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Species-specific profiles of per- and polyfluoroalkyl substances (PFAS) in small coastal sharks along the South Atlantic Bight of the United States

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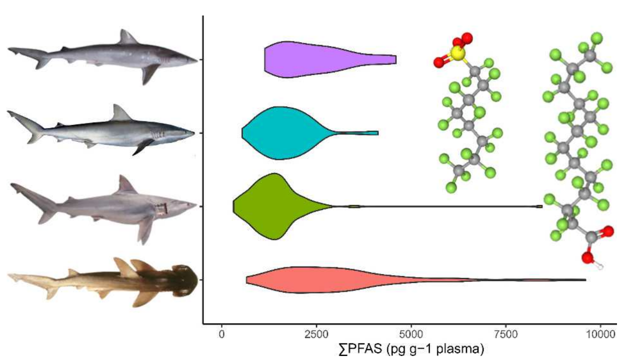
HIGHLIGHTS

- PFAS was determined in the plasma of 315 live-captured sharks.
- Species-specific differences of ∑PFAS were investigated, with bonnethead sharks exhibiting the highest PFAS levels.
- PFDA and PFUdA in Atlantic sharpnose, and PFTrDA in blacknose sharks showed 100 % detection rates.
- Significant variations in select PFAS were observed between sexes of bonnetheads and Atlantic sharpnose sharks.

GRAPHICAL ABSTRACT



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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) have gained widespread commercial use across the globe in various industrial and consumer products, such as textiles, firefighting foams, and surface coating materials. Studies have shown that PFAS exhibit a strong tendency to accumulate within aquatic food webs, primarily due to their high bioaccumulation potential and resistance to degradation. Despite such concerns, their impact on marine predators like sharks remains underexplored. This study aimed to investigate the presence of 34 PFAS in the plasma ($n = 315$) of four small coastal sharks inhabiting the South Atlantic Bight of the United States (U.S). Among the sharks studied, bonnetheads (*Sphyrna tiburo*) had the highest ∑PFAS concentration (3031 ± 1674 pg g − 1 plasma, $n = 103$), followed by the Atlantic sharpnose shark (*Rhizoprionodon terraenovae*, 2407 ± 969 pg g − 1, $n = 101$), blacknose shark (*Carcharhinus acronotus*, 1713 ± 662 pg g − 1, $n = 83$) and finetooth shark (*Carcharhinus isodon*, 1431 ± 891 pg g − 1, $n = 28$). Despite declines in the manufacturing of perfluorooctane sulfonate (PFOS)

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and perfluorooctanoic acid (PFOA), the long-chain (C8 – C13) perfluoroalkyl acids (PFAAs) were frequently detected, with PFOS, perfluorodecanoic acid (PFDA), and perfluorotridecanoic acid (PFTrDA) present as the most dominant PFAS. Furthermore, males exhibited significantly higher ∑PFAS concentrations than females in bonnetheads ($p < 0.01$), suggesting possible sex-specific PFAS accumulation or maternal offloading in some species. The results of this study underscore the urgency for more extensive biomonitoring of PFAS in aquatic/marine environments to obtain a comprehensive understanding of the impact and fate of these emerging pollutants on marine fauna.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS), a class of synthetic chemicals comprised predominantly of carbon – fluorine bonds, have gained significant attention due to their environmental persistence over a long period of time (Buck et al., 2011; Lindstrom et al., 2011; Johnson et al., 2021). These compounds have been widely utilized in industrial and consumer products such as food packaging, textiles, clothing, pesticides, firefighting foams, cosmetics, and stain-resistant materials, due to their unique amphiphilic properties (Glüge et al., 2020; Whitehead et al., 2021; Gaines, 2023). It is estimated that there are currently over 9000 PFAS in existence with myriad applications, and, as a result, they are found ubiquitously in environments worldwide (Cordner et al., 2021). Once released into the environment, PFAS are dispersed globally through oceanic currents and atmospheric pathways, enabling their transport from source locations to distant, remote regions (Kwok et al., 2013; Hartz et al., 2023). The transport process also likely induces a transformation in volatile precursors, such as fluorotelomer alcohols (FTOH) and perfluoroalkyl sulfonamido ethanols (FASE), leading to their conversion into end groups known as perfluoroalkyl acids (PFAAs) (Ellis et al., 2004; Young et al., 2007; Wang et al., 2020). PFAAs, which include perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), are considered "terminal PFAS" that don't further transform under typical environmental conditions and they have been recognized for their tendency to accumulate in biological systems and pose potential adverse health risks to both wildlife and humans (Conder et al., 2008a; Bell et al., 2021; De Silva et al., 2021). In response to their toxicity and bioaccumulation potential, several PFAAs, specifically perfluorohexane sulfonic acid (PFHxS), PFOS, and PFOA, have been phased-out of use and added to the list of persistent organic pollutants (POPs) by the Stockholm convention (Fiedler et al., 2022). Unlike lipophilic POPs, PFAS exhibit a distinct behavior by binding with plasma-bound proteins more so than accumulating within lipid-rich reservoirs. Still, some PFAS have been noted to have strong biomagnification potential within food webs (Bangma et al., 2022) and higher levels of some PFAS have been reported in apex predators (Houde et al., 2011; Androulakakis et al., 2022; Khan et al., 2023).

Top predators, such as raptors, marine mammals, and sharks, serve as sentinel species in the continually expanding field of pollution monitoring and wildlife toxicology. These predators assume a significant role by integrating and reflecting long-term contaminant exposure due to their extended lifespans and expansive foraging territories (Alves et al., 2016; Juan-Jordá et al., 2022; Treu et al., 2022). The tendency of sharks to accumulate detectible and often elevated levels of contaminants, coupled with their ecological and socioeconomic significance, make them suitable focal species for biomonitoring studies (Alves et al., 2022). During the last few decades, some sharks have witnessed a significant decline in their populations, which raises concerns about the potential risk of extinction at a global scale (Roff et al., 2018; Pacoureau et al., 2021; Juan-Jordá et al., 2022); however, in the U.S. waters many populations are showing signs of recovery from overfishing (Peterson et al., 2017). Despite their ecological significance, there has been a lack of comprehensive research examining the accumulation of PFAS in these crucial species.

The southeastern region of the United States encompasses a vast and diverse coastline, extending from North Carolina to Florida and supports a wide range of marine fauna (Adams, 1902). In recent years, several studies have been conducted along this region to investigate the presence of PFAS in both abiotic (Ahmadireskety et al., 2021; Griffin et al., 2022; Ehsan et al., 2023) and biotic regimes (De Silva et al., 2016; Bangma et al., 2017; Fair et al., 2019; Lynch et al., 2019; Palmer et al., 2019). PFAS were detected in all matrices throughout the coastline, with hotspots near areas with historic aqueous film-forming foam (AFFF) use. However, studies specifically focusing on PFAS accumulation in apex marine predators, like sharks, are lacking. The main objective of the present study was to investigate the prevalence of PFAS in a variety of small coastal sharks along the South Atlantic Bight of U.S. and assess any potential species-specific bioaccumulation patterns. Potential relationships between biological parameters, specifically body size and sex and PFAS profiles in the sharks, were also explored.

2. Materials and methods

2.1. Sampling

Four species of sharks were captured using bottom longlines and gillnets as part of fishery-dependent and -independent sampling efforts conducted along the South Atlantic Bight of the United States (US) from Winyah Bay, South Carolina to the Florida Keys, during the years of 2010 to 2017. Sampling occurred monthly in estuaries and nearshore coastal waters. Following capture, precaudal length (PCL; tip of rostrum to precaudal pit), fork length (FL, tip of the rostrum to fork in caudal fin) and stretched total length (STL, tip of the rostrum to the posterior end of the extended caudal fin) were measured in centimeters (cm). Blood was collected from sharks via caudal venipuncture using sterile syringes and 16- or 18-gauge needles, transferred into vacutainer tubes containing anticoagulant, and held on ice during transport. In the laboratory, the blood was centrifuged at 1300*g* for 5 min to separate plasma, which was then stored at −20 °C until further analysis. Following blood collection, most sharks obtained from fishery-independent surveys were tagged and released for studies on movement patterns. The four species included in this study were bonnethead (*Sphyrna tiburo*; $n = 103$), finetooth shark (*Carcharhinus isodon*; $n = 101$), blacknose shark (*Carcharhinus acronotus*; $n = 83$), and Atlantic sharpnose shark (*Rhizoprionodon terraenovae*; $n = 28$). Sampling locations and biological information are detailed in (Tables S1-S4) and depicted in (Fig. 1).

2.2. Standards and reagents

All PFAS standards, including non-labeled and isotopically-labeled analogs, were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada) or obtained from SynQuest Laboratories and Oakwood Products Inc. Water and methanol, both Optima grade, were purchased from Fisher Scientific (Waltham, MA, USA). Detailed information on target PFAS ($n = 34$) and isotopically-labeled standards can be found in supplementary information (Tables S5 and S6, respectively).

2.3. Extraction

A method for PFAS extraction in shark plasma previously published by our laboratory was adapted for this study (Da Silva et al., 2020). In brief, 0.2 g of plasma samples (gravimetrically weighed) were aliquoted into 96-well plates and spiked with an isotopically-labeled internal standard mixture. The plates were vortexed for 5 min at 450 rpm. Then, 380 μL of methanol was added to each well and the plates were vortexed for another 5 min. To facilitate phase separation, the plates underwent centrifugation at 4000 rpm for 25 min. Finally, 100 μL of the resulting supernatant from each well was removed and transferred into an autosampler vial for PFAS analysis.

2.4. Instrumental analysis

Samples were analyzed for 34 PFAS using a Thermo Scientific Vanquish Ultra -High Performance Liquid Chromatography (UHPLC) system coupled to a Thermo Scientific Quantis triple quadrupole mass spectrometer operated in negative polarity employing electrospray and selected reaction monitoring (SRM) scanning mode. Chromatographic separation was accomplished using a Gemini C18 column (100 mm × 2 mm; 3 μm; Phenomenex, Torrance, CA, USA). The mobile phases consisted of water (A) and methanol (B), both containing 5 mM ammonium acetate. Additional details regarding UHPLC-MS/MS conditions can be found in (Table S7). If possible, two transitions were monitored for target analytes. The most intense transition was used to quantify detected PFAS, while the second transition was used to confirm identification. The SRM transitions, chromatographic retention times, and other optimized parameters for all native and labeled PFAS can be found in (Table S8).

2.5. Quality assurance and quality control (QA & QC)

To avoid contamination, all fluoropolymer materials were avoided in experimental procedures and instrumental analyses, including a PFAS-free LC kit. Procedural blanks were carried out every ten samples to assess and mitigate background contamination. No PFAS were detected in the blanks except 6:2 fluorotelomer sulfonate (6:2 FTS), which was excluded from reporting due to blank contamination. During instrumental analysis, solvent blanks (methanol) were employed after every five samples to monitor potential carryover. Commercially available plasma-based matrix, SRM 1950 – Metabolites in Frozen Human Plasma, was extracted in triplicate (100 μL each) and analyzed alongside samples. Method accuracy was evaluated by comparing the experimentally-derived PFAS concentrations in the SRM 1950 matrix to reference values established by the National Institute of Standards and Technology (NIST). Accuracy and precision values can be found in (Table S9).

2.6. Data analysis/statistics

R studio (version 4.2.3) was used to characterize the distribution of PFAS across all shark species under investigation. Nonparametric statistical tests were used to analyze the data after Shapiro-Wilk tests determined that all data were not normally distributed ($p \leq 0.05$). When analyzing the comparisons and correlations, the concentrations below the limit of quantitation (LOQ) were replaced with the LOQ/$\sqrt{2}$. The Spearman correlation test was employed to examine the correlation strength among the measured PFAS and also the relationship between concentrations of both total and individual PFAS with shark FL within each species. The Wilcoxon Mann-Whitney *U* test was used to compare PFAS concentrations between male and female sharks, while the Kruskal-Wallis test was applied to compare sum ($\sum$) PFAS concentrations among different shark species. In cases where the Kruskal-Wallis test yielded a statistically significant result ($p < 0.05$), the Dunn test (post-hoc) was employed to identify which species differed from the others.

Peak integration was achieved using Thermo Xcalibur software v 4.1. Calibration curves constructed for the quantitation of each detected PFAS had regression coefficients (r^2) above 0.995. For analytes without

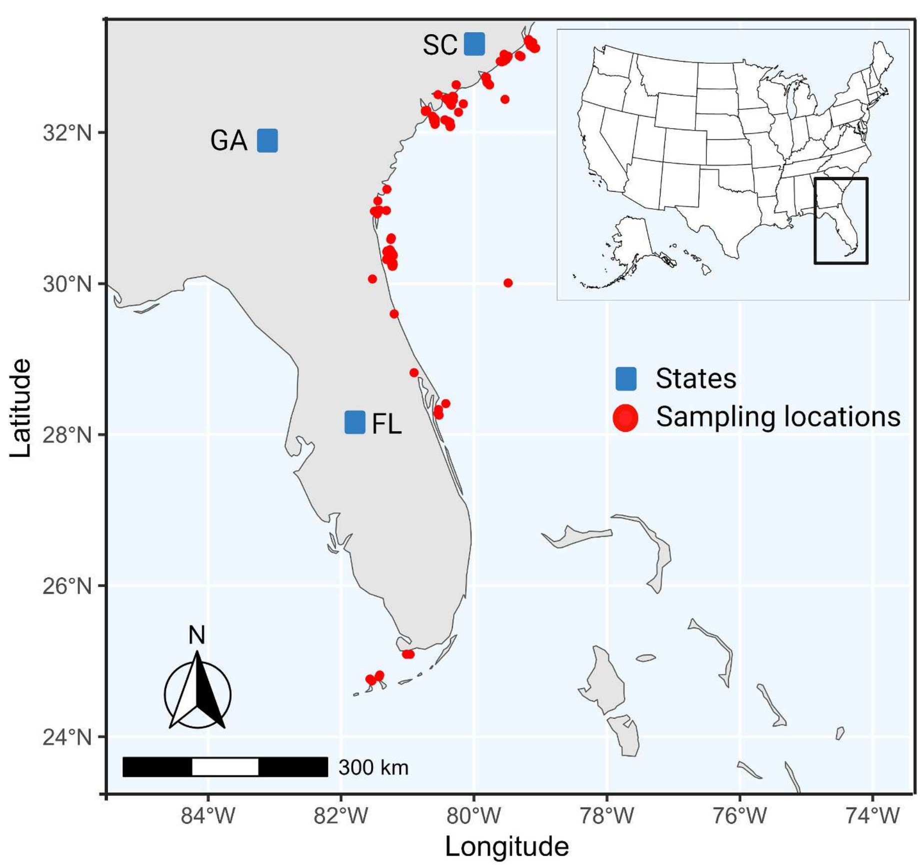

Fig. 1. Graphical depiction of the shark sampling locations along the South Atlantic Bight of the United States. SC: South Carolina, GA: Georgia, FL: Florida.

a mass-labeled homologue, the internal standard that was closest in retention time was utilized for quantitation. The LOQ, detailed in (Table S5) was set for each target PFAS as the lowest calibration curve level whose peak was both Gaussian in shape and had a signal-to-noise ratio (S/N) of 10. Concentrations that were above the limit of detection (or 3× S/N) but below LOQ were noted as "< LOQ" in (Tables S10-S14), which detail individual concentrations for all detected PFAS in each shark species. Concentration data were normalized per weight of each sample and reported in picogram (pg) PFAS per g of shark plasma.

3. Results and discussion

3.1. Occurrence of PFAS in sharks

Of the 34 target PFAS analyzed in plasma samples ($n = 315$) from four shark species (bonnethead, finetooth shark, blacknose shark, and Atlantic sharpnose shark), only 10 PFAS were quantifiable in one or more samples: perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), PFDA, perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), PFTrDA, perfluorotetradecanoic acid (PFTeDA), and PFOS. The detection rates (%), mean ± SD concentrations, and ranges of individual and total concentrations ($\sum$PFAS) measured (in pg g^{-1}) detected in shark plasma are presented in (Table 1), while the specific concentrations of individual PFAS for each shark are outlined in (Tables S10 – S13). The $\sum$PFAS differed among the shark species and ranged from 309 to 9606 pg g − 1 plasma and interestingly, every shark analyzed had detectable levels of PFAS, providing further support that these contaminants are ubiquitous in the environment (Houde et al., 2011). The highest $\sum$PFAS among all species were observed in bonnetheads, with mean ± SD of 3031 ± 1674 pg g^{-1}, followed by Atlantic sharpnose sharks (2407 ± 969 pg g^{-1}), blacknose sharks (1713 ± 662 pg g^{-1}), and finetooth sharks (1431 ± 891 pg g^{-1}) (Table 1).

Interestingly, similar to previous findings in various sharks (Senthil Kumar et al., 2009; Alves et al., 2016; Zafeiraki et al., 2019; Chynel et al., 2021; Boldrocchi et al., 2022), PFOS and long-chain PFCAs were identified as the predominant PFAS in this study. Bonnetheads and Atlantic sharpnose sharks shared a similar pattern of select individual PFAS by concentration with PFOS (mean ± SD of 847 ± 1007 and 472 ± 327), followed by PFTrDA (714 ± 264 and 464 ± 147), respectively. For finetooth and blacknose sharks, PFTrDA exhibited the highest concentration (861 ± 553 and 836 ± 343) followed by PFHxA (298 ± 109 and 295 ± 65) respectively (Table 1). PFOS and a myriad of PFCAs dominate PFAS levels in wildlife due to limited environmental degradation, widespread global use in industries, and their tendency to bioaccumulate in marine life (Giesy and Kannan, 2001; Prevedouros et al., 2006).

The relative abundance (%) of individual PFAS to the $\sum$PFAS in each shark species is displayed in (Fig. 2). Among the detected PFAS, PFOS demonstrated dominance over all other PFAS in bonnetheads and Atlantic sharpnose sharks, accounting for over 23% and 16%, respectively. Interestingly, in finetooth sharks and blacknose sharks, PFTrDA was the most prevalent with 34 and 33%, respectively. Notably, PFCAs were the most abundant PFAS class, encompassing >75% of the total PFAS in all shark species in this study. Previous studies have illustrated that the bioaccumulation factor of PFCAs increases with increasing carbon-chain length (Martin et al., 2003; Conder et al., 2008b; Kwadijk et al., 2010; Fang et al., 2014). Within the category of short-chain PFAS, only PFHxA and PFHpA were detectable, exhibiting comparatively lower detection percentages across all four-shark species. The limited detection of these short-chain PFAS may be attributed to their low bioaccumulation potential; however, this could also be related to diet. Future research should examine prey items for these sharks to delineate the potential trophic transfer of PFAS in sharks.

3.2. Species-specific differences of PFAS

Significant inter-species variations were observed in $\sum$PFAS concentrations, suggesting differing bioaccumulation patterns among these shark species (Fig. 3). The most substantial disparities were noted between bonnethead and both finetooth and blacknose sharks. Conversely, the difference between bonnethead and Atlantic sharpnose sharks exhibited slight differentiation but were not statistically significant (Fig. 3). These variations may arise from several factors, such as specific contamination sources within their geographical foraging ranges, dietary preferences unique to each species, distinct toxicokinetics, and the degree of maternal transfer of contaminants to offspring, which can be affected, for example, by maternal parity (Keller et al., 2005; Galatius et al., 2013; Babut et al., 2017; Chynel et al., 2021).

Bonnethead sharks have been found to consume a diet largely

Table 1
Summary of concentrations (pg g^{-1} plasma) of PFAS measured in various shark species collected from the South Atlantic Bight of the United States.

PFAS	Bonnethead (n = 103)[a]			Finetooth (n = 101)			Blacknose (n = 83)			Sharpnose (n = 28)		
	DR (%)[b]	Mean ± SD[c]	Range	DR (%)	Mean ± SD	Range	DR (%)	Mean ± SD	Range	DR (%)	Mean ± SD	Range
PFHxA	50	339 ± 165	<LOQ[d]-1237	50	298 ± 109	<LOQ-826	17	295 ± 65	<LOQ-455	25	404 ± 165	<LOQ-1058
PFHpA	14	114 ± 52	<LOQ-265	4	62 ± 21	<LOQ-94	2	65 ± 23	<LOQ-81	14	57 ± 9	<LOQ-69
PFOA	88	337 ± 162	<LOQ-1057	24	201 ± 64	<LOQ-495	36	193 ± 24	<LOQ-305	96	232 ± 56	<LOQ-364
PFNA	52	272 ± 121	<LOQ-747	12	170 ± 84	<LOQ-427	29	179 ± 83	<LOQ-503	79	243 ± 91	<LOQ-409
PFDA	85	364 ± 215	<LOQ-1209	61	223 ± 47	<LOQ-426	87	282 ± 191	<LOQ-1718	100	416 ± 224	191–1009
PFUdA	93	238 ± 186	<LOQ-884	63	110 ± 53	<LOQ-285	96	175 ± 169	<LOQ-1475	100	331 ± 222	72–1034
PFDoA	90	267 ± 79	<LOQ-534	39	209 ± 33	<LOQ-310	72	221 ± 33	<LOQ-320	89	274 ± 77	<LOQ-501
PFTrDA	99	714 ± 264	<LOQ-1348	93	861 ± 553	<LOQ-3571	100	836 ± 343	275–1875	89	464 ± 147	<LOQ-808
PFTeDA	59	183 ± 100	<LOQ-600	8	183 ± 554	<LOQ-808	8	110 ± 17	<LOQ-127	21	103 ± 32	<LOQ-165
PFOS	96	847 ± 1007	<LOQ-5455	45	245 ± 94	<LOQ-2132	67	181 ± 123	<LOQ-726	96	472 ± 327	<LOQ-1525
$\sum$PFAS[e]		3031 ± 1674	650–9606		1431 ± 891	309–8454		1713 ± 662	535–4124		2407 ± 969	1138–4597

[a] Number of samples analyzed.
[b] Detection rate.
[c] Standard deviation.
[d] Limit of quantification.
[e] Sum of all detected PFAS.

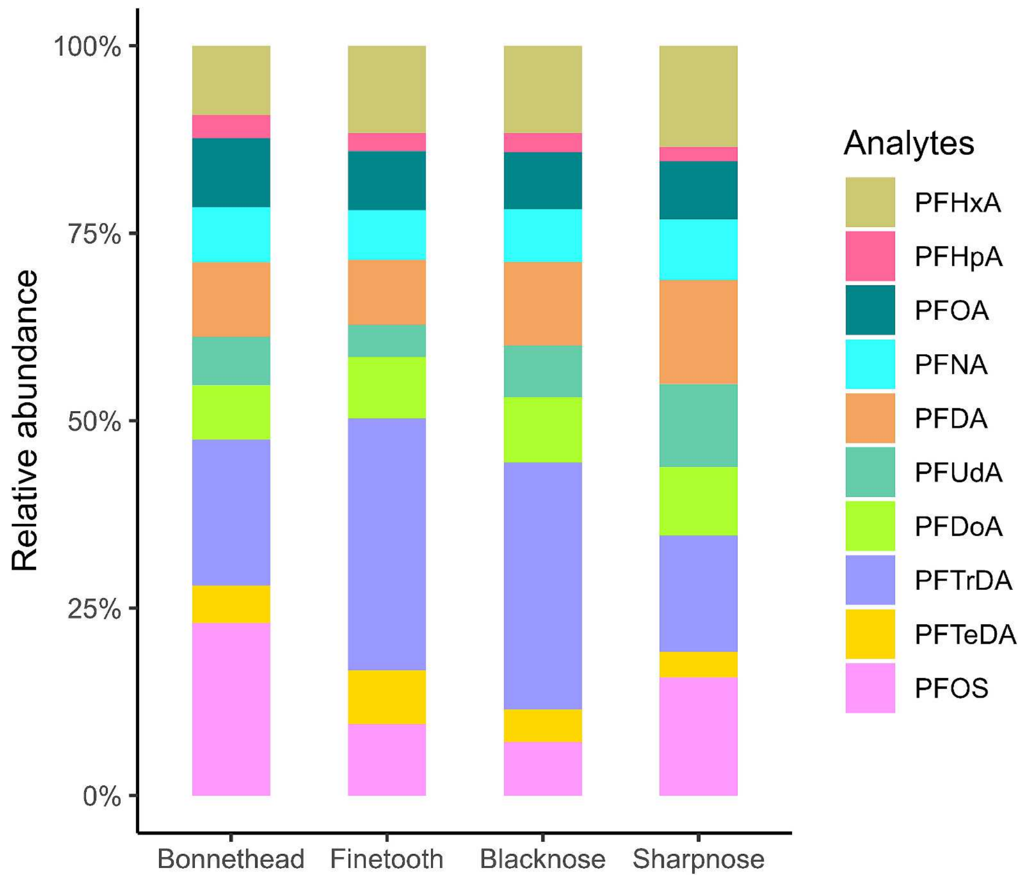

Fig. 2. Comparison of the relative abundance profiles of detected PFAS in plasma samples of various shark species collected along the South Atlantic Bight of the United States.

dominated by crabs, shrimp, and fish (Cortes et al., 1996; Bethea et al., 2007, 2011; Branham et al., 2022). Finetooth sharks primarily feed on filter-feeding fish, particularly menhaden (*Brevoortia patronus*) (Castro, 1993). Blacknose sharks have a more diverse diet, encompassing fish, shrimp, and octopus, while Atlantic sharpnose sharks consume a combination of fish, crabs, and shrimp (Bethea et al., 2004, 2006). Relevant data evaluating the intake of PFAS from prey species to the sharks in the South Atlantic Bight of the U.S remains is not currently available. Nevertheless, the beforementioned dietary sources from previous investigations exhibit substantial overlap, suggesting that there may be additional exposure routes that also contribute to the species-specific burdens of PFAS.

Estuarine areas have been shown to be PFAS “hotspots” as they are typically close to a wide variety of possible sources of contamination (Avellán-Llaguno et al., 2021; Miranda et al., 2021). In this study, bonnethead shark samples were primarily obtained from estuaries while the other sharks were predominantly sourced from coastal areas. The preference/tendency of bonnetheads for estuarine environments (Driggers et al., 2014) could be another possible explanation for the greater PFAS accumulation in these species.

Thus, we hypothesize that the type/location of habitat and dietary selection of these sharks may both be underpinning factors that correlate with ∑PFAS detected in their plasma.

3.3. PFAS associations with biological parameters

A Wilcoxon Mann-Whitney *U* test revealed that bonnetheads displayed a significantly higher concentration of ∑PFAS in male specimens ($n = 24$) when contrasted with their female counterparts ($n = 79$) ($p = 0.001$) (Fig. 4). No significant differences in ∑PFAS between sexes were observed in the other shark species: finetooth sharks ($p = 0.914$) males ($n = 41$), females ($n = 60$); blacknose sharks ($p = 0.525$), with males ($n = 23$), females (n = 60); and Atlantic sharpnose sharks ($p = 0.089$), with males ($n = 18$) and females ($n = 10$) (Fig. 4). Further, we investigated sex-based differences in all sharks for those individual PFAS detected at a rate of ≥75 % to determine which PFAS were driving observed sex-based differences (Fig. S1). No statistically significant differences were noted for individual PFAS among sex groups of finetooth sharks and blacknose sharks. This agrees with prior studies conducted on sharks inhabiting the Atlantic Ocean (Alves et al., 2016) and the eastern Mediterranean Sea (Zafeiraki et al., 2019), where no significant differences in PFAS levels were observed between male and female individuals. However, in the case of bonnetheads, significantly higher levels in males were observed for PFOA ($p = 0.0067$), PFDA ($p = 0.0016$), PFUdA ($p = 0.046$), and PFOS ($p = 0.00015$. Similarly, in Atlantic sharpnose sharks, males exhibited elevated levels of PFOA (p = 0.0067), PFNA ($p = 0.000093$), and PFTrDA ($p = 0.019$) compared to females. The notable sex-specific disparities observed in ∑PFAS levels among bonnetheads (Fig. 4), as well as in individual PFAS levels in both bonnetheads and Atlantic sharpnose sharks (Fig. S1), suggest the possibility that females may undergo PFAS offloading during pregnancy and/or there are other factors such as sex-based dietary or locational differences This is supported by Chynel et al. (2021), who reported that viviparous sharks experience maternal offloading of PFAS to embryos during the gestation period, leading to lower concentrations in females. While our study is the first to report significant sex-based differences in multiple PFAS in small coastal sharks, further research is recommended to gain a deeper understanding of the underlying mechanisms responsible for these sex differences in these select species.

We also investigated the association between concentrations of PFAS

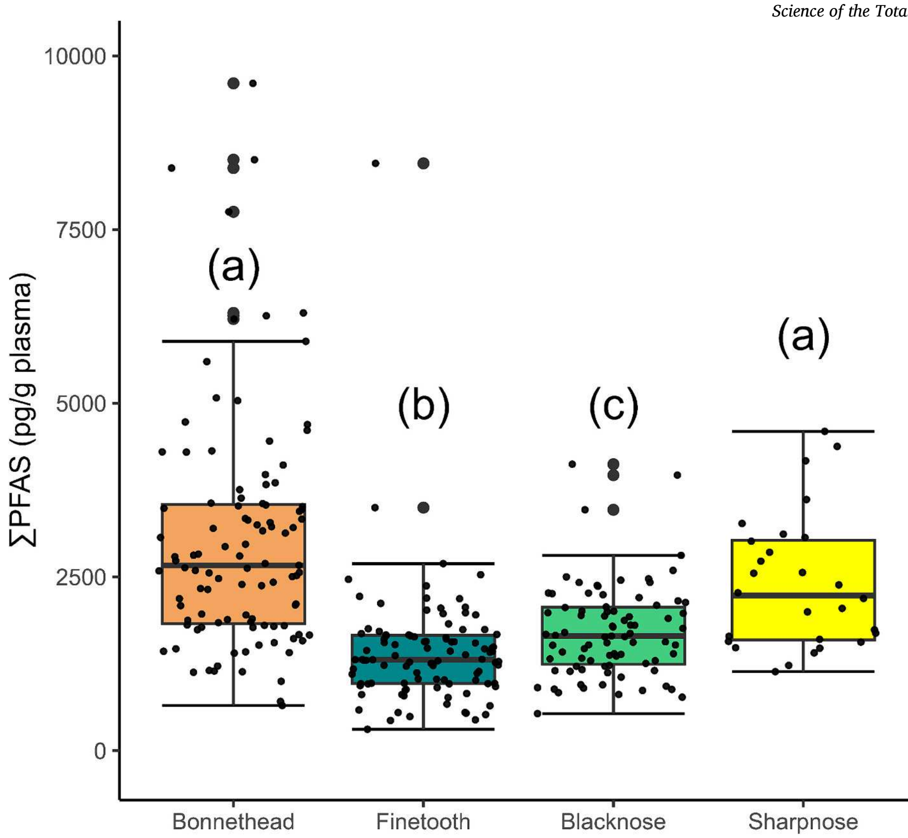

Fig. 3. Total PFAS comparison based on the Kruskal-Wallis along with the Dunn post-hoc tests among the individuals of shark species: bonnethead (n = 103), finetooth (n = 101), blacknose (n = 83), Atlantic sharpnose (n = 28) collected from the South Atlantic Bight of the United States. Bonnethead: finetooth (p.adj = 1.94×10^{-21}), bonnethead: blacknose (p.adj = 1.42×10^{-09}), finetooth: blacknose (p.adj = 7.8×10^{-03}), bonnethead: Atlantic sharpnose (p.adj = 2.12×10^{-01}), finetooth: Atlantic sharpnose (p.adj = 1.28×10^{-06}), blacknose: Atlantic sharpnose (p.adj = 7.1×10^{-03}). Solid line in the boxplot indicates the median, whiskers represent the range while the small-dots represent individual species in each group of sharks and the solid-dots indicate the outliers. Letters (a,b,c) point to significant differences among species in ∑PFAS (pg g-1 plasma).

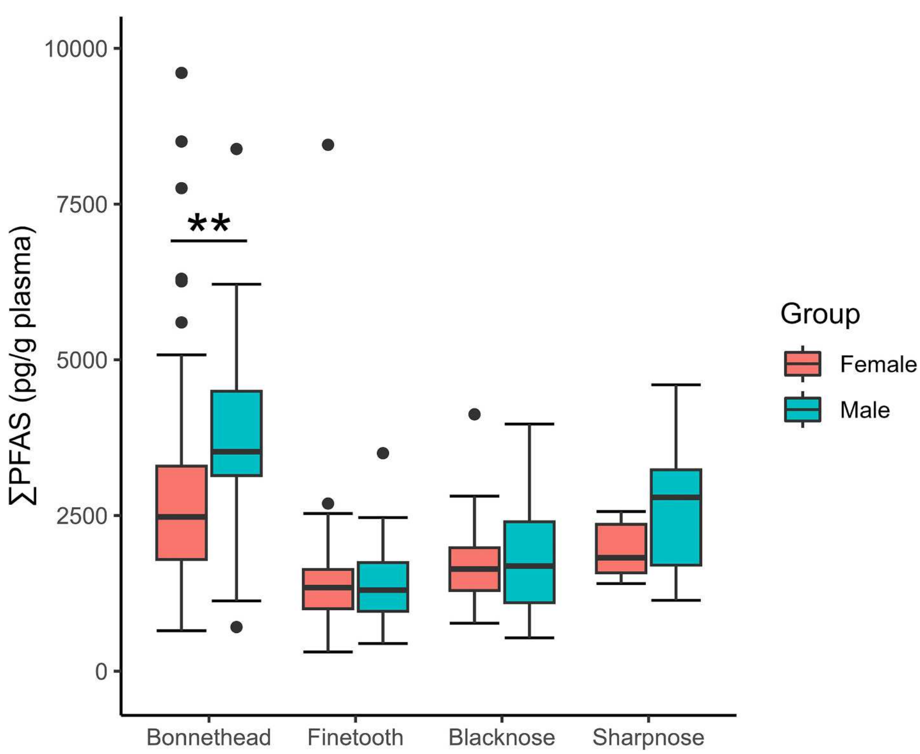

Fig. 4. Mann-Whitney U test comparison profiles of ∑PFAS between male and female groups of various shark species. (Asterisks indicate significant differences between the sex groups: *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$). Solid line in the boxplot indicates the median, whiskers represent the range while the solid-dots display the outliers.

in plasma and shark length using Spearman's rank correlation coefficient (r) analysis, as depicted in (Figs. S2 – S6). In Bonnethead, PFOA, PFOS, and ∑PFAS were statistically significant but exhibited weak negative associations. No strong correlation of ∑PFAS or individual PFAS between the length of sharks was observed for all species studied. This is consistent with several sharks studied by Zafeiraki et al. (2019), where no correlation was observed in relation to body size of sharks.

3.4. Associations among PFAS

The Spearman correlation analysis revealed significant associations among the measured PFAS to each other in the plasma of sharks, particularly emphasizing robust correlations within longer chain PFAS ($C \geq 8$) (Fig. S7). However, PFTrDA stood out as an exception, displaying no correlation with any other PFAS across all the four-shark species investigated.

Upon species-specific examination, bonnethead sharks exhibited the strongest correlation for PFUdA with PFDA and PFDoDA ($r = 0.91$ and $r = 0.89$, respectively). In finetooth sharks, a significant correlation was observed between PFOS and PFDA ($r = 0.72$). Blacknose sharks displayed a predominant correlation between PFUdA and PFDA ($r = 0.85$). Atlantic sharpnose sharks, on the other hand, demonstrated the highest correlations for PFDA with PFOS and PFUdA ($r = 0.94$ and 0.92, respectively). Overall, these findings indicate a common source of exposure for longer chain PFAS in the studied shark species, with the exception of PFTrDA. The lack of correlation for PFTrDA suggests a potential different source of exposure or properties for this specific PFAS compared to the other PFAS in these sharks.

3.5. Global comparison of PFAS in sharks

To provide context for this study, we undertook a comprehensive comparative analysis of prior studies encompassing diverse shark species across the globe and PFAS burden. PFAS have been examined in a range of shark tissues and organs, such as liver, gills, gonads, heart, muscle and skin (Senthil Kumar et al., 2009; Alves et al., 2016; Zafeiraki et al., 2019; Chynel et al., 2021; Boldrocchi et al., 2022), as shown in (Table S14). Within the studied tissues of sharks worldwide, the presence of PFOS and PFCAs with carbon chain lengths (C8 – C13) have been consistently documented. PFOS emerges as the most extensively studied PFAS in wildlife and commonly is implicated as having a high potential for bioaccumulation within the marine food web on a global scale (Miranda et al., 2022). However, long chain PFCAs appear to hold the dominant presence within most studied shark tissues. Within the global cohort of studied sharks, the most elevated concentration of a single PFAS ever documented was 27,100 pg g^{-1} wet weight (ww) of PFTrDA, found in the liver of an individual bigeye thresher shark (*Alopias superciliosus*) in the Mediterranean Sea, which supports the high bioaccumulation tendency for PFCAs in sharks (Table S14). The highest recorded levels of ∑PFAS at 84,200 pg g − 1 ww were detected in the liver of an angular roughshark (*Oxynotus centrina*) from the Mediterranean Sea, surpassing the ∑PFAS levels observed in any other shark species. As shown in this study, bonnetheads exhibited the highest ∑PFAS concentration in plasma (9606 pg g − 1), among the sharks studied from the U.S. South Atlantic Bight. The elevated PFAS levels in the liver of an angular roughshark and the plasma of bonnethead sharks could be attributed to their distinct benthic feeding behavior (Kousteni and Megalofonou, 2016; Plumlee and Wells, 2016). Remarkably, both species, known for their benthic foraging, showed the highest PFAS contamination in liver and plasma tissues compared to other shark species studied (Table S14). This phenomenon reinforces the significance of shark feeding ecology in relation to the accumulation of PFAS.

The comprehensive understanding of PFAS distribution within complete organisms is a topic that lacks substantial clarity and summarization, especially across species. In this capacity, prior studies that have focused on sharks have highlighted significant variations in the distribution patterns of PFAS across distinct tissue types (Table S14). This trend remains consistent across a diverse range of shark species investigated on a global scale, regardless of their specific taxonomic classifications. Thus far, data suggests that the liver is a prominent site for the accumulation of ∑PFAS (Fig. S8). Interestingly, the liver is predominantly comprised of proteins and PFAS have been shown to forming complexes with proteins in blood-rich tissues (Fliedner et al., 2020; Bangma et al., 2022). Given the liver's pivotal role in investigating PFAS dynamics, this distinctive pattern extends to other protein-rich tissues such as gills, gonads, and the heart (Fig. S8).

In this study, we highlight the presence of distinct PFAS variants detected in plasma that have also been found in other major organs of various sharks studied globally (Table S14). Traditionally, ecotoxicological studies have relied on lethal sampling (Marsili et al., 2016), yet harvesting major organs poses potential repercussions on wildlife populations, as well as the structure and functioning of marine ecosystems (Barnett et al., 2010). In light of the increasing focus on the conservation of vulnerable wild species susceptible to overexploitation, the need for non-lethal sampling methods in ecotoxicological studies is imperative (Awruch et al., 2008). Hence, collection of plasma from live specimens, as demonstrated in this study, could be a viable and ethical non-lethal method for assessing PFAS burden in potentially vulnerable and/or endangered shark species.

4. Conclusions

The present study provides data in research gaps concerning the presence of PFAS in plasma samples of small coastal sharks inhabiting the South Atlantic Bight of the U.S. The analysis of 315 plasma samples from 4 different shark species showed the presence of at least one individual PFAS in all analyzed sharks. We observed differences in the detection rates and accumulation pattern of PFAS, among the shark species examined, suggesting species-specific variation. Bonnethead sharks showed the highest ∑PFAS likely due to their benthic feeding behavior. Consequently, it can be inferred that different shark species may exhibit distinct vulnerabilities to PFAS contamination. In addition, this study also uncovered significant variations of PFAS concentrations between sexes for select species but no significant association was observed for PFAS vs shark length. To gain a comprehensive understanding of PFAS exposure in different shark species, future research should investigate influential factors such as feeding ecology, habitat preferences, and metabolic rates. Overall, this study highlights the need for assessing PFAS contamination in sharks and other apex marine organisms across different geographical locations. The implications of the findings extend to the conservation and management of shark populations, as PFAS exposure has the potential to adversely affect wildlife health and reproductive success. Therefore, concerted efforts should be made to minimize the release of PFAS into the marine environments and develop effective strategies for the remediation and removal of these contaminants in marine ecosystems. Furthermore, future research should also delve into the maternal offloading and trophic magnification of PFAS and evaluate the broader ecological concerns of these contaminants in marine ecosystems. To effectively mitigate PFAS contamination in the environment, further research is warranted to identify the sources and pathways. This knowledge will be instrumental in developing effective mitigation strategies aimed at safeguarding marine ecosystems and the organisms that inhabit them.

CRediT authorship contribution statement

Qaim Mehdi: Writing – original draft, Software, Resources, Investigation, Formal analysis, Data curation, Conceptualization. **Emily K. Griffin:** Writing – review & editing, Data curation. **Juliette Esplugas:** Writing – review & editing, Formal analysis, Data curation. **Jim Gelsleichter:** Writing – review & editing, Data curation, Conceptualization. **Ashley S. Galloway:** Writing – review & editing, Data curation. **Bryan**

S. Frazier: Writing – review & editing, Data curation. **Alina S. Timshina:** Writing – review & editing, Data curation. **R. Dean Grubbs:** Writing – review & editing, Data curation. **Keyla Correia:** Writing – review & editing, Formal analysis, Data curation. **Camden G. Camacho:** Writing – review & editing, Methodology, Formal analysis, Data curation. **John A. Bowden:** Writing – review & editing, Visualization, Supervision, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they do not possess any known financial interests or personal associations that may have influenced the findings presented in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.171758.

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