng L⁻¹; mean: 1.61 ng L⁻¹), PFBS (< MDL-4.12ng L⁻¹; mean: 1.42 ng L⁻¹), PFOA (< MDL-2.94 ng L⁻¹, mean: 1.36 ng L⁻¹), and PFBA (< MDL-4.02 ng L⁻¹; mean: 1.84 ng L⁻¹). The detection rates of PFBS, PFPeA, PFPeS, PFHxA, PFHxS, PFHpA, PFOA, and PFOS, ranged from 70 to 90%, while the detection rates of PFBA, FBSA, PFHpS, PFNA, PFDA, PFDaA, and PFTrDA ranged from 10–50%. The composition of PFAS congeners of each sample is shown in Figure S1. Overall, PFHpA accounts for 16.6% of total PFAS detected, followed by PFPeA (14.8%), PFBA, PFBS, FBSA, PFHxA, PFHxS, PFOA, and PFOS ranged from 6.38–9.67%, while other PFAS contributed with less than 4.12%.

3.3 Spatial distribution and potential sources of PFAS in surface waters

Higher concentrations of PFAS are mostly observed in samples from polluted rivers, or samples near coastal estuaries, and point sources, such as military airbases, WWTPs, airports, etc. These water bodies pass through highly urbanized areas with large populations, businesses, in which various chemicals and waste discharges, drainage and runoffs might all end up to. The highest concentration in surface water was observed in the C103 canal (HB: 169 ng L⁻¹) at 2 km from the Homestead Air Reserve Base, where the historical use of AFFF containing PFAS is well known, and whereas the sample from the same canal on the west side close to ENP is nearly 5-fold lower, suggesting the potential impact of this point source

on PFAS levels. The highest levels in Biscayne Bay surface water were found in Miami River (98.9 ng L⁻¹; Sep 2021), Little River (91.7 ng L⁻¹; Sep 2021), and BC-8 canal (103 ng L⁻¹; Aug 2020), which were previously also reported as polluted waterways in South Florida with high levels of wastewater tracers, pharmaceutical and personal care products (PPCPs), and steroid hormones (Blair & Kemp, 2004; Ng et al., 2021).

The ENP adjacent canals presented PFAS levels ranging from 30 to 60 ng L⁻¹. These freshwater canals on the eastern boundaries serve as a buffer zone that separates the wetlands of ENP from highly productive subtropical agricultural lands and urban development areas (Quinete et al., 2013). Therefore, potential sources are likely to be a mixture of rainfall and runoffs from urban and agricultural areas of southeast Florida, such as from the usage of PFAS containing insecticides and fertilizers (Savvaides et al., n.d.) (Borthakur et al., 2022). Since there are no studies to date performed inside the ENP preserved area, the impact of PFAS in the Everglades water quality is still uncertain.

Key West and Miami beach surface waters showed concentrations below 20 ng L⁻¹. Though the sample locations include tourist beaches, marinas, drainage openings from apartment buildings, which could have contributed with PFAS input, it still presented a relatively low PFAS pollution level. These samples are associated with the highest salinities observed in this study, one possible reason is that PFAS levels can be substantially lowered by the dilution effect in seawater (Wang et al., 2019).

North Tampa Bay (where Tampa city is located) surface water showed slightly higher concentration than samples from central Tampa Bay followed by samples from South Tampa Bay, which coincides with the population in this area decreasing from North to South, for example, North Tampa Bay (Tampa city) has a population of 383,959, followed by Central Tampa Bay (St. Petersburg) with a population of 258,308, and South Tampa Bay (Palmetto City) with a population of 13,323. (census.gov, April 1, 2020). In addition, airports (Tampa International Airport, Clearwater International Airport, and Peter O. Knight Airports), military bases (MacDill Air Force Base), landfills (Pinellas County Solid Waste Disposal), wastewater treatment plants (St Petersburg Wastewater Treatment and Howard F. Curren Advanced Wastewater Treatment Plant) are all found concentrated in North Tampa Bay, which could have contributed to PFAS input in this area. In April 2021, 814 million liters of legacy phosphate mining wastewater and marine dredge water from Piney Point Mining Phosphate Facility were discharged into South Tampa Bay and Port Manatee. Our sampling trip was conducted about one month after the incident, whereas the wastewater input and runoff it carried over might have contribute to the water quality deterioration in this area, potentially affecting the PFAS levels as well.

PFAS concentrations identified in each sampling area are compared and presented in Fig. 5. The identified predominant PFAS included PFOS, PFPeA, PFHxA, PFBA, PFOA, PFHxA, PFHpA, PFHxS, PFNA, PFHpS, PFPes, and 6 – 2 FTS. As seen in Fig. 5, in general, highest concentration of PFAS were found in Biscayne Bay and canals waters followed by Tampa Bay, ENP canals, and Key West for most of the congeners, except for PFBA, which was higher in ENP canals, and PFHpA, which showed the highest level in Tampa Bay.

3.4 Spatial distribution and potential sources of PFAS in tap water from Florida

To better address PFAS spatial distribution, tap water samples collected in this study from Central Florida and the West coast of South Florida are compared to samples collected from the metropolitan area on the East coast of South Florida previously published in Li et al., 2022 using the same method. The average PFAS concentration of the samples from the same region were calculated for comparison and displayed in Fig. 6. The regions in Florida were divided into three groups: Central Florida (St. Lucie, Okeechobee, Osceola, Orange counties; N = 4); West coast of South Florida (Sarasota, Hillsborough, Pinellas, Charlotte, Lee, Collier counties; N = 6), and East coast of South Florida (Palm Beach, Broward, Miami Dade counties; N = 22, data from Li et al. 2022). The total PFAS concentrations were the highest in the East coast of South Florida (mean: 83.0 ng L⁻¹), followed by the West coast of South Florida (mean: 14.4 ng L⁻¹), and Central Florida (mean: 8.00 ng L⁻¹) as shown in Figure S2. This trend coincides with the increased population in the defined groups: East coast of South Florida with a population of 5.6 million followed by West coast of South Florida with 3.6 million, and Central Florida with 1.7 million. Though PFAS levels could be associated with demographics factors (higher population number) and related human activities (higher production and discharge of industrial and domestic wastewater, landfills disposals, among others), the number of samples assessed in other regions and counties were low and further studies including a larger number of samples are needed to allow a more comprehensive and better understanding on the occurrence, distribution, and fate of PFAS in Florida.

The concentrations of most PFAS congeners were higher on the East coast of South Florida, followed by West coast of South Florida, and Central Florida as shown in Fig. 6, except for PFPeS, GenX, PFHpA, and Adona. Adona is an emerging PFAS substitute of PFOA and PFOS which was not detected in any East coast samples but showed concentration up to 6.50 ng L⁻¹ in the West Coast and Central Florida tap waters. PFBA, PFOS, PFPeA, and PFHxA levels on the East coast showed higher concentration trend compared to the other regions in Florida.

The source of tap water in most of the cities in South and Central Florida such as Miami, Orlando, Fort Meyers, Naples, and Port St. Lucie is primarily from the Floridian aquifer, whereas the sources of tap water in Tampa region which include Tampa city, St. Peterburg, Sarasota, Port Charlotte in this study, are diverse coming from surface water from rivers and canals, groundwater from Floridian aquifer, and desalinated seawater (Tampa.gov, April 1, 2020). However, studies on PFAS occurrence and levels in Floridan aquifers and surface water sources used for drinking purposes are still lacking to be able to draw any conclusion on the contamination source of PFAS in drinking water. It was found that the PFAS level in drinking water is higher than that of surface water in the east coast samples, which could arise from precursors breakdown processes during the water treatment and contamination during distribution processes (Li et al., 2022), but in the West coast and Central Florida water, more samples are needed to evaluate the difference on PFAS levels in surface water and tap waters.

3.5 Principal Component Analysis (PCA)

The Principal Component Analysis (PCA) determined the total variance of the dataset explained by the principal components (PCs) and their eigenvalues in both surface and tap waters. The number of PCs was determined using the Kaiser criterion (eigenvalues > 1; (Mooi & Sarstedt, 2011)). Eight PCs were extracted from the surface waters' dataset, displaying a cumulative variance of 84.71%. As for the tap waters' dataset, eleven PCs were extracted, exhibiting a cumulative variance of 83.55%.

A representation of the results of the PCA is given by the PCA biplots in Fig. 7. These plots display loadings of the variables (i.e., vectors), determining how strongly each of the variables influence a PC. The further away these vectors are from a PC origin, the higher the influence they have on that PC. Small angles in these loadings indicate positive correlations, while large angles indicate negative correlations, and a 90° angle indicates no correlation. In Fig. 7A, which represents the PCA results for surface waters, a higher loading of the congeners 4 - 2 FTS, 6 - 2 FTS, and 8 - 2 FTS was noted, showing a high influence of these congeners, especially in the Biscayne Bay area. These congeners displayed a strong positive correlation, suggesting they have similar sources. The PCA biplot also showed clusters of samples based on their similarities. Samples from the same areas clustered in groups suggest shared similarities in compounds' composition, which was especially true in Key West.

In Fig. 7B, which represents the PCA results for tap waters, multiple high loadings were noted, including total PFAS (Σ PFAS), and the congeners PFOA, PFHpA, PFHxA, PFBA, PFNA, PFHxS, and PFOS. This shows a higher influence of these congeners in the data variability, especially in the East coast of South Florida region. Interestingly, all of these congeners are from the same two categories: perfluoroalkyl carboxylic acid (PFCA, including PFOA, PFHpA, PFHxA, PFBA, and PFNA) and perfluoroalkyl sulfonic acid (PFSA; including PFHxS, and PFOS), indicating similar composition and potential sources.

3.6 Ecological and human health risk assessment

PFAS have been identified as Contaminants of Emerging Concern (CEC), which their ubiquitous presence may pose ecological and public health risks. Levels of PFOA and PFOS found here in tap water are below the health advisory guideline from the U.S EPA, which the sum of PFOA and PFOS should not be above 70 ng L⁻¹. Nevertheless, this level is being currently re-evaluated considering more recent scientific data and new analyses which indicate that negative effects might occur in levels lower than the established advisory value (Mccarthy et al., 2017; Post, 2021). Seafood consumption is another important route of dietary exposure to humans, as PFAS were found in fish tissues including Striped Mullets (*Mugil Cephalus*) which is a native Floridian fish (Bangma et al., 2018; Denys et al., 2014). Though there are no federal established guidelines that monitor surface water contamination for PFAS in the U.S., currently, the Florida Department of Environmental Protection (FDEP) has developed provisional surface water screening values of 1300 µg L⁻¹ of PFOA and 37 µg L⁻¹ of PFOS for fresh-water systems, and 13 µg L⁻¹ of PFOS in saltwater systems, considering the protection of human health for the consumption of freshwater and estuarine finfish and shellfish (FDEP, 2021). The levels of PFOA ranged from 0.265 ng L⁻¹ to 10.2 ng L⁻¹, and PFOS ranged from 0.68 ng L⁻¹ to 25.7 ng L⁻¹ in surface water samples from Biscayne Bay, Tampa Bay, ENP, and Key West covered in this study, which are all below these screening

levels. However, considering that coastal Florida supports heavy seafood production and consumption, PFAS monitoring on these areas is needed for further human health risk assessment.

In addition, these aquatic ecosystems that support indispensable biomes are incessantly stressed due to these anthropogenic pollutants. As PFAS were identified in Florida coastal water samples, previous study evaluated West Indian manatees inhabiting three coastal sites in Florida (Brevard County, Crystal River, and ENP), where PFOS was detected in the plasma of every Manatee (N = 69) with concentrations up to 166 ng/g ww. Coastal area covered in this study are natural habitats for manatees (Deutsch et al., 2003), and PFOS was also found to be the most predominant PFAS determined in our surface water samples, which suggest the potential environmental impact on these vulnerable and endangered species. Moreover, another study showed that corals, a crucial component to wildlife, tourism, and storm control, can rapidly bioconcentrate and eliminate PFOS, and exposure to PFOS (100 ng L⁻¹) was associated with increased oxidative stress (Bednarz et al., 2022). When combined with elevated temperature, PFOS can exacerbate the oxidative stress response leading to impaired photosynthesis in corals, which indicates that interactive effects of PFOS exposure with other environmental stressors can induce additional biological effects (Bednarz et al., 2022).

The levels of PFOS found in this study are above most of strict thresholds recommended in Europe, Australia, and New Zealand (0.23 to 23 ng L⁻¹) for the purpose of protecting aquatic biota. Though PFOS is the most prevalent PFAS detected in our study, PFBA, PFBS, and PFPeA were also predominant in the aquatic environment, therefore, it is important to take into consideration the potential PFAS synergetic effects on aquatic wildlife, which are currently not well understood and demands further assessments.

4. Conclusion

This study investigated PFAS occurrence, concentration, composition, and potential sources in tap water and surface water in Central and South Florida environments. For tap waters, PFAS concentrations showed the highest in the East coast of South Florida (mean: 83.0 ng L⁻¹), followed by the West Coast of South Florida (mean: 14.4 ng L⁻¹), and Central Florida (mean: 8.0 ng L⁻¹). It could be associated with population and related human activities that have potential impact on the quality of groundwater as drinking water source through water cycle. PFOS, PFPeA, PFHpA, PFHxA, PFHxS, PFBA, and PFBS are found predominant in tap water samples. Studies on PFAS occurrence and levels in Floridan aquifers, groundwater, and surface water sources used for drinking purposes are still needed to further elucidate the source of PFAS to drinking water supply. In surface water, higher PFAS concentrations (> 60 ng/L) are mostly observed from polluted rivers or coastal estuaries in Biscayne Bay, and sites collected nearby points source (military airbases, WWTPs, airports, etc.). Predominant PFAS in surface waters included PFOS, PFPeA, PFHxA, PFBA, PFOA, PFHpA, and PFHxS, which followed the trend Biscayne Bay > Tampa Bay > ENP canals > Key West. PFAS levels observed in tap waters were below the health advisory limit set by the U.S. EPA, although it does not mean that observed levels could not potentially constitute human health risks. Though the levels of PFOA (up to 22.9 ng L⁻¹) and PFOS, (up to 25.7 ng L⁻¹) found in this

study are below the provisional surface water screening level for both fresh water and saltwater systems set up by FL DEP for the protection of human health from consumption of freshwater and estuarine finfish and shellfish, they are above most of strict thresholds recommended in Europe, Australia and New Zealand (0.23 to 23 ng L⁻¹ for PFOS) for the purpose of protecting aquatic biota. Other PFAS frequently found in the aquatic environment should be taken into consideration in further toxicology studies to better understand PFAS synergetic effects on aquatic wildlife, allowing a more comprehensive and sensitive assessment of ecological risks. PCA was able to identify similarity in potential sources of PFAS that have strong correlations or show geographic clustering, which can be a powerful tool for investigating the fate and source of PFAS.

Declarations

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Availability of data and materials

All data used in the current study are available from the corresponding author on reasonable request.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

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Consent for publication: Not applicable.

Author Contributions

All authors contributed to the study conception and design. Methodology, investigation, and formal analysis were performed by Xuerong Li and Morgan Fatowe. Data visualization and statistical tests were performed by Xuerong Li and Leila Lemos. Data curation and validation were performed by Xuerong Li and Natalia Quinete. Supervision, resources, project administration and funding were performed and obtained by Natalia Quinete. The first draft of the manuscript was written by Xuerong Li and Morgan Fatowe and all authors edited and made revisions of the manuscript. All authors read and approved the final manuscript.

Web reference:

United States Census Bureau. [census.gov](https://www.census.gov), accessed on April 1, 2020

City of Tampa. [Tampa.gov](https://www.tampa.gov), accessed on April 1, 2020

References

1. Ahrens, L., & Bundschuh, M. (2014). Fate and effects of poly- and perfluoroalkyl substances in the aquatic environment: A review. *Environmental Toxicology and Chemistry*, *33*(9).
<https://doi.org/10.1002/etc.2663>
2. Bangma, J. T., Reiner, J. L., Jones, M., Lowers, R. H., Nilsen, F., Rainwater, T. R., Somerville, S., Guillette, L. J., & Bowden, J. A. (2017). Variation in perfluoroalkyl acids in the American alligator (*Alligator mississippiensis*) at Merritt Island National Wildlife Refuge. *Chemosphere*, *166*, 72–79.
<https://doi.org/10.1016/J.CHEMOSPHERE.2016.09.088>
3. Bangma, J. T., Reiner, J. L., Lowers, R. H., Cantu, T. M., Scott, J., Korte, J. E., Scheidt, D. M., McDonough, C., Tucker, J., Back, B., Adams, D. H., & Bowden, J. A. (2018). Perfluorinated alkyl acids and fecundity assessment in striped mullet (*Mugil cephalus*) at Merritt Island national wildlife refuge. *Science of The Total Environment*, *619–620*, 740–747.
<https://doi.org/10.1016/J.SCITOTENV.2017.11.141>
4. Baran, J. R. (2001). Fluorinated Surfactants and Repellents: Second Edition, Revised and Expanded Surfactant Science Series. Volume 97. By Erik Kissa (Consultant, Wilmington, DE). Marcel Dekker: New York. 2001. xiv + 616 pp. \$195.00. ISBN 0-8247-0472-X. *Journal of the American Chemical Society*, *123*(36). <https://doi.org/10.1021/ja015260a>
5. Bednarz, V. N., Choyke, S., Marangoni, L. F. B., Otto, E. I., Béraud, E., Metian, M., Tolosa, I., & Ferrier-Pagès, C. (2022). Acute exposure to perfluorooctane sulfonate exacerbates heat-induced oxidative stress in a tropical coral species. *Environmental Pollution*, *302*, 119054.
<https://doi.org/10.1016/J.ENVPOL.2022.119054>
6. Blair, S., & Kemp, S. (2004). *Miami River Basin Water Quality Improvement Report: Action Item Matrix Quarterly Progress Report*. Department of Environmental Resource Management (DERM), Miami-Dade County.

7. Borthakur, A., Leonard, J., Koutnik, V. S., Ravi, S., & Mohanty, S. K. (2022). Inhalation risks of wind-blown dust from biosolid-applied agricultural lands: Are they enriched with microplastics and PFAS? *Current Opinion in Environmental Science & Health*, 25, 100309. <https://doi.org/10.1016/J.COESH.2021.100309>
8. Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Allan, #, Jensen, A., Kannan, K., Mabury, S. A., & Pj Van Leeuwenkk, S. (2011). Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integr Environ Assess Manag*, 7, 513–541. <https://doi.org/10.1002/ieam.258>
9. Caccia, V. G., & Boyer, J. N. (2005). Spatial patterning of water quality in Biscayne Bay, Florida as a function of land use and water management. *Marine Pollution Bulletin*, 50(11), 1416–1429. <https://doi.org/10.1016/J.MARPOLBUL.2005.08.002>
10. Cui, D., Li, X., & Quinete, N. (2020). Occurrence, fate, sources and toxicity of PFAS: What we know so far in Florida and major gaps. *TrAC Trends in Analytical Chemistry*, 130, 115976. <https://doi.org/10.1016/j.trac.2020.115976>
11. Denys, S., Fraize-Frontier, S., Moussa, O., Bizec, B. le, Veyrand, B., & Volatier, J. L. (2014). Is the fresh water fish consumption a significant determinant of the internal exposure to perfluoroalkylated substances (PFAS)? *Toxicology Letters*, 231(2), 233–238. <https://doi.org/10.1016/J.TOXLET.2014.07.028>
12. Deutsch, C. J., Reid, J. P., Bonde, R. K., Easton, D. E., Kochman, H. I., & O'Shea, T. J. (2003). Seasonal Movements, Migratory Behavior, and Site Fidelity of West Indian Manatees along the Atlantic Coast of the United States. *Wildlife Monographs*, 151, 1–77. <http://www.jstor.org/stable/3830830>
13. FDEP. (2021). *Florida Department of Environmental Protection PFAS Dynamic Plan* .
14. Grandjean, P., & Clapp, R. (2015). Scientific Solutions Perfluorinated Alkyl Substances: Emerging Insights Into Health Risks. *NEW SOLUTIONS: A Journal of Environmental and Occupational Health Policy*, 25(2), 147–163. <https://doi.org/10.1177/1048291115590506>
15. Grønnestad, R., Pe, B., Va, rez, Arukwe, A., B Jaspers, V. L., Munro Jenssen, B., Karimi, M., Lyche, J. L., & Krøkje, Å. (2019). *Levels, Patterns, and Biomagnification Potential of Perfluoroalkyl Substances in a Terrestrial Food Chain in a Nordic Skiing Area*. <https://doi.org/10.1021/acs.est.9b02533>
16. Kato, K., Kalathil, A. A., Patel, A. M., Ye, X., & Calafat, A. M. (2018). Per- and polyfluoroalkyl substances and fluorinated alternatives in urine and serum by on-line solid phase extraction–liquid chromatography–tandem mass spectrometry. *Chemosphere*, 209, 338–345. <https://doi.org/10.1016/J.CHEMOSPHERE.2018.06.085>
17. Li, X., Fatowe, M., Cui, D., & Quinete, N. (2022). Assessment of per- and polyfluoroalkyl substances in Biscayne Bay surface waters and tap waters from South Florida. *Science of the Total Environment*, 806. <https://doi.org/10.1016/j.scitotenv.2021.150393>
18. Lopez-Espinosa, M. J., Mondal, D., Armstrong, B., Bloom, M. S., & Fletcher, T. (2012). Thyroid function and perfluoroalkyl acids in children living near a chemical plant. *Environmental Health Perspectives*, 120(7). <https://doi.org/10.1289/ehp.1104370>

19. McCarthy, C., Kappelleman, W., & Diguisseppi, W. (2017). *Ecological Considerations of Per- and Polyfluoroalkyl Substances (PFAS)*. <https://doi.org/10.1007/s40726-017-0070-8>
20. Mooi, E., & Sarstedt, M. (2011). Factor Analysis. In E. Mooi & M. Sarstedt (Eds.), *A Concise Guide to Market Research: The Process, Data, and Methods Using IBM SPSS Statistics* (pp. 201–236). Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-12541-6_8
21. Ng, B., Quinete, N., Maldonado, S., Lugo, K., Purrinos, J., Briceño, H., & Gardinali, P. (2021). Understanding the occurrence and distribution of emerging pollutants and endocrine disruptors in sensitive coastal South Florida Ecosystems. *Science of the Total Environment*, 757. <https://doi.org/10.1016/j.scitotenv.2020.143720>
22. Podder, A., Sadmani, A. H. M. A., Reinhart, D., Chang, N. bin, & Goel, R. (2021). Per and poly-fluoroalkyl substances (PFAS) as a contaminant of emerging concern in surface water: A transboundary review of their occurrences and toxicity effects. *Journal of Hazardous Materials*, 419, 126361. <https://doi.org/10.1016/J.JHAZMAT.2021.126361>
23. Post, G. B. (2021). Recent US State and Federal Drinking Water Guidelines for Per-and Polyfluoroalkyl Substances. *Environmental Toxicology and Chemistry*, 40(3), 550–563. <https://doi.org/10.1002/etc.4863>
24. Quinete, N., Castro, J., Fernandez, A., Zamora-Ley, I. M., Rand, G. M., & Gardinali, P. R. (2013). *Occurrence and Distribution of Endosulfan in Water, Sediment, and Fish Tissue: An Ecological Assessment of Protected Lands in South Florida*. <https://doi.org/10.1021/jf403140z>
25. Quinete, N., Lavandier, R., Dias, P., Taniguchi, S., Montone, R., & Moreira, I. (2011). Specific profiles of polybrominated diphenylethers (PBDEs) and polychlorinated biphenyls (PCBs) in fish and tucuxi dolphins from the estuary of Paraíba do Sul River, Southeastern Brazil. *Marine Pollution Bulletin*, 62(2), 440–446. <https://doi.org/10.1016/J.MARPOLBUL.2010.11.021>
26. Rahman, M. F., Peldszus, S., & Anderson, W. B. (2014). Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Research*, 50, 318–340. <https://doi.org/10.1016/J.WATRES.2013.10.045>
27. Sardiña, P., Leahy, P., Metzeling, L., Stevenson, G., & Hinwood, A. (2019). Emerging and legacy contaminants across land-use gradients and the risk to aquatic ecosystems. *Science of The Total Environment*, 695, 133842. <https://doi.org/10.1016/J.SCITOTENV.2019.133842>
28. Savvaides, T., Koelmel, J. P., Zhou, Y., Lin, E. Z., Stelben, P., Aristizabal-Henao, J. J., Bowden, J. A., Godri Pollitt, K. J., & Pollitt, K. J. G. (n.d.). *Prevalence and Implications of Per- and Polyfluoroalkyl Substances (PFAS) in Settled Dust*. 1, 3. <https://doi.org/10.1007/s40572-021-00326-4>
29. Skutlarek, D., Exner, M., & Färber, H. (2006). Perfluorinated surfactants in surface and drinking waters. *Environmental Science and Pollution Research*, 13(5). <https://doi.org/10.1065/espr2006.07.326>
30. Team, R. C. (2019). *R: A language and environment for statistical computing*. Vienna, Austria.
31. Vieira, V. M., Hoffman, K., Shin, H. M., Weinberg, J. M., Webster, T. F., & Fletcher, T. (2013). Perfluorooctanoic acid exposure and cancer outcomes in a contaminated community: A geographic analysis. *Environmental Health Perspectives*, 121(3). <https://doi.org/10.1289/ehp.1205829>

32. Wang, Q., Tsui, M. M. P., Ruan, Y., Lin, H., Zhao, Z., Ku, J. P. H., Sun, H., & Lam, P. K. S. (2019). Occurrence and distribution of per- and polyfluoroalkyl substances (PFASs) in the seawater and sediment of the South China sea coastal region. *Chemosphere*, *231*, 468–477. <https://doi.org/10.1016/J.CHEMOSPHERE.2019.05.162>
33. Winchell, L. J., Wells, M. J. M., Ross, J. J., Fonoll, X., Norton, J. W., Kuplicki, S., Khan, M., & Bell, K. Y. (2021). Analyses of per- and polyfluoroalkyl substances (PFAS) through the urban water cycle: Toward achieving an integrated analytical workflow across aqueous, solid, and gaseous matrices in water and wastewater treatment. *Science of The Total Environment*, *774*, 145257. <https://doi.org/10.1016/J.SCITOTENV.2021.145257>
34. Wood, C., Balazs, G. H., Rice, M., Work, T. M., Jones, T. T., Sterling, E., Summers, T. M., Brooker, J., Kurpita, L., King, C. S., & Lynch, J. M. (2021). Sea turtles across the North Pacific are exposed to perfluoroalkyl substances. *Environmental Pollution*, *279*, 116875. <https://doi.org/10.1016/J.ENVPOL.2021.116875>
35. Yamashita, Y., Jaffé, R., Maie, N., & Tanoue, E. (2008). *Yamashita, Y., et al. Assessing the dynamics of dissolved organic matter (DOM) in coastal environments by excitation emission matrix fluorescence and parallel factor analysis (EEM-PARAFAC). Limnol. Oceanogr.*, *53*(5), 2008, 1900–1908.
36. Yang, Y. Y., Toor, G. S., Wilson, P. C., & Williams, C. F. (2017). Micropollutants in groundwater from septic systems: Transformations, transport mechanisms, and human health risk assessment. *Water Research*, *123*, 258–267. <https://doi.org/10.1016/J.WATRES.2017.06.054>
37. Web reference:
38. United States Census Bureau. [census.gov](https://www.census.gov), accessed on April 1, 2020
39. City of Tampa. [Tampa.gov](https://www.tampa.gov), accessed on April 1, 2020

Figures

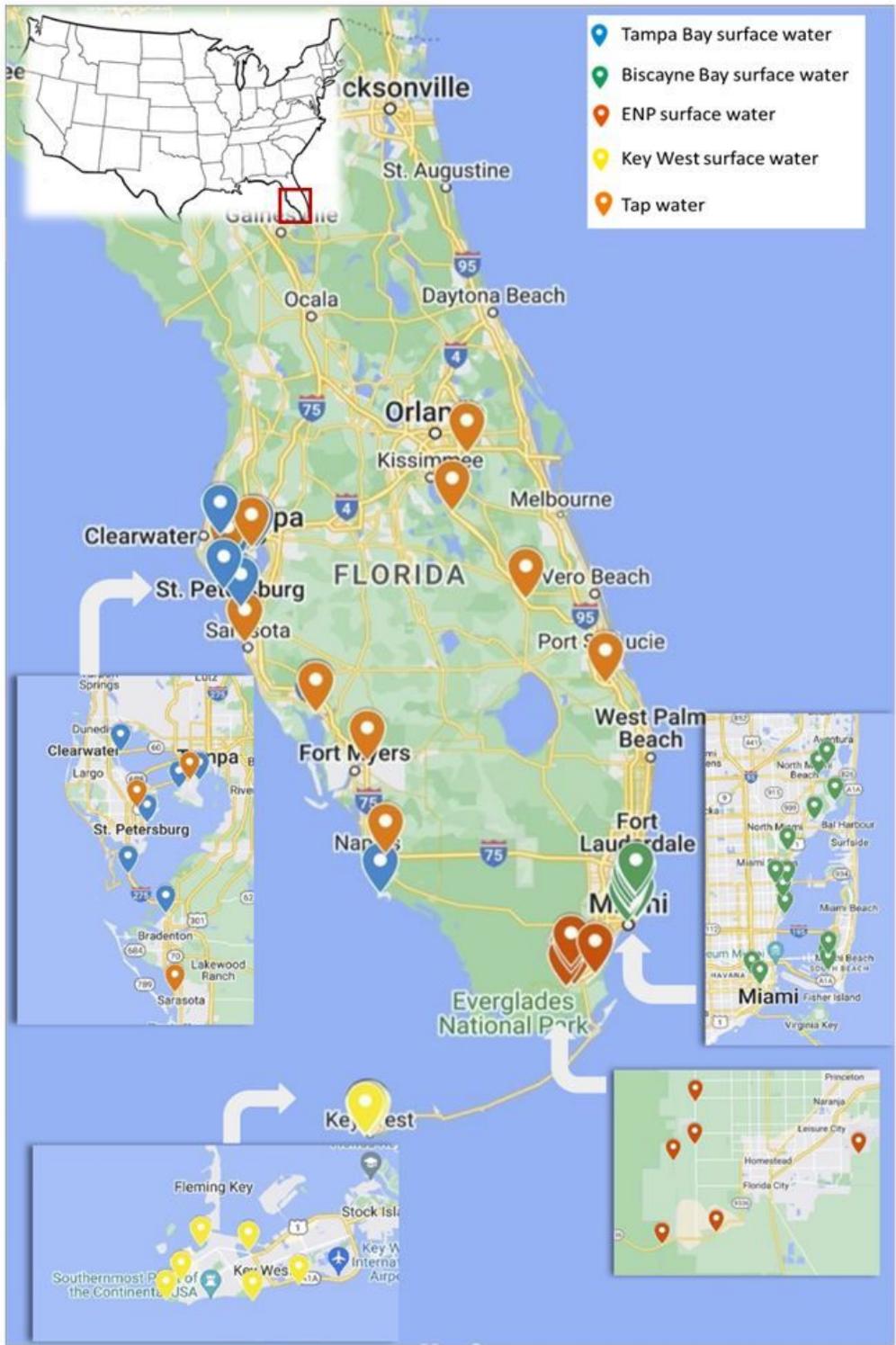


Figure 1

PFAS surface water and tap water sampling sites across Central and South Florida

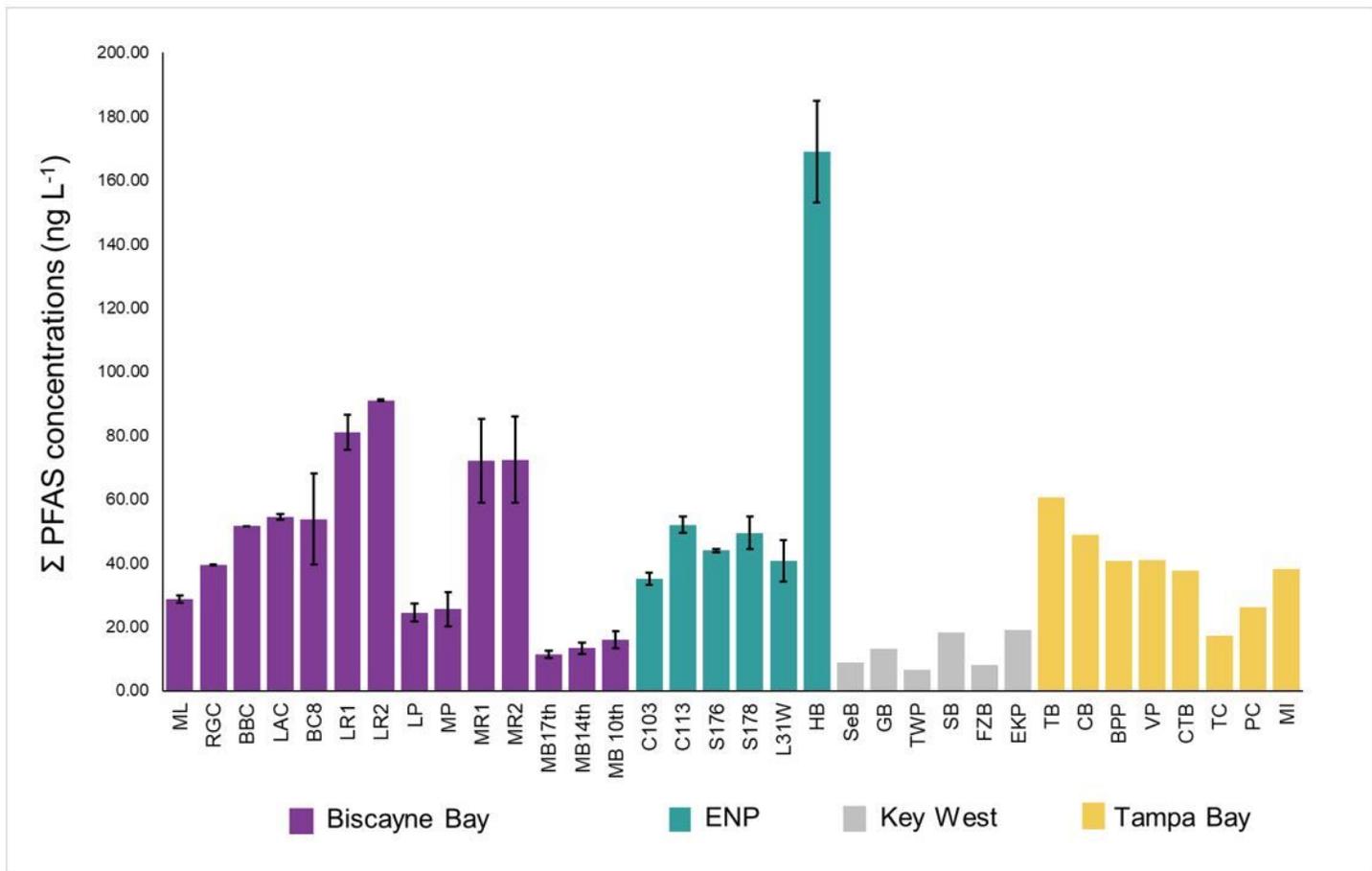


Figure 2

Average of total PFAS concentrations in samples collected from Biscayne Bay, ENP, Key West, and Tampa Bay. The variability of the data from the same sampling sites collected ≥ 2 times is presented as error bar.

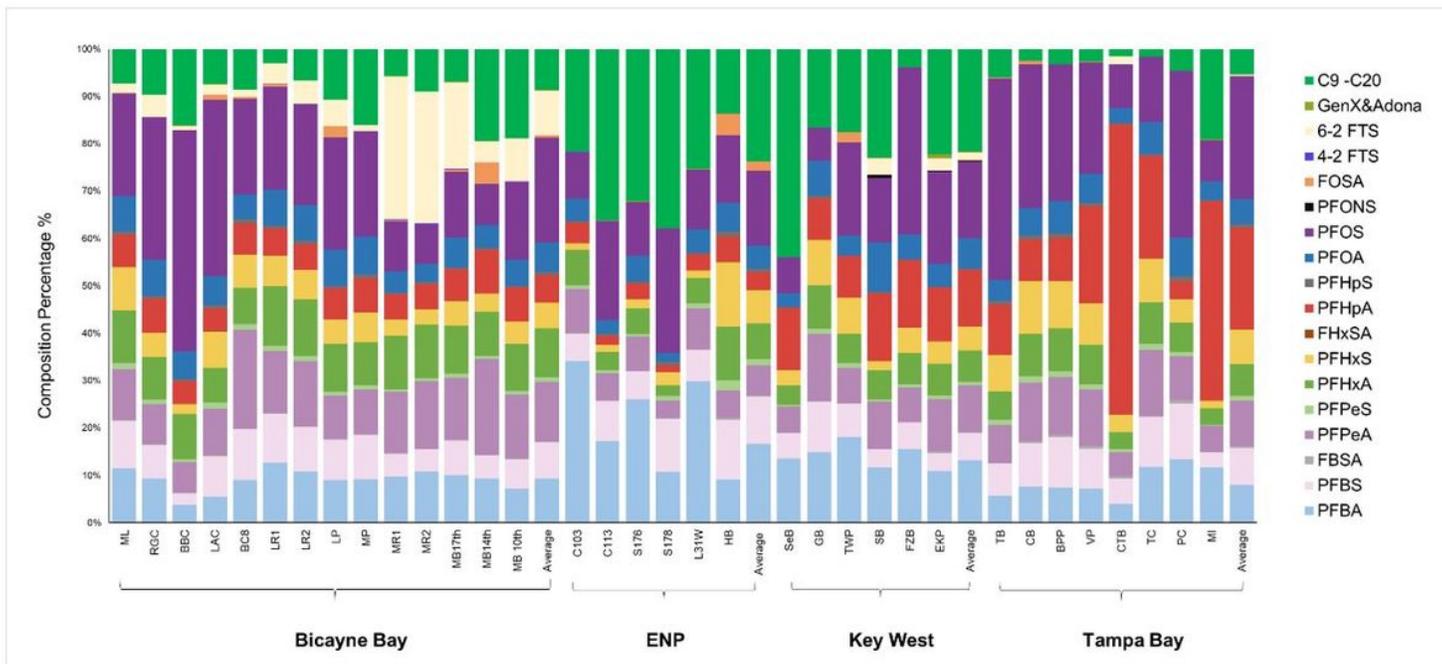


Figure 3

PFAS composition percentage in surface water sample along Biscayne Bay, ENP, Key West, and Tampa Bay. Group C9-C20 combined PFAS congeners with carbon chain ≥ 9 in each sample. PFAS classes and carbon chain length groups can be found in Table S1.

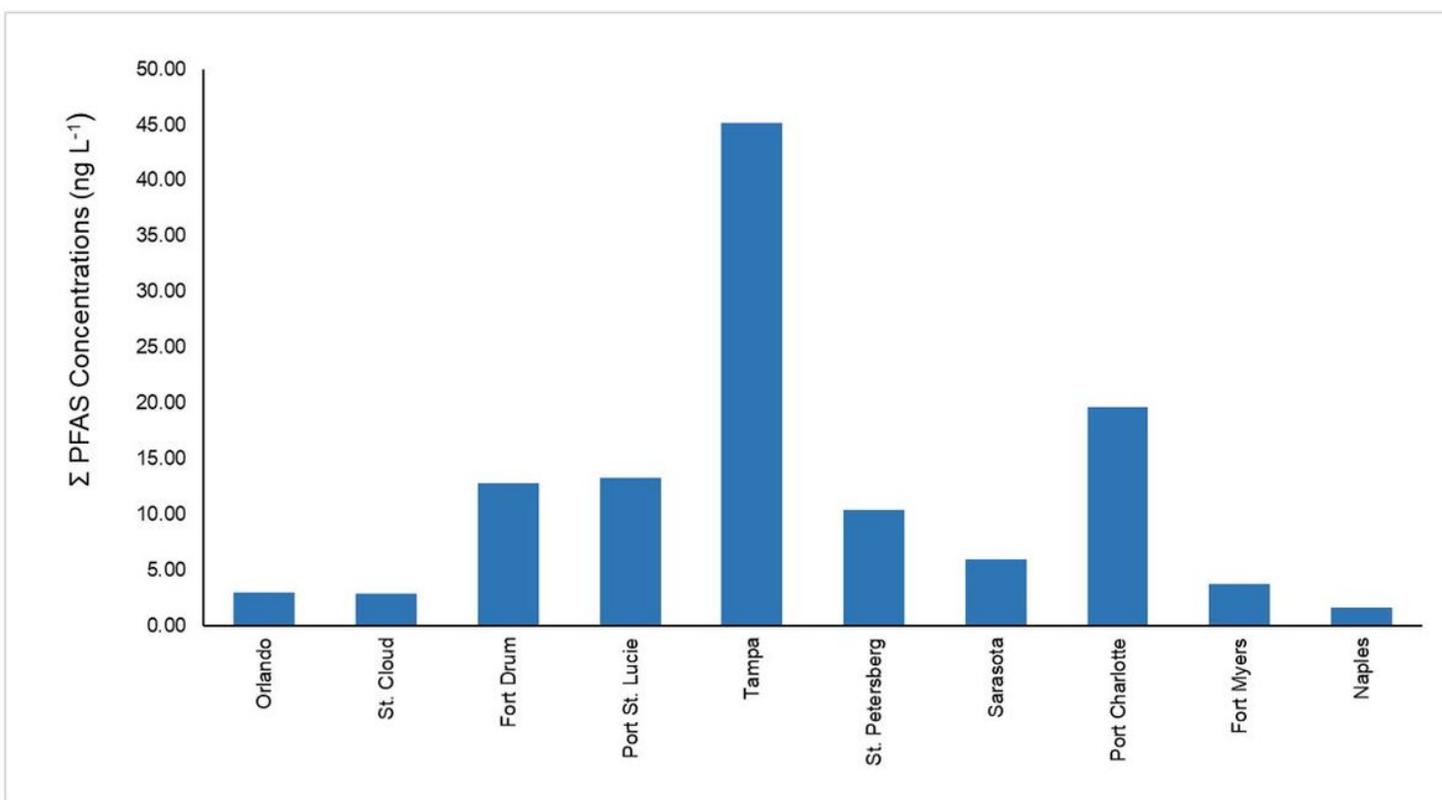


Figure 4

Total PFAS concentration of tap water samples from major cities on the West coast and Central Florida.

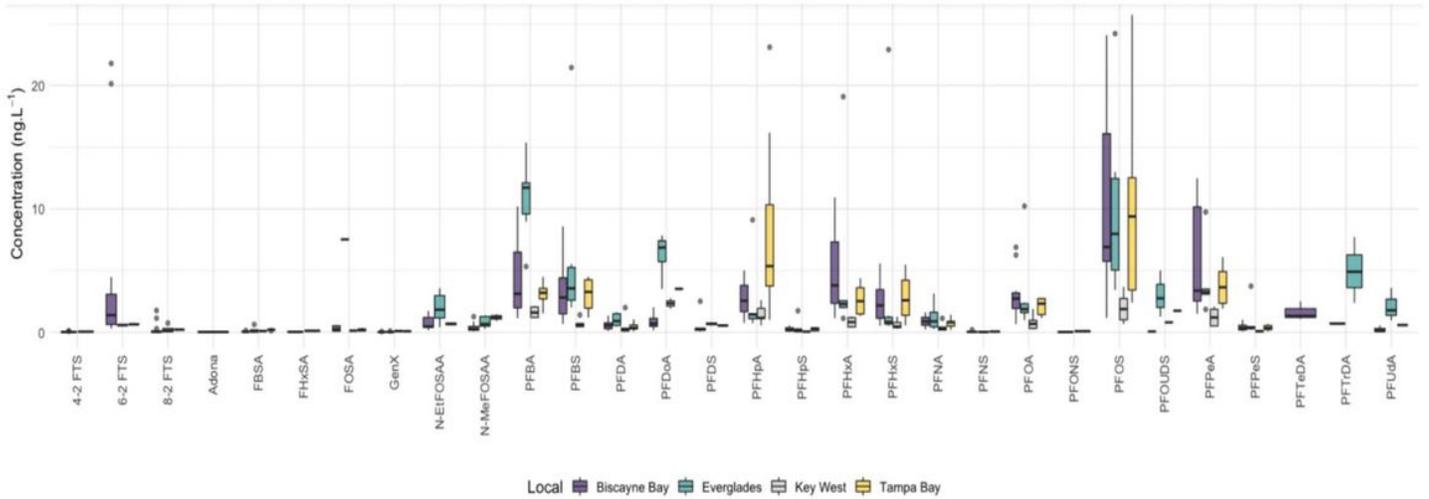


Figure 5

Boxplot of PFAS concentration in surface water from Biscayne Bay, ENP canals, Tampa Bay, and Key West. Median (the middle line), minimum and maximum values excluding outliers (upper and lower whiskers) are shown in the boxplot. The circles represent outliers.

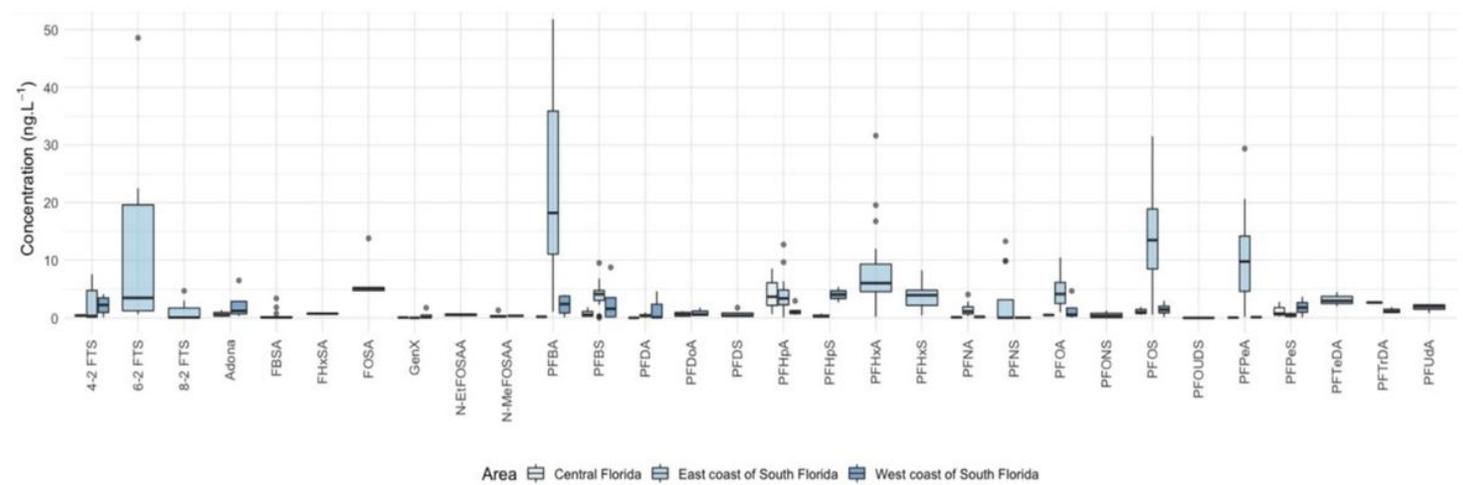


Figure 6

Boxplot of PFAS concentration of tap water samples in defined Central Florida, West coast of South Florida, and East coast of South Florida. Median (the middle line), minimum and maximum values

