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Assessing per- and polyfluoroalkyl substances (PFAS) in sediments and fishes in a large, urbanized estuary and the potential human health implications

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The primary source of chronic exposures to per- and polyfluoroalkyl substances (PFASs) in humans is through the ingestion of contaminated foods and drinking water, with fish and other seafood being a major contributor. Nevertheless, there is scant literature on the dietary exposure to PFASs for the general United States (U.S.) population. The Tampa Bay (Florida, USA) region has the highest population density in the State and communities and their attendant support services are arrayed in an urban to semi-rural continuum from the head of the Bay to the ocean mouth. Tampa Bay supports productive recreational and commercial fisheries, providing a diverse community of species. A variety of potential PFAS sources surround Tampa Bay including airports, industry, wastewater treatment plants, fire-fighting training areas and military installations. The objective of this study is to quantify PFASs in sediment and fishes collected from Tampa Bay to further estimate human health risks from dietary exposures. Sediment ($n = 17$) and fish (24 species, $n = 140$) were collected throughout Tampa Bay in 2020 and 2021 and analyzed for 25 PFAS compounds. Concentrations of PFASs in sediments and edible tissues of fish ranged from 36.8 to 2,990 ng kg⁻¹ (dry weight) and 307 to 33,600 ng kg⁻¹ (wet weight), respectively. Generally, levels were highest in Old Tampa Bay and decreased south towards the Gulf of Mexico. Profiles in both matrices were generally dominated by perfluorooctane sulfonic acid (PFOS) with variations by location. Estimated human health risks from the consumption of contaminated fish collected in Tampa Bay exceeded concentration thresholds for minimum risk levels (MRLs) and tolerable weekly intake (TWIs) values for adults and youths. Additionally, concentrations of PFOS in edible fish tissues of several recreationally important species collected in Tampa Bay exceeded consumption guideline

levels established by several governmental agencies. In the current context, the elevated levels of PFAS in Tampa Bay and the exceedances of available thresholds for potential human health risks are a cause for concern and justify a more intensive examination especially for more heavily utilized species, particularly those used in subsistence-level fishing, which, as elsewhere may be significantly under documented.

KEYWORDS

tier 1 original research PFAS, sediment, fish, risk assessment, dietary exposure, consumption advisories

1 Introduction

Per- and polyfluorinated alkyl substances (PFASs) were first developed in the 1940s and later manufactured for product applications in the 1950s (3M, 2021). PFASs are a group of over 9,000 synthetic chemicals comprised of materials with properties that include electrical insulating and oil, water, temperature, chemical and fire resistance. These characteristics are appealing to a variety of industries resulting in their extensive use as surfactants and coatings in major applications including packaging, nonstick cookware, aqueous film forming foams (AFFF) for firefighting, electronic devices, aircraft and vehicle applications, and various textiles (e.g., carpets, leather products, furniture, clothing, surgical gowns, etc.). Since PFAS compounds are extremely pervasive, persistent, and environmentally stable, they have been detected globally in all environmental media (air, water, soil), wildlife, food items, and humans (Buck et al., 2011; ATSDR, 2018; Nakayama et al., 2019; Podder et al., 2021; Fiedler et al., 2022; Sims et al., 2022).

One of the most commonly used PFASs, perfluorooctanoate acid (PFOA) is a possible human carcinogen (IARC, 2017). Additionally, another common PFAS, perfluorooctanesulfonic acid (PFOS) and a replacement compound, known as GenX (aka HFPO-DA), both have carcinogenic potential (USEPA, 2016b; 2018). Major concerns regarding the persistence and toxicity of PFASs have led to regulatory actions to phase-out the manufacturing and emissions of PFOS and PFOA related compounds; however, replacement chemicals are equally persistent, and their inherent toxicity is often unknown (USEPA, 2000; Buck et al., 2011). Primary routes of exposures in humans are through ingestion of contaminated food, food-packaging, water, dust, and hand-to-mouth transfer from carpets (Trudel et al., 2008; Carnero et al., 2021; Curtzweiler et al., 2021). Although the United States Environmental Protection Agency (USEPA) has issued non-enforceable drinking water health advisories for individual and combined concentrations (70 ng L^{-1}) of PFOA and PFOS, there are currently no maximum contaminant levels (MCLs) established for any PFASs (USEPA, 2009; OECD/UNEP, 2013; USEPA,

2016a). The lack of federal guidelines has resulted in seven states adopting their own drinking water guidelines ranging from 14 to $1,000 \text{ ng L}^{-1}$ (Cordner et al., 2019).

Considering the greatest source of chronic exposures to PFOS and PFOA in the general population is through the ingestion of contaminated food and drinking water, there are, surprisingly, no published studies on the dietary exposure of PFAS for the general United States (U.S.) population, nor has the U.S. established any consumption guidelines for contaminated foods, such as daily or weekly intake values. However, intermediate-duration oral minimal risk levels (MRL) have been derived in the United States for five PFASs, PFOA ($0.000003 \text{ mg kg}^{-1} \text{ day}^{-1}$), PFOS ($0.000002 \text{ mg kg}^{-1} \text{ day}^{-1}$), PFNA ($0.000003 \text{ mg kg}^{-1} \text{ day}^{-1}$), and PFHxS ($0.00002 \text{ mg kg}^{-1} \text{ day}^{-1}$); (ATSDR, 2015). In addition, the USEPA has derived reference doses (RfD) for noncancerous health effects based on oral exposures of PFOS ($0.00002 \text{ mg kg}^{-1} \text{ day}^{-1}$), PFOA ($0.00002 \text{ mg kg}^{-1} \text{ day}^{-1}$), and PFBS ($0.0003 \text{ mg kg}^{-1} \text{ day}^{-1}$) (USEPA, 2017; 2021). These RfDs have been utilized by several states to develop fish advisories based on PFAS concentrations measured in local fish. For instance, the Great Lakes Consortium has recommended dietary restrictions on fish containing greater than $10 \mu\text{g kg}^{-1}$ of PFOS in edible tissues (GLCFCA, 2019). More extensive research evaluating food and dietary exposures has been conducted mainly outside the United States including in Europe, Asia, and Canada. Fish and other seafoods were found to be the most important contributor to PFOA and PFOS exposure followed by eggs, meat and fruit (EFSA, 2020). In 2020, the European Food Safety Authority (EFSA) updated their 2018 guidance on PFAS levels in food and established new recommended total weekly intake (TWI) values of $4.4 \text{ ng kg}^{-1} \text{ bw}^{-1}$ (bw = body weight) per week for the sum of four PFAS compounds: PFOA, PFOS, PFNA, and PFHxS (EFSA, 2020).

Tampa Bay is Florida's largest open-water estuary, inhabited by over 200 fish species, including dozens that support fisheries. The State of Florida is considered a prime recreational and commercial fishing destination resulting in \$38 million in annual saltwater license sales and providing \$14 billion in economic impact from both saltwater and freshwater recreational fishing (<https://myfwc.com/conservation/value/saltwater-fishing/>). Tampa Bay is a popular fishing destination

for the four million state-wide anglers in Florida. There are various potential PFAS sources surrounding the Tampa Bay region including military installations, airports, and wastewater treatment plants. Thus, it is surprising there are currently no available data on PFAS levels in fish from this region, considering the popularity of fishing in this area.

The objectives of the present study were to: (1) determine if PFASs were present in sediments and edible tissues of fish collected in Tampa Bay, and (2) compare detectable levels of PFASs in the edible tissues of fishes to available consumption guidelines to estimate potential human health risks from fish consumption. Consequently, we expect this research will guide future research needs regarding PFAS contamination in Florida, and particularly focus attention on species presenting elevated risks for consumption. This information will assist resource managers in determining if fish consumption advisories should be considered in the Tampa Bay region.

2 Materials and methods

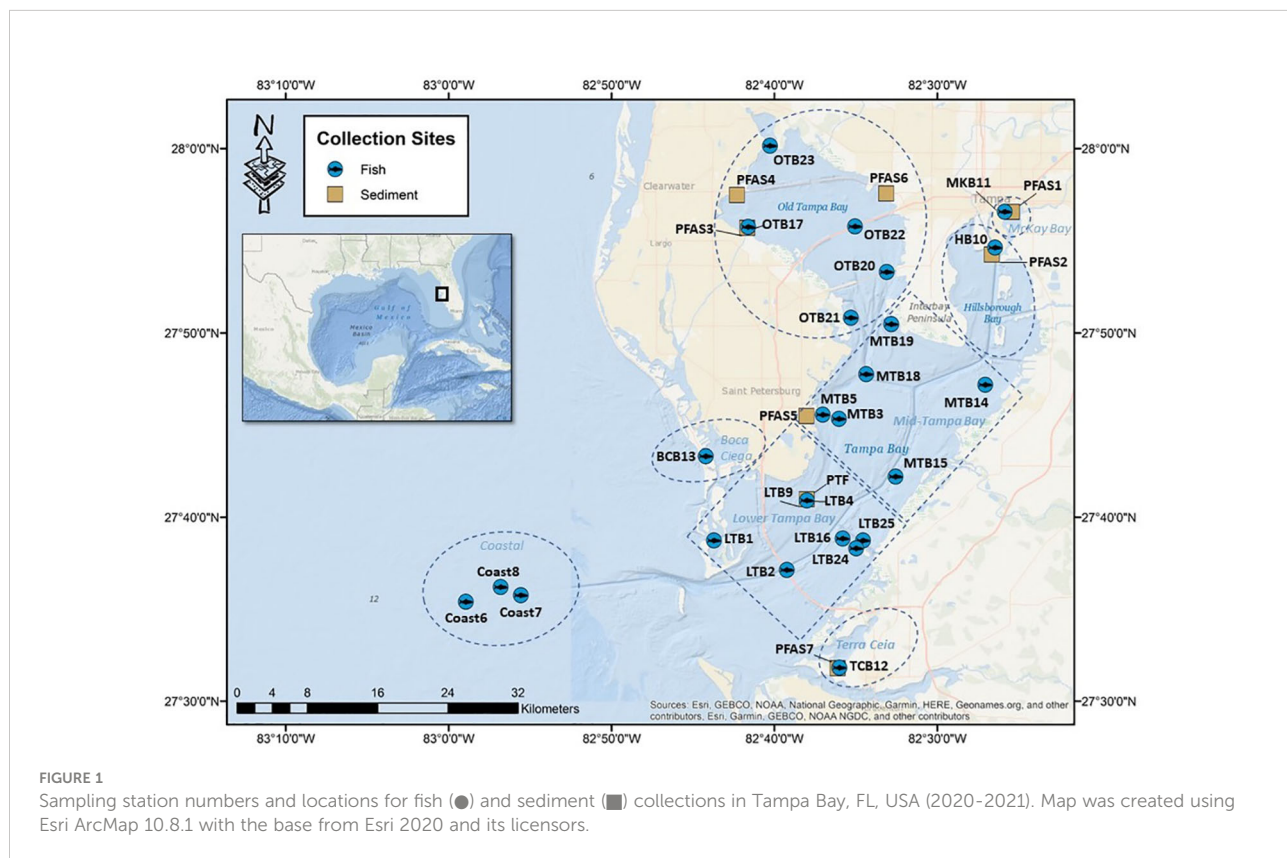
2.1 Site description

Tampa Bay is located on the central west coast of Florida and is the largest open water estuary in the state. The Bay has a surrounding watershed of 5,700 km², covers a surface area of

approximately 1,030 km², with a mean depth of 3 m, and a maximum depth of 13.3 m. Tampa Bay consists of eight segments, Old Tampa Bay, Hillsborough Bay, McKay Bay, Middle Tampa Bay, Lower Tampa Bay, Manatee River, Terra Ceia Bay and Boca Ciega Bay (Figure 1) (Karlen et al., 2015). The greater Tampa Bay area is considered a humid subtropical climate with annual temperatures typically ranging from 11 to 32°C. The region's human population in 2019 was estimated at 3.1 million with a 2% annual growth rate for the region which currently outpaces the national average (1.5% annual growth rate per year) (www.census.gov/usapopulation.org/tampa-population/). There are five major airports surrounding the region, a number of military bases, and wastewater treatment (mostly secondary) outfalls throughout the region producing ~ 242 thousand m³/day of effluent (www.tampa.gov/wastewater/info/advanced-wastewater-treatment-plant/facts-of-interest). Other potential sources of PFASs to the bay include fire-fighting training facilities, manufacturing urbanization with Hillsborough and Old Tampa Bay being the most urbanized, and the southeast portion of the Bay being more rural.

2.2 Standards and reagents

Acetonitrile (ACN, Optima LC/MS grade), methanol (MeOH, Optima LC/MS grade), acetic acid (Optima LC/MS grade), formic acid 99% purity (Optima LC/MS grade) and



ammonium hydroxide (ACS grade) were purchased from Fisher Scientific (Waltham, MA, USA). Water was purified through a Millipore water purification system (Bedford, MA, USA) with a 0.22 μm membrane filter and a specific resistance of 18 $\mu\Omega$. Individual native compounds (chemical purities of > 98%), and mass-labelled internal and surrogate standards (chemical purities of > 98% and isotopic purities of \geq 99%) were purchased through Wellington Laboratories (Guelf, ON, Canada).

2.3 Sediment collection, composition and extraction methodology

2.3.1 Sample collection

In 2020, sediments were collected from six segments of the Bay and focused on areas adjacent to airports and wastewater treatment plants (WWTP) throughout Tampa Bay. Specific site selections followed the Tampa Bay Benthic Monitoring Program which employs a stratified-random sampling strategy adopted from the EPA's Environmental Monitoring and Assessment Program – Estuaries (EMAP-E) design (Karlen et al., 2015). Sediment samples were collected from seven sites in duplicate and one site in triplicate for a total of 17 sediment samples (Figure 1). Sediments were collected at each site using a Young-Modified Van Veen grab sampler aboard an aluminum cabin boat operated by the Environmental Protection Commission of Hillsborough County. The grab sampler and all sampling utensils were field cleaned with Alconox detergent, rinsed with ambient seawater and decontaminated with isopropyl alcohol prior to collections at each site. The grab sample was taken from a sediment depth of 15 cm, covering an area of 0.04 m². Wearing gloves, the top layer (~2 cm) of sediment was removed from each grab using a stainless-steel spoon, placed in a stainless-steel beaker and homogenized by stirring. The homogenized surface sediments were then transferred to certified I-Chem high density polyethylene (HDPE) jars (Fisher Scientific, Waltham, MA, USA), immediately placed in a cooler on bagged ice for transport back to the laboratory for storage at -20°C until further analysis.

2.3.2 Sediment composition

Sediment composition was determined following the high-temperature combustion method (Standard Methods Committee of the American Public Health Association) and EPA 620/R-95/008 (Strobel et al., 1995) outlined in the Field and Laboratory Methods Manual for Tampa Bay National Estuary Program (Versar, 1993). Briefly, sand and clay particles were separated by wet-sieving through a 63 μm stainless steel sieve and weighed using standard procedures (Plumb, 1981). Approximately 45-50 g wet weight for predominantly sandy sediments or 20-25 g for predominantly silty sediments were used for the percent silt and clay composition analysis. The

sediments were combined with 20ml of the dispersant solution (100 mg of hexametaphosphate) and 30 ml distilled water and stirred for 1-5 minutes using a small spatula to disperse sediment aggregates. The homogenized sample was wet sieved through a 63 μm sieve using the minimal amount of distilled water as possible. The retained fraction (>63 μm) was transferred to a pre-weighed glass beaker and dried at 100°C for 24 hrs. and then weighed. The <0.63 μm filtrate was transferred to a 1000 ml graduated cylinder and the volume was filled to the next highest 50 ml mark with distilled water and homogenized by stirring. A 40 ml subsample was transferred to a pre-weighed glass beaker with a volumetric pipette and dried at 100°C for 24 hrs., then weighed. Weighed samples were dried for an additional 24 hrs. and then reweighed as a check on the stability of the original measurement. Unused sediments from each sample were stored at 4°C for future QA/QC analysis. Total organic carbon was analyzed using a Shimadzu TOC-L Series SSM. Samples were filtered and dried overnight at 100°C then ground and dried again at 100°C and reground. A total of 600 mg of ground sediment was weighed (300 mg for both Total Carbon and Inorganic Carbon measurements). The total carbon fraction was combusted at 900°C for 10-15 minutes, and the inorganic carbon fraction was combusted at 250°C for 8-10 minutes.

2.3.3 Sediment extractions

Freeze dried sediment samples were extracted following the American Society for Testing and Materials (ASTM) 7968 method (ASTM, 2017). Briefly, two grams of freeze-dried sediments were added to a 15 mL polypropylene (PP) test tube (Fisher Scientific, Waltham, MA, USA) followed by 10 mL of 1:1 Millipore water:MeOH and adjusted to a pH of 9 – 10 using ammonium hydroxide. Samples were then vortexed, placed on a mechanical shaker at 400 rpm for one hour and centrifuged at 1,900 rpm for 10 minutes. The entire supernatant was then filtered into a clean 15 mL PP test tube using disposable polypropylene syringe with a 0.2 μm polypropylene filter with a regenerated cellulose membrane (Captiva, Agilent Technologies, Santa Clara, CA, USA). Following filtration, the extract pH was adjusted to 3.5 – 4.0 using acetic acid. An aliquot of each sample was transferred to a PP autosampler vial and sealed with a PP cap (Agilent Technologies, Santa Clara, CA, USA). Internal standards were added to the final extracts (1 mL) prior to injection.

2.4 Fish collections and extraction methodology

Twenty-four species of fish (Table 1) were collected onboard either chartered (2020) or Florida Fish and Wildlife Research Institute vessels (2021) using hook and line, baited traps, nets or 183 m center bag haul seines at 25 locations from seven segments of Tampa Bay near potential sources, such as

TABLE 1 Common and scientific names for the fish collected in Tampa Bay (2020–2021).

Common name	Scientific name
Atlantic Bumper	<i>Chloroscombrus chrysurus</i>
Black Sea Bass	<i>Centropristis striata</i>
Blue Runner	<i>Caranx crysos</i>
Channel Catfish	<i>Ictalurus punctatus</i>
Common Snook	<i>Centropomus undecimalis</i>
Crevalle Jack	<i>Caranx hippos</i>
Gafftopsail Catfish	<i>Bagre marinus</i>
Gag	<i>Mycteroperca microlepis</i>
Gulf Toadfish	<i>Opsanus beta</i>
Hardhead Catfish	<i>Ariopsis felis</i>
Ladyfish	<i>Elops saurus</i>
Little Tunny	<i>Euthynnus alletteratus</i>
Gray Snapper	<i>Lutjanus griseus</i>
Pinfish	<i>Lagodon rhomboides</i>
Round Scad	<i>Decapterus punctatus</i>
Southern Flounder	<i>Paralichthys lethostigma</i>
Southern Puffer	<i>Sphoeroides nephelus</i>
Spanish Mackerel	<i>Scomberomorus maculatus</i>
Spanish Sardine	<i>Sardinella aurita</i>
Spotted Seatrout	<i>Cynoscion nebulosus</i>
Striped Mullet	<i>Mugil cephalus</i>
Thread Herring	<i>Opisthonema oglinum</i>
Tomtate	<i>Haemulon aurolineatum</i>
White Grunt	<i>Haemulon plumieri</i>

airports, wastewater treatment plants and military installations (Figure 1). Biometrics of each fish were recorded in the field (Table S1), the animals then placed in polypropylene bags (ULINE, Pleasant Prairie, WI, USA) and stored in coolers on bagged ice for transport back to the laboratory. A total of 140 individual fish ($n = 140$) from 24 species were collected in Tampa Bay and analyzed for 25 target PFASs.

The extraction of fish tissue followed Pulster and Giardina (2022). Briefly, filets of muscle tissues from individual fish were excised using solvent rinsed knives, placed in amber jars and homogenized by finely mincing using solvent rinsed dissection scissors. Two grams of homogenized tissue was then placed in a 50 mL polypropylene test tube; surrogate standards were added and allowed to sit at room temperature for 15 minutes (Pulster and Giardina, 2022). A ceramic homogenizer and 2 mL of water with 1% formic acid was then added and homogenized for 2 min at 1500 rpm (1600 Mini G, SPEX SamplePrep), followed by 8 mL of cold ACN containing 2% formic acid and homogenized for an additional 5 min (1500 rpm) and then centrifuged for 5 minutes at 5,000 rpm. An aliquot of 2.4 mL of the extract supernatant was then transferred to a 3 mL Captiva EMR Lipid cartridge (Agilent Technologies, Santa Clara, CA, USA) and allowed to elute *via* gravity. Once the extract was no longer visible, 600 μ L of 80:20

Acetonitrile (ACN):Millipore water was added and eluted by gravity until dry then vacuum was applied until completely dry. The extract was mixed, and then 500 μ L of the clean extract was transferred to a polypropylene autosampler vial; internal standards were added, and 300 μ L of water was added for a final extract volume of 800 μ L.

2.5 Targeted PFAS analysis

Prior to analysis, the liquid chromatography tandem mass spectrometer (LC/MS/MS, Agilent 1290 Infinity II LC – 6470 MS/MS) was configured to reduce system background contamination (i.e., peek tubing and pump seals, inline filter and delay column) following industry recommendations (Anumol et al., 2017). The concentrations of 25 targeted PFAS (Table S2) were confirmed and quantified using liquid chromatography tandem mass spectrometry (LC/MS/MS) with a negative electrospray ionization (ESI) source (Agilent Jet Stream) and operating under the dynamic multiple reaction monitoring (dMRM) mode. Twenty microliters of sediment and fish extracts were injected at a flow rate of 300 μ L min^{-1} and analyte separation was achieved using a Zorbax Eclipse Plus C18 column (2.1 mm x 100 mm, 1.8 μ m, Agilent Technologies) with a gradient mobile phase consisting of 20 mM ammonium acetate in 95: 5 water: ACN (mobile phase A) and 10 mM ammonium acetate in 95: 5 ACN: water (mobile phase B; Table S3). A 14 min post-run time at 100% mobile phase A was incorporated to ensure full column equilibration. The LC/MS/MS instrument conditions and acquisition parameters are further detailed in Tables S4, S5. Four PFASs were not detected in any of the sediment samples and are reported as the total of 21 PFAS (T_{21} PFAS) in dry weight (d.w.). PFEEESA was not detected in any of the fish samples, therefore concentrations are reported as the total of 24 PFAS (T_{24} PFAS) in wet weight (w.w.) for the fish muscle samples.

2.6 Human health risk assessment for fish consumption

The concentrations of four select PFAS in the edible muscle tissues of fish (all species combined) were used to estimate chronic and sub-chronic human health risks from seafood consumption in four sections of Tampa Bay: Old Tampa Bay, Hillsborough Bay, Mid-Tampa Bay, and Lower Tampa Bay. Boca Ciega, and Terra Ceia were not included due to the small sample sizes ($n < 10$). Chronic and sub-chronic human health risks were also assessed for the consumption of Striped Mullet (*Mugil cephalus*) collected in Old Tampa Bay. The 95% upper confidence limit (UCL, without non-detects) of PFAS concentrations measured in fish collected in Tampa Bay was determined using USEPA ProUCL software (V5.1). The 95%

UCL concentrations were used to estimate weekly intake (EWI) and the estimated daily dose (EDD) for sub-chronic (3 meals/week) and chronic (7 meals/week) lifetime exposures from the consumption of PFAS contaminated fishes collected from Tampa Bay. Risks were assessed for various demographic characteristics, including age, gender, race, income, and region/coastal zone (USEPA, 2011b; 2014). Results for the risks by income and region/coastal are not included herein but can be found elsewhere (USF Digital Commons doi: 10.5038/y6w7cf53m9). Health risks were estimated for the four selected PFASs: PFOS, PFOA, PFNA, and PFHxS with detectable levels in edible tissues of fish and have available consumption advisories or thresholds (e.g., minimal risk level [MRL], TWI). The following formulas were used to calculate the estimated daily dose (EDD) and estimated weekly intake (EWI):

$$EDD \text{ (mg/kg/day)} = \frac{C_{ef} \times IR \times EF \times ED}{BW \times LT}$$

where, C_{ef} is the 95% ProUCL concentration (mg g^{-1}) in the edible fish filets of an individual PFAS, ingestion rate for the consumption of estuarine fish (IR, g day^{-1}), exposure frequency ($\text{EF, days year}^{-1}$), exposure duration (ED, years), body weight (BW, kg) and days over a lifetime to assume chronic exposure (LT, days). All exposure factors ($\text{IR, EF, ED, BW, LT}$) provided in Tables S6, S7 are the USEPA recommended values (USEPA, 2011b; 2014).

$$EWI \text{ (ng/kg/bw)} = \frac{C_{ef} \times IR}{BW}$$

where, C_{ef} is the 95% ProUCL concentration (ng g^{-1}) in the edible fish filets of an individual PFAS, ingestion rates are the usual fish consumption rate (UFCR) estimates specifically for estuarine finfish (IR, g week^{-1}) and body weight (BW, kg).

2.7 Quality assurance and quality control

A QA/QC program following the ASTM and EPA methodology (USEPA, 2011a; ASTM, 2017; Shoemaker and Tettenhorst, 2018) was implemented to ensure data quality. Surrogate recoveries and 25 target PFAS were quantified using a quadratic regression fit analysis of a five-point external calibration curve (10-fold dilution, 1 – 1000 ng L^{-1}) ($R^2 = 0.9979 - 1.00$; Table S5). Recoveries for the fish ($M_3\text{PFBA: } 101 \pm 15\%$; $M_2\text{PFOA: } 92 \pm 12\%$; $M_2\text{PFDA: } 114 \pm 16\%$; $M_4\text{PFOS: } 113 \pm 13\%$) and sediment ($M_3\text{PFBA: } 95 \pm 14\%$; $M_2\text{PFOA: } 72 \pm 9\%$; $M_2\text{PFDA: } 96 \pm 15\%$; $M_4\text{PFOS: } 102 \pm 17\%$) were within acceptable ranges. The method quantitation limit (MQL) was considered the lowest standard with all compounds resolved.

2.8 Data analysis

All statistical analyses were performed using JMP Pro Version 16.0.0 (SAS Institute Inc, 1989-2021) and MATLAB R2021a (The Mathworks, 1994-2022) with the Fathom Toolbox (Jones, 2017). Differences in mean PFAS concentrations in fish and sediments by Bay segment and species were assessed using a modified permutational multivariate analysis of variance (PERMANOVA) and pair-wise modified PERMANOVA with 1,000 iterations (Anderson et al., 2017). The level of significance was set at $\alpha = 0.05$ and adjusted using the Bonferonni correction to protect against Type I errors. To evaluate associations between PFAS concentrations and biometric parameters, permutation-based Pearson's correlations were calculated using biometrics and ΣPFAS or individual PFAS concentrations. The strength of relationships was considered very weak ($r < 0.30$), weak ($r = 0.30$ to 0.50), strong ($r = 0.50$ to 0.70), or very strong ($r > 0.70$).

3 Results

3.1 PFAS levels and patterns in sediments

The composition of sediment in Tampa Bay ranged from mud to medium grained sand; the TOC ranged from 0.2 to 12% (Table 2). Four of the target PFAS compounds (NaDONA, 3,6-OPFHpA, PFPeS and PFEESA) were not found in any of the sediment samples collected in Tampa Bay. Generally, the $T_{21}\text{PFAS}$ concentrations for sediment decreased in the Bay from northeast to southwest and ranged from 36.8 to 2,990 ng kg^{-1} (d.w.). Mean concentrations of the $T_{21}\text{PFAS}$ (Figure 2A) were highest in the sediments collected in Old Tampa Bay ($1,000 \pm 1,140 \text{ ng kg}^{-1}$ d.w.) followed by Hillsborough Bay ($982 \pm 681 \text{ ng kg}^{-1}$ d.w.), Mid-Tampa Bay ($636 \pm 371 \text{ ng kg}^{-1}$ d.w.), Lower Tampa Bay ($634 \pm 296 \text{ ng kg}^{-1}$ d.w.), McKay Bay ($221 \pm 8.22 \text{ ng kg}^{-1}$ d.w.) and Terra Ceia Bay ($78.7 \pm 59.3 \text{ ng kg}^{-1}$ d.w.). Concentrations varied by collection site within each of the Bay segments (Figure S1). The small sample sizes did not allow for statistically significant differences to be detected between segment locations in the Bay. In general, compositional profiles of the sediment (Figure 3) collected in four of the five Bay segments were dominated by PFOS (50 - 72%); however, profiles varied by station. For example, Terra Ceia Bay sediments collected at station PFAS7-2 were dominated by 6:2 FTS (87%). Significant, moderate ($r = 0.40 - 0.60$) to strong ($r > 0.70$) positive relationships were detected between some individual and $T_{21}\text{PFAS}$ concentrations and moisture content, total organic carbon, total carbon and grain size (Table 3).

TABLE 2 The percent (%) composition of total organic carbon (TOC), total inorganic carbon (TIC), total carbon (TC) and silt-clay of sediment collected in various segments of Tampa Bay, 2020.

Bay segment	Field ID	TOC (%)	TIC (%)	TC (%)	Silt-Clay (%)	Silt-Clay category
Old Tampa Bay	PFAS3-1	6.00	0.25	6.30	70.1	Mud
	PFAS3-2	0.20	0.25	0.10	62.1	Mud
	PFAS4-1	0.40	0.25	0.40	5.70	Fine
	PFAS4-2	0.70	0.25	0.80	10.5	Fine
	PFAS6-1	0.40	0.25	0.50	8.40	Fine
	PFAS6-2	0.40	0.25	0.50	9.50	Fine
Hillsborough Bay	PFAS2-1	2.25	3.15	5.45	50.2	Mud
	PFAS2-2	2.30	0.25	2.40	19.00	Very Fine
	PFAS2-3	N/A	N/A	N/A	N/A	N/A
McKay Bay	PFAS1-1	0.80	0.25	0.90	9.30	Fine
	PFAS1-2	0.60	0.25	0.70	9.60	Fine
Mid-Tampa Bay	PFAS5-1	8.30	0.25	8.30	54.3	Mud
	PFAS5-2	11.9	0.25	11.9	49.2	Mud
Lower Tampa Bay	PTF11	0.05	0.05	2.50	4.20	Medium
	PTF15	0.50	0.05	4.00	3.20	Medium
Terra Ceia Bay	PFAS7-1	1.10	0.25	1.10	7.30	Fine
	PFAS7-2	0.20	0.25	0.30	2.70	Medium

(N/A, Not analyzed).

3.2 PFAS levels and patterns in edible muscle tissue of fish

Fish were collected from 24 locations throughout Tampa Bay during 2020 and early 2021. Muscle tissue from 140 individual fish from 24 species were analyzed for 25 target PFASs. Fish ranged from 13 to 69 cm in length and 0.03 to 3.7 kg in weight (Table S1). The T_{24} PFAS in muscle tissue of fish collected in Tampa Bay ranged from 307 to 33,600 ng kg⁻¹ (w.w.). Mean concentrations of T_{24} PFAS (Figure 2B) were highest in edible muscle tissues collected in Old Tampa Bay (15,600 ± 9,240 ng kg⁻¹ w.w.), followed by McKay Bay (11,100 ± 4,860 ng kg⁻¹ w.w.), Hillsborough Bay (8,720 ± 4,570 ng kg⁻¹ w.w.), Mid Tampa Bay (7,870 ± 6,600 ng kg⁻¹ w.w.), Boca Ciega (6,620 ± 4,980 ng kg⁻¹ w.w.), Lower Tampa Bay (5,300 ± 4,100 ng kg⁻¹ w.w.), Terra Ceia Bay (4,670 ng kg⁻¹ w.w.), and coastal areas (2,030 ± 1,390 ng kg⁻¹ w.w.). These comparisons use all species combined due to limited samples sizes and the lack of similar species collected from all locations. This precluded the comparison of individual species across segments of the Bay, therefore, interpretive caution should be used. Levels of PFAS in fishes also varied by station location (Figure S2A). The highest concentrations of T_{24} PFAS in muscle tissue of fish were found at stations OTB20, OTB17, MTB19, and OTB21. There were also species-specific differences observed in the mean total PFAS concentrations with the highest levels in the bottom dwelling (e.g., catfishes) and upper trophic level species (e.g., Crevalle Jack, Spotted Seatrout) (Figure S2B). Tomtate (655 ± 286 ng kg⁻¹ w.w.) and Pinfish (1,640 ± 1,080 ng kg⁻¹ w.w.) had the lowest

mean concentrations PFASs. Like sediments, fish profiles were generally dominated by PFOS (68 ± 17%), with variation by station (Figure 4). Sample sizes and length classes were not sufficient to evaluate relationships for individual species. For all species combined, significant associations were observed between fish length and T_{24} PFAS, PFHxS, PFHpS, PFOS, PFOA, PFNA, PFDA, PFUnDA, and PFDoA (Table S8). Elevated levels of PFOS in the edible tissues of some species require further research to determine effects of fish size and sex and if consumption advisories need to be considered.

3.3 Risk assessment

3.3.1 Sub-chronic and chronic exposures: Estimated daily dose

Assuming residents are consuming three meals per week consisting of fish collected from Old Tampa Bay, the EDDs for sub-chronic exposures of PFOS is either equal to or exceeds (by up to 3x) the recommended ATSDR MRL (0.000002 mg kg⁻¹ day⁻¹) (ATSDR, 2015) for all adult age, gender and race classes and exceeded the MRL by up to a factor of two for youth age classes (<11 years old) and race (black and other race; Figures 5, 6). For fish collected in Hillsborough Bay, the calculated sub-chronic EDDs were approaching, equal or exceeded the recommended MRL for adult males and several race and children between one and six years of age (Figures 5, 6). The EDDs for sub-chronic exposures from fish collected in Mid-Tampa Bay all exceeded the MRL for adults of other race

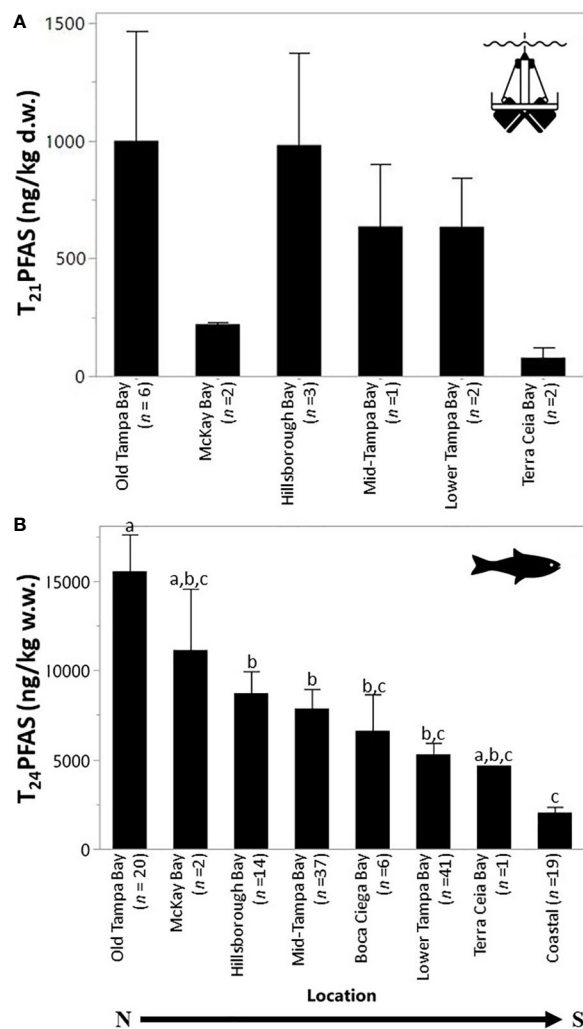


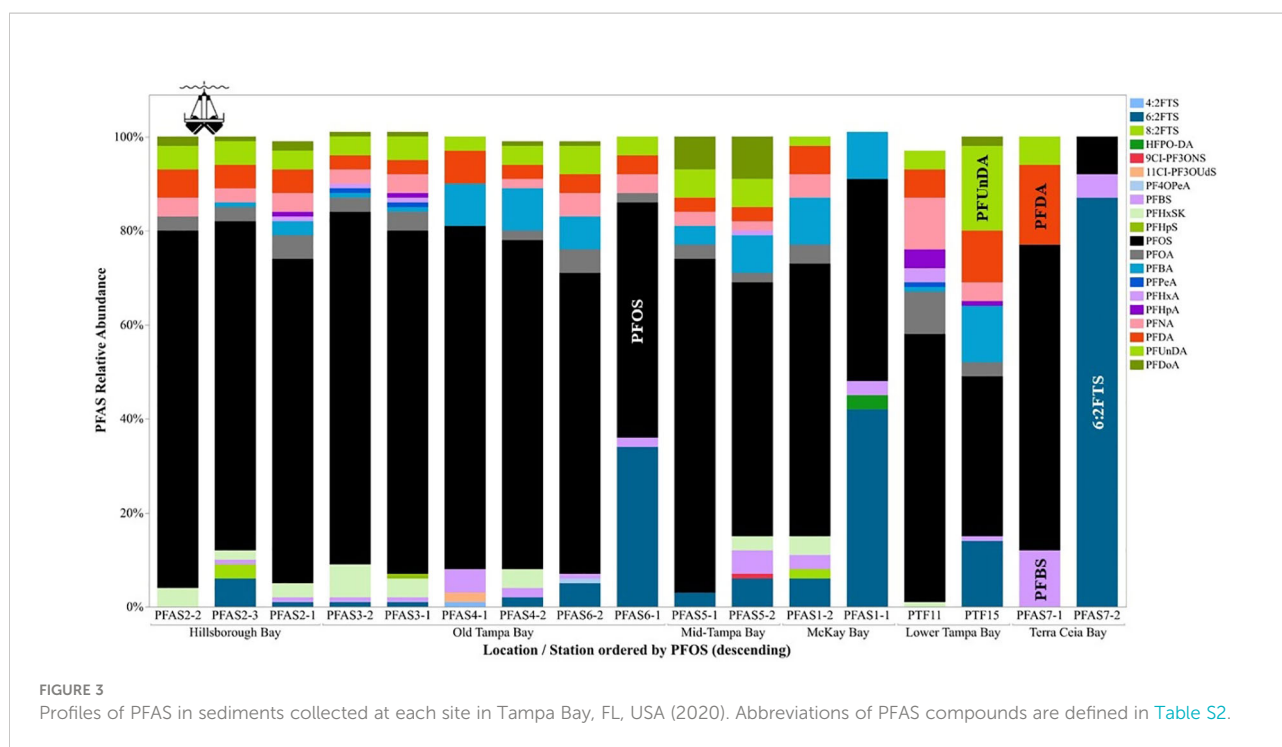
FIGURE 2

Total mean PFAS concentrations in sediment (A) and fish (B) collected by segments within Tampa Bay, FL, USA. Segments are ordered from north to south. Each error bar was constructed using 1 standard error from the mean. There were no significant differences between sediment concentrations throughout the Bay. Fish concentrations by segments not connected by the same letter are significantly different.

(Figure 6). For youth of all age and race, the sub-chronic EDDs for PFOS exposure from fish collected in Lower and Mid-Tampa Bay were all below the recommended MRL (Figures 5, 6). The calculated daily dose for sub-chronic exposures of PFOA, PFNA, and PFHxS from fish collected in all segments of Tampa Bay were below the ATSDR derived MRLs by up to 3 orders of magnitude for youth and adults of all ages and race (Figures S3, S4). Additionally, the calculated daily doses for sub-chronic exposures of PFOS from the consumption of Striped Mullet only collected in Old Tampa Bay were also below the available MRL for PFOS, PFOA, PFNA, and PFHxS exposures for all youth and adult age and race classes (Figures S5, S6).

The EDDs for chronic exposures of PFOS, assuming seven meals per week consisting of fish collected in all four Bay

segments evaluated were either approaching or up to six times higher than the derived ATSDR MRL for all adult demographics (age, race, gender, Figures 5, 6). Chronic exposures of PFOS in youth of all ages and race (except non-Hispanic white) from the consumption of fish collected in Old Tampa Bay were three times higher than the recommended MRL (Figures 5, 6). MRLs were also exceeded for youth (all ages, black or other race) consuming fish collected in Hillsborough Bay. In Mid-Tampa Bay, the MRLs were exceeded for chronic PFOS exposures for certain youth age classes (<11 years old) and race (black) whereas the MRLs were only exceeded for youth less than six years of age from fish collected in Lower Tampa Bay. For PFOA, PFNA, and PFHxS the calculated daily dose for chronic exposures from the consumption of fish collected in all



segments of Tampa Bay were as much as three orders of magnitude below the ATSDR derived MRLs for all youth and adult demographics (Figures S7, S8). The calculated daily dose for chronic PFOS exposure from consuming just Striped Mullet collected in Old Tampa Bay was approaching the MRL for youths less than six years of age and exceeded the derived MRL for other race adults and was approaching the derived MRL for several other demographic classes of adults (Figures S5, S6). The calculated daily dose for chronic exposures of PFOA, PFNA, and PFHxS from the consumption of Striped Mullet collected in Old Tampa Bay were all below the ATSDR derived MRLs (Figure S5, S6).

3.3.2 Estimated weekly intake

The EWIs for the combined exposures of PFOS, PFOA, PFNA, and PFHxS from the consumption of fish (all species combined) collected in all segments of Tampa Bay exceeded the EFSA TWI derived for food ($4.4 \text{ ng kg}^{-1} \text{ bw}$) for all demographics of youths and adults (Figure S9). Adults of other race and youth less than three years old had the highest EWIs in all segments of Tampa Bay. For adults of other race, the EWIs were 7.5, 10, 13, and 24 times higher than the EFSA guidelines in Lower Tampa Bay, Mid-Tampa Bay, Hillsborough, and Old Tampa Bay, respectively. For youth less than three years of age, the EWIs were five, seven, nine, and 17 times higher than the recommended TWIs in Lower Tampa Bay, Mid-Tampa Bay, Hillsborough, and Old Tampa Bay, respectively. Additionally, the EWIs for the exposures of PFOS, PFOA, PFNA, and PFHxS from the consumption of Striped Mullet collected only from Old

Tampa Bay also exceeded the EFSA derived TWI for all demographics of youths and adults (Figure 7). The EWIs for youths less than three years and adults of other race consuming Striped Mullet from Old Tampa Bay were a factor of seven and 10 times higher, respectively, than the EFSA TWI guidelines.

3.3.3 Consumption advisories

Concentrations of PFOS in edible tissues of fish collected in Tampa Bay ranged from 0.92 to 30.1 ng g^{-1} (w.w.). These measured concentrations of PFOS were compared to consumption advisories issued in the State of Michigan (Figure 8). Recreationally important species such as Crevalle Jack, Spotted Seatrout, Gray Snapper, and Spanish Mackerel have PFOS levels that may indicate the need to consider fish advisories in Tampa Bay as they are close to or exceed similar advisories elsewhere.

4 Discussion

Sediments and fish were collected in the urbanized Tampa Bay estuary system to assess PFAS levels and potential human health risks from consumption of contaminated fishes. In general, PFAS concentrations in both sediment and fish were highest in Old Tampa Bay and Hillsborough Bay and decreased southeastward towards the Gulf of Mexico. Sediment concentrations differed between sites within a segment. For instance, the highest mean concentrations of T_{21} PFAS in sediments collected from Old Tampa Bay were measured at

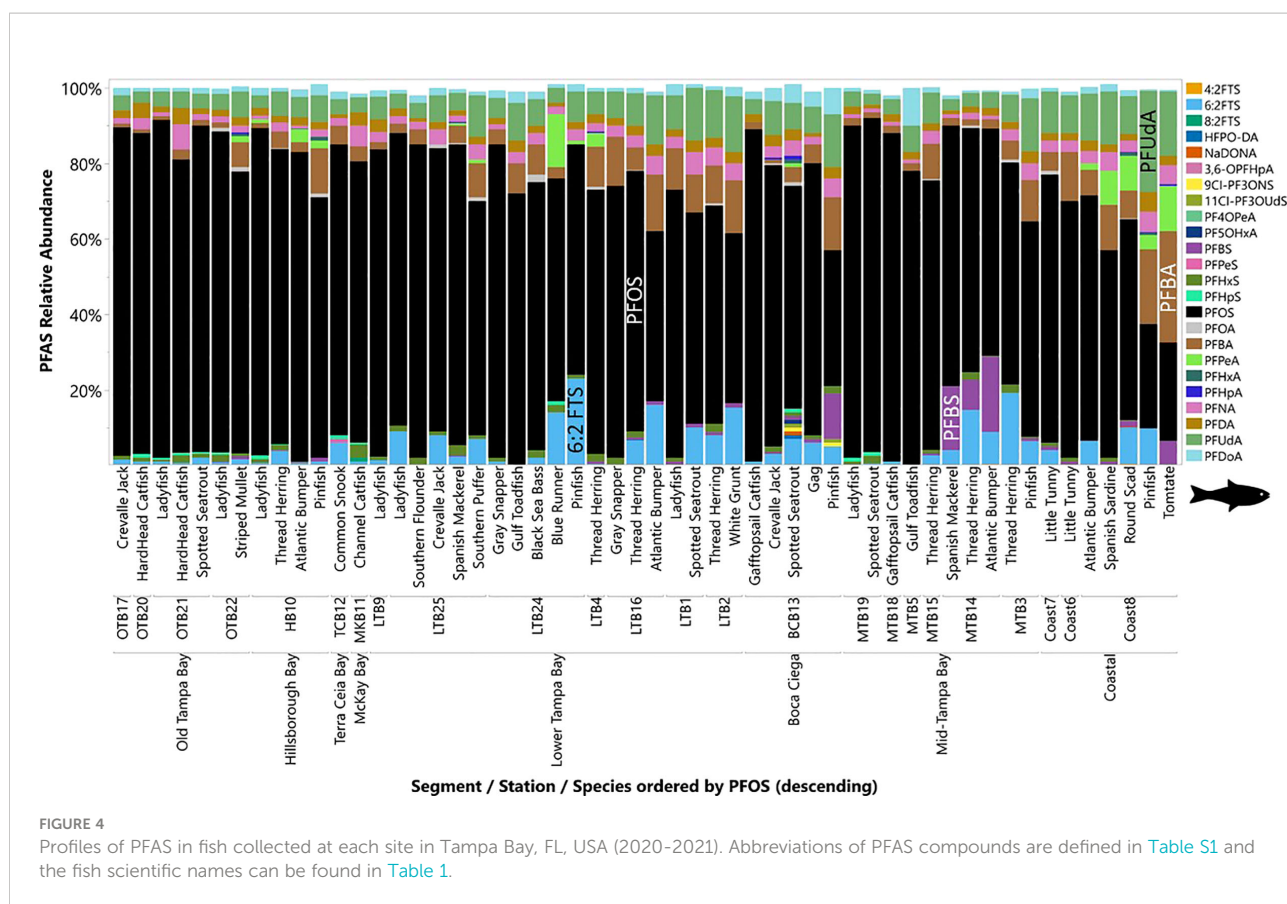
TABLE 3 Correlation coefficients (*r*), probability values (*p*-value) between PFAS and composition of sediments collected in Tampa Bay, FL, USA (2020).

Compound	Statistic	% Moisture	Dry Wt.	% TOC	% TIC	% TC	% Silt/Clay
4:2FTS	<i>r</i>	0.0429	-0.0441	-0.1034	-0.1059	-0.1894	0.3614
	<i>p</i> -value	0.8703	0.8665	0.7139	0.6963	0.499	0.169
6:2FTS	<i>r</i>	-0.1795	0.1867	-0.0996	-0.1322	-0.0893	-0.2533
	<i>p</i> -value	0.4906	0.473	0.7239	0.6255	0.7516	0.3439
8:2FTS	<i>r</i>	0.3022	-0.3017	0.1584	-0.0815	0.0911	0.0719
	<i>p</i> -value	0.2384	0.2392	0.5728	0.764	0.7467	0.7914
9Cl-PF3ONS	<i>r</i>	0.1907	-0.1981	0.7435	-0.0567	0.6961	0.2836
	<i>p</i> -value	0.4635	0.4461	0.0015*	0.8348	0.0039*	0.2871
11Cl-PF3OUdS	<i>r</i>	0.0835	-0.0857	-0.2429	-0.1353	-0.1821	-0.2991
	<i>p</i> -value	0.7502	0.7437	0.383	0.6175	0.516	0.2604
PF4OPeA	<i>r</i>	-0.3561	0.3476	-0.1704	0.2182	-0.2619	-0.057
	<i>p</i> -value	0.3469	0.3593	0.7149	0.6036	0.5704	0.8933
PF5OHxA	<i>r</i>	-0.1261	0.121	-0.204	-0.1872	-0.0307	-0.2879
	<i>p</i> -value	0.6296	0.6438	0.4659	0.4876	0.9135	0.2796
PFBS	<i>r</i>	0.2973	-0.3039	0.4321	0.1144	0.3918	0.6563
	<i>p</i> -value	0.2466	0.2357	0.1077	0.673	0.1486	0.0058*
PFHxSK	<i>r</i>	0.3234	-0.3269	0.1241	0.0865	0.0927	0.7486
	<i>p</i> -value	0.2054	0.2003	0.6595	0.7501	0.7424	0.0008*
PFHpS	<i>r</i>	0.2662	-0.2684	0.1973	-0.0767	0.147	0.6583
	<i>p</i> -value	0.3018	0.2976	0.4809	0.7777	0.6012	0.0056
PFOS	<i>r</i>	0.5375	-0.5404	0.2627	0.1361	0.2664	0.8061
	<i>p</i> -value	0.0261*	0.0251*	0.3442	0.6152	0.3372	0.0002*
PFOA	<i>r</i>	0.4784	-0.4839	0.1654	0.1861	0.2653	0.6012
	<i>p</i> -value	0.052*	0.049*	0.5558	0.4903	0.3393	0.0138*
PFBA	<i>r</i>	0.3776	-0.3851	0.3012	0.1254	0.4382	0.2466
	<i>p</i> -value	0.1351	0.1269	0.2753	0.6436	0.1023	0.3572
PFPeA	<i>r</i>	0.2198	-0.2241	0.1061	-0.0813	0.1249	0.5552
	<i>p</i> -value	0.3967	0.3872	0.7065	0.7648	0.6574	0.0256*
PFHxA	<i>r</i>	0.2859	-0.2922	0.0774	0.0524	0.197	0.3863
	<i>p</i> -value	0.266	0.255	0.784	0.847	0.4817	0.1394
PFHpA	<i>r</i>	0.323	-0.3287	-0.0041	0.1894	0.1689	0.2989
	<i>p</i> -value	0.206	0.1977	0.9883	0.4824	0.5474	0.2609
PFNA	<i>r</i>	0.4293	-0.4353	0.1225	0.1034	0.2285	0.5384
	<i>p</i> -value	0.0855	0.0807	0.6637	0.7031	0.4128	0.0314*
PFDA	<i>r</i>	0.5211	-0.5271	0.1286	0.2325	0.3064	0.5872
	<i>p</i> -value	0.032*	0.0297*	0.6479	0.3863	0.2667	0.0168*
PFUnDA	<i>r</i>	0.4819	-0.4871	0.2818	0.0345	0.3818	0.6658
	<i>p</i> -value	0.0501*	0.0473*	0.3089	0.899	0.1602	0.0049*
PFDoA	<i>r</i>	0.8353	-0.8341	0.8014	0.1107	0.7762	0.8439
	<i>p</i> -value	<.0001*	<.0001*	0.0003*	0.6832	0.0007*	<.0001*
T21PFAS	<i>r</i>	0.536	-0.5394	0.2629	0.1308	0.2897	0.7869
	<i>p</i> -value	0.0266*	0.0255*	0.3439	0.6292	0.2949	0.0003*

Abbreviations of PFAS compounds are defined in Table S2. TOC, Total organic carbon; TIC, Total inorganic carbon; TC, Total carbon. Statistically significant correlations are indicated with an asterisk next to the *p*-value.

the mouth of the Cross Bayou inlet (PFAS3; $2,360 \pm 891$ ng kg⁻¹ d.w.). There are a number of industries and military installations located on the peninsula bordering this inlet that may be contributing to these levels, including wastewater treatment

plant outfalls, civilian and military airports and other military facilities. The second highest mean sediment concentrations by site were collected near wastewater treatment discharge outfall in Hillsborough Bay (PFAS2; 980 ± 680 ng kg⁻¹ d.w.). However,

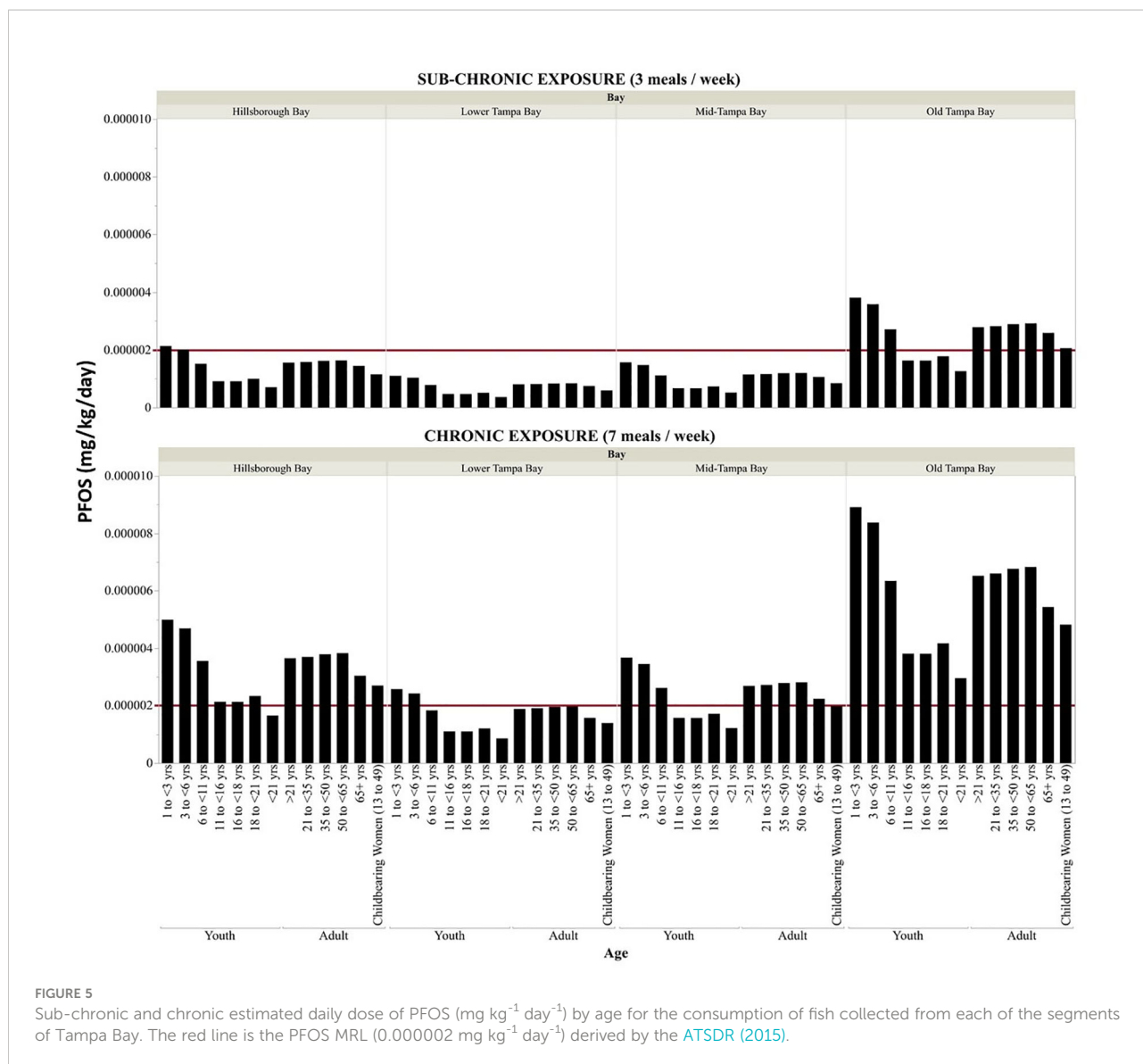


there are a number of other industries and container loading facilities in the direct vicinity. Sediments collected near wastewater treatment plants (PFAS7-2), airports (PFAS6-1), fire-fighting training facilities and waste incinerators (PFAS1-1) had elevated levels of 6:2FTS, an alternative to PFOS and PFOA that is widely used as a co-formulant in AFFFs and as a chrome mist suppressant in the electroplating industry. Measured PFAS in sediments collected in Tampa Bay (T_{21} PFAS 0.037 – 2.99 ng g⁻¹ d.w.) were similar to sediments collected in the Seine River, France (Σ PFAS 0.78 – 6.7 ng g⁻¹ d.w.) (Macorps et al., 2022), and Korean river and lake systems (Σ PFAS 0.03 – 1.09 ng g⁻¹ d.w.) (Lam et al., 2014). Furthermore, Tampa Bay sediments were as much as 30 times lower than sediments collected in the Great Lakes (Codling et al., 2018) and 25 times lower than AFFF impacted sediments (0.8 – 76 ng g⁻¹ d.w.) collected in Sweden (Mussabek et al., 2019).

Elevated concentrations of T_{24} PFAS in muscle tissue of fish were located at stations near a major thoroughfare (Gandy Bridge OTB20), the Cross Bayou inlet (OTB17), a military facility (MTB19), and at the mouth of Old Tampa Bay adjacent to Weedon Island Preserve (OTB21). Profiles in the edible tissues of fish were mainly dominated by PFOS however, fish collected adjacent to the TECO Big Bend Power Station (MTB15) had elevated levels of PFBS. PFBS is considered a replacement

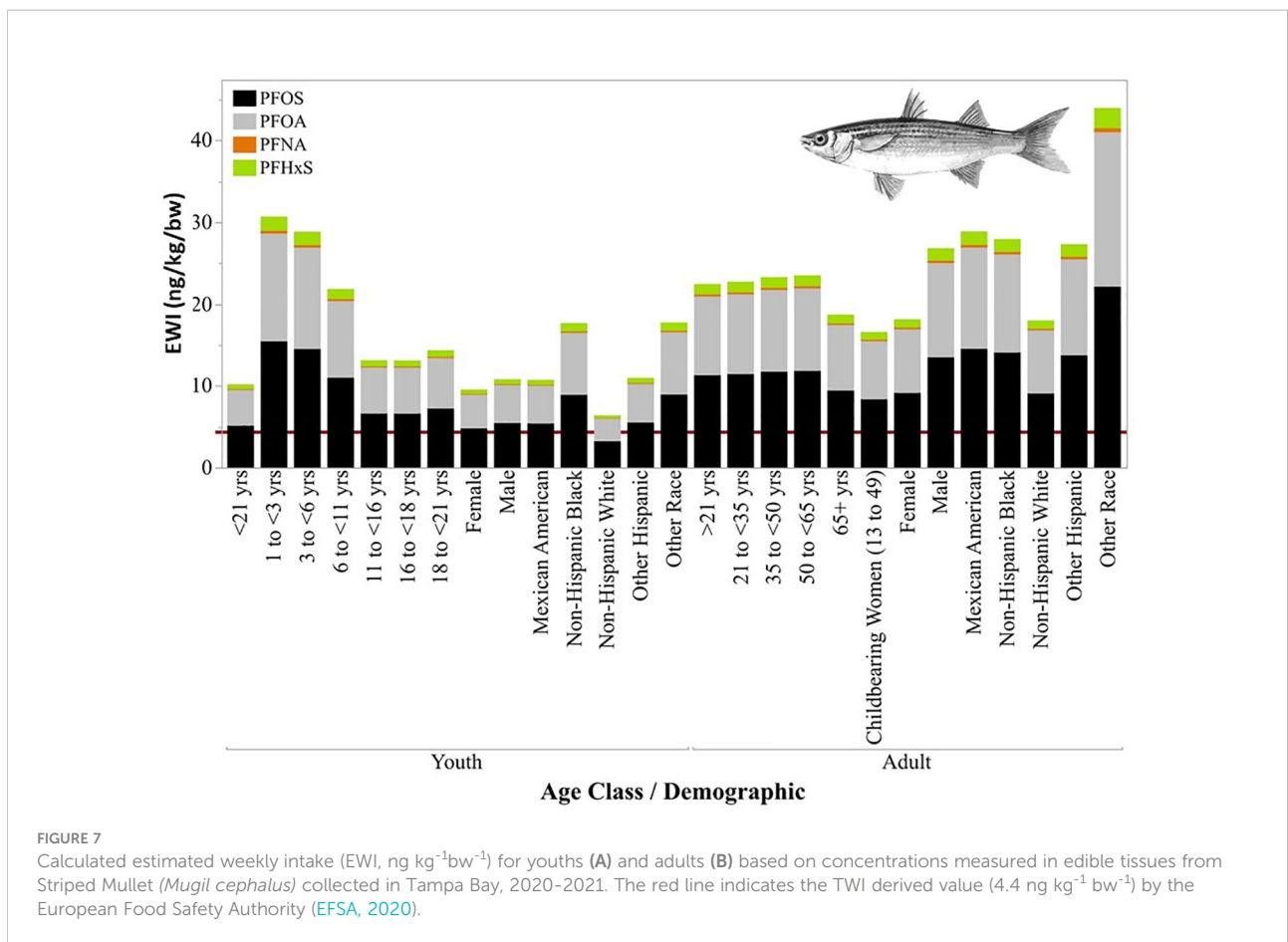
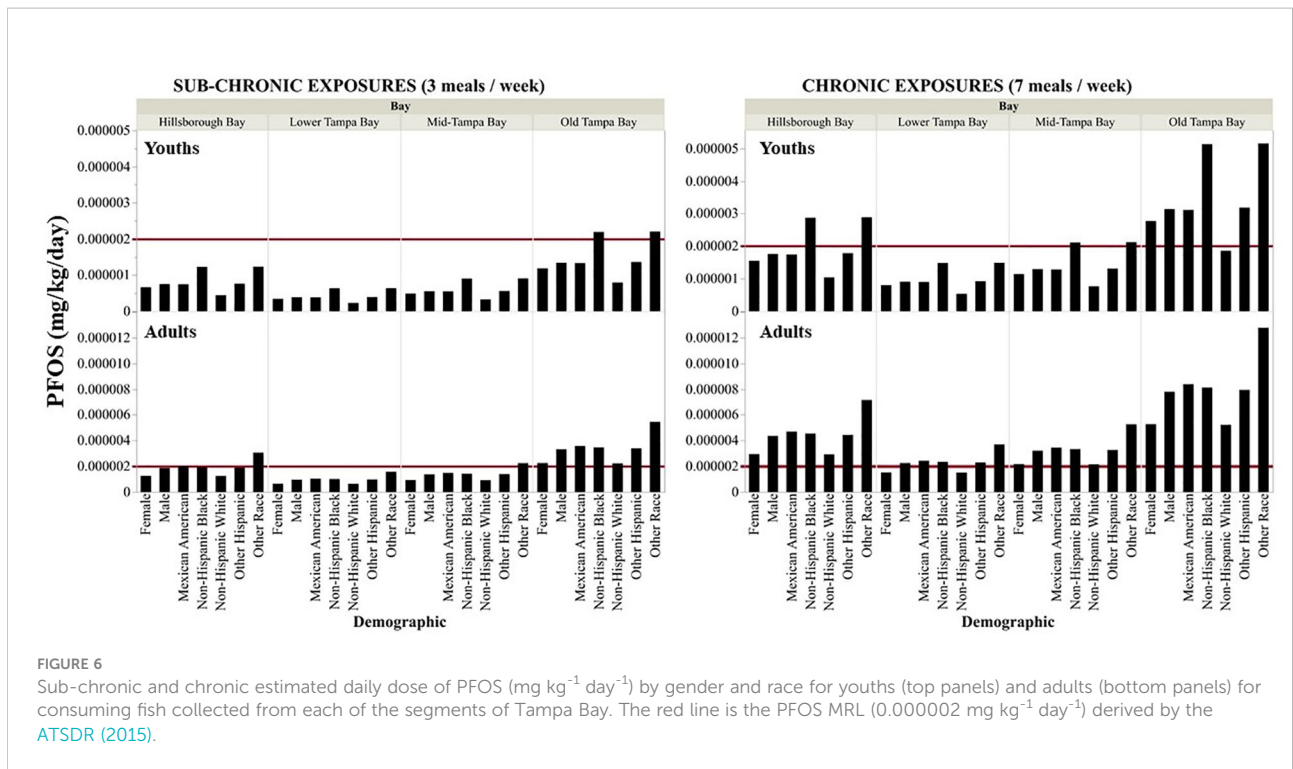
compound for PFOS-related compounds and can be directly released into the environment as PFBS or can be a final degradation product of perfluorobutane sulfonyl fluoride (PBSF)-based surfactants. Fish collected near a wastewater treatment plant in Boca Ciega Bay (BCB13) had elevated levels of other PFAS replacement compounds such as Gen-X (HFPO-DA), NaDONA, and F53B (9Cl-PF3ONS, 11Cl-PF3OUdS). The range of total PFAS measured in Tampa Bay fish (T_{24} PFAS 0.31 – 33.6 ng g⁻¹ w.w.) were similar to the edible tissues of fish collected in the Seine River (Σ PFAS 0.22 – 3.8 ng g⁻¹ w.w.), Great Lakes (0.09 – 90.7 ng g⁻¹ w.w.), Lake Vättern (PFAS < MDL – 23.1 ng g⁻¹ w.w.), and the Baltic Sea (< MDL – 3.34 ng g⁻¹ w.w.) (Berger et al., 2009; Point et al., 2021; Macorps et al., 2022). However, PFOS levels in edible fish tissues collected in the Great Lakes region (2.40 – 206 ng g⁻¹ w.w.) (Point et al., 2021) were up to seven times higher than those reported in Tampa Bay fishes (0.92 – 30.1 ng g⁻¹ w.w.).

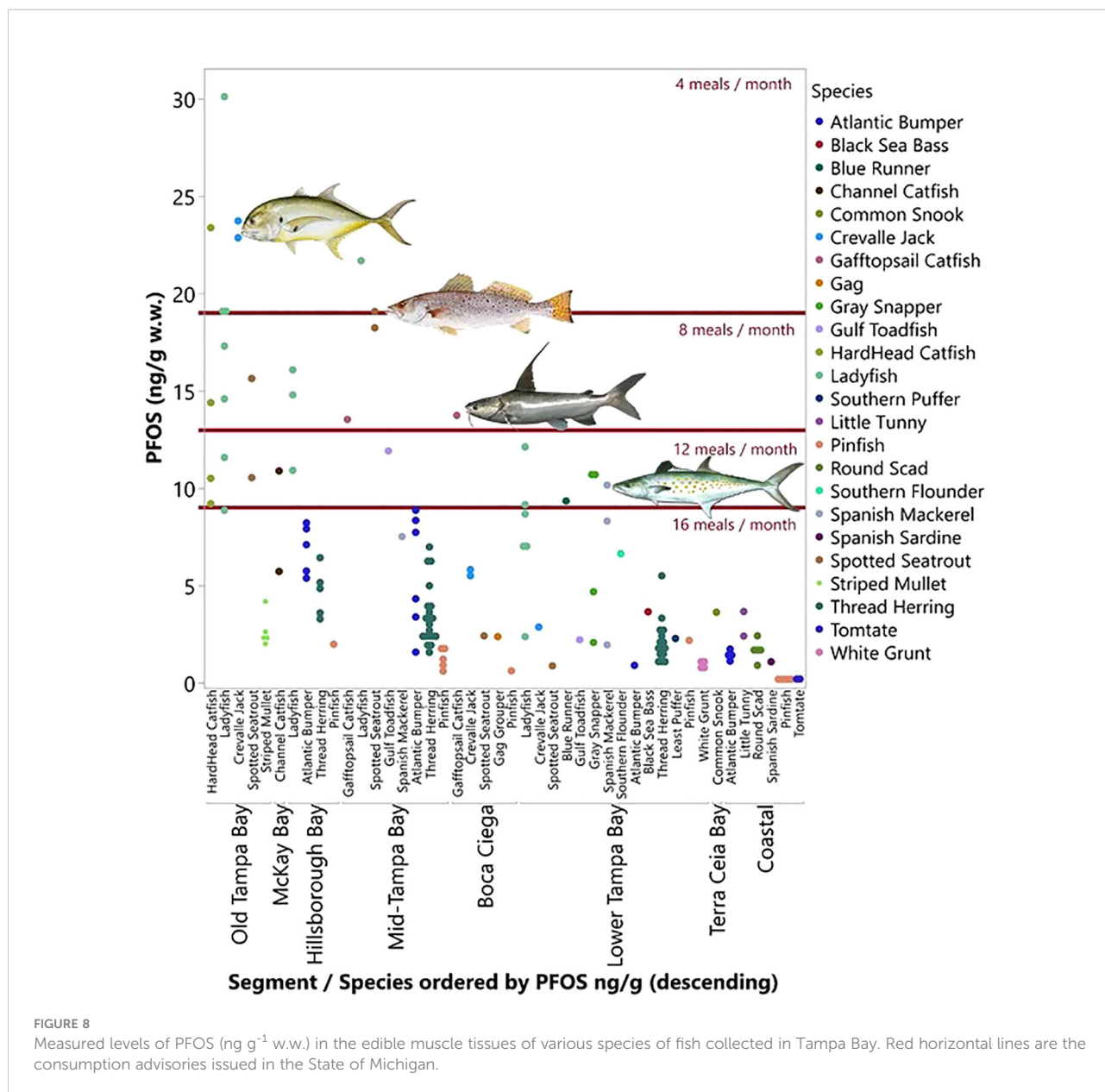
Concentration ratios of PFOS to long-chain PFCAs (PFOS/ Σ LC-PFCA) of > 1 have been used as a proxy for direct water emission sources, while a ratio of < 1 indicate atmospheric PFAS sources (Ali et al., 2021; Valsecchi et al., 2021). In this study, the mean PFOS/ Σ LC-PFCA ratios in edible tissues of fish (5.7 ± 3.1) and sediments (3.4 ± 1.6) indicate the presence of local contamination sources (e.g., wastewater treatment plant, military installations, airports, etc.) in Tampa Bay.



Potential human health risks of PFAS (PFOS, PFOA, PFNA, and PFHxS) exposures from the consumption of contaminated fish collected in Tampa Bay were estimated. Estimated daily doses of PFOS and estimated weekly intake values exceeded available concentration thresholds (MRLs, TWIs) for adult and youth demographics. Exceedances of thresholds (MRLs and TWIs) were highest in Old Tampa Bay and Hillsborough Bay and decreased southward towards the Gulf of Mexico. Available thresholds were also exceeded for the consumption of Striped Mullet only for adult and youth demographics. PFASs measured in Striped Mullet were lower than other recreationally important species (e.g., Spotted Seatrout, Spanish Mackerel, Crevalle Jack) collected in Tampa Bay, yet the sample sizes for species other than Striped Mullet did not allow for the assessment of dietary risks. Hepatic, immune, and developmental endpoints were the most sensitive targets in laboratory animals exposed to PFOS

and PFOA (ATSDR, 2015). The most sensitive targets were hepatic and thyroid endpoints for PFHxS and developmental endpoints for PFNA (ATSDR, 2015). Minimal risk levels (MRLs) are used as an estimate of daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects. These are strictly used as screening levels and do not define action or remediation levels. The EFSA derived TWI is expected to be protective for potential critical endpoints (increase in serum cholesterol, reduced birth weight and high serum levels of ALT). It should also be noted the estimates were based on the assumption that populations are consuming three or seven meals a week of fish collected from Tampa Bay. Although these may not be accurate estimations for the wider population, the risk assessment conducted herein suggests these may be applicable estimations for those populations' subsistence fishing in Tampa Bay.





Concentrations of PFOS in edible fish tissues of several recreationally important species (e.g., Spotted Seatrout) collected in Tampa Bay also exceeded consumption guidelines issued in Michigan and other states in the Great Lakes Region. A number of other states (AL, CT, IN, MA, ME, MN, NJ, NY, OR) have also issued consumption advisories (1 meal/week) for the general population for fish with PFOS levels ranging from ≤ 3.5 to 200 ng g^{-1} . More restrictive consumption advisories have also been issued sensitive populations in several states (≤ 1.56 to $34 \text{ ng PFOS g}^{-1}$ = one meal/week). Additionally, 'do not eat' advisories have been issued for PFOS levels ranging from 17 – 800 ppb. The concentration of PFOS used to issue advisories span three orders of magnitude and incorporate different criteria, making it difficult to assess the need for consumption restrictions from state to state.

The concentrations of PFOS measured in edible fillets in this study (range: 0.09 to 30 ng g^{-1} ; mean: 5.69 ng g^{-1}) exceeded many of the consumption advisories (4 to 16 meals per month) issued by various states. Additionally, the exceedances of the derived ATSDR MRL and EFSA TWI in Tampa Bay may indicate a need for consumption advisories for certain demographics, recreationally important species, and areas of the Bay (e.g., < three meals per week) (ATSDR, 2015; EFSA, 2020).

This study was initiated as a first-level surveillance survey to understand the scale and extent of PFAS pollution in sediments and across a range of fish species. Because sample sizes of each species sampled were relatively low, caution should be used in interpreting the results from any one species. Furthermore, because not every species was sampled in every Bay segment,

and there were species related differences in contamination levels, these factors may confound clear interpretation of species and location-related differences. Nevertheless, our study found significant PFAS-related pollution in Bay sediments and fishes that should stimulate additional more intensive studies to resolve these issues. Expanding the research in Tampa Bay to include larger sample sizes and additional recreationally important species would be beneficial. This information will more accurately estimate exposure risks based on species-specific consumption. Nevertheless, the elevated levels in fish from this study and their exceedances of available MRLs, TWIs, and current consumption advisories issued in other states will help to inform state resource managers of environmental levels of PFAS in Tampa Bay and aid in the consideration of consumption advisories in this region.

Data availability statement

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession number(s) can be found at The University of South Florida Libraries Digital Commons (doi: [10.5038/y6w7cf53m9](https://doi.org/10.5038/y6w7cf53m9)).

Ethics statement

The animal study was reviewed and approved by University of South Florida Institutional Animal Care & Use Committee (Protocol #W IS00008294).

Author contributions

EP performed all analytical and data analysis and generated the original manuscript draft with contributions from all authors. EP, KR, SG, TA, BG, KC, and SAM all assisted with sample collections. SM was responsible for characterizing sediment compositions. SAM and EP conceived and completed the study design. All authors contributed to the article and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmars.2022.1046667/full#supplementary-material>

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