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Journal

ACS ES&T Water, 3(5)

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Publication Date

2023-04-19

DOI

10.1021/acsestwater.2c00296

Peer reviewed

Published in final edited form as:
ACS ES T Water. 2023 April 19; 3(5): 1243–1259. doi:10.1021/acsestwater.2c00296.

Occurrence and Bioaccumulation Patterns of Per- and Polyfluoroalkyl Substances (PFAS) in the Marine Environment

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic compounds used in commercial applications, household products, and industrial processes. The concern around the environmental persistence, bioaccumulation and toxicity of this vast contaminant class continues to rise. We conducted a review of the scientific literature to compare patterns of PFAS bioaccumulation in marine organisms and identify compounds of potential concern. PFAS occurrence data in seawater, sediments, and several marine taxa was analyzed from studies published between the years 2000 and 2020. Taxonomic and tissue-specific differences indicated elevated levels in protein-rich tissues and in air-breathing organisms compared to those that respire in water. Long-chain perfluoroalkyl carboxylic acids, particularly perfluoroundecanoic acid, were detected at high concentrations across several taxa and across temporal studies indicating their persistence and bioaccumulative potential. Perfluorooctanesulfonic acid was elevated in various tissue types across taxa. Precursors and replacement PFAS were detected in several marine organisms. Identification of these trends across habitats and taxa can be applied towards biomonitoring efforts, determination of high-risk taxa, and criteria development. This review also highlights challenges related to PFAS biomonitoring including (i) effects of environmental and biological variables, (ii) evaluation of protein binding sites and affinities, and (iii) biotransformation of precursors.

GRAPHICAL ABSTRACT

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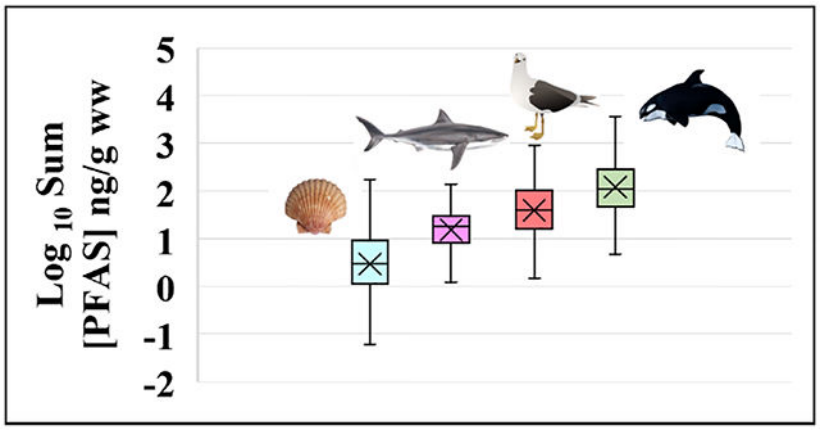
Conflict of Interest Statement- The authors declare no conflict of interest.



1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are anthropogenic organic compounds with over 8000 unique known structures in the Toxic Substances Control Act Inventory.[1, 2] They have been used in commercial and industrial applications since the 1940s. Due to their widespread use in commercial products such as food packaging, water-repellent textiles and coatings, fire-fighting foams, and others, PFAS are ubiquitous in the environment. PFAS have been described as the "forever chemicals"[3] for their persistence in the environment and resistance to degradation; they are particularly difficult to break down because of the strength of their carbon-fluorine bonds. Unlike other persistent organic pollutants (POPs) like polychlorinated biphenyls (PCBs) and chlorinated pesticides, PFAS are amphiphilic and, therefore, their binding affinities and partitioning properties are different from other organic contaminants.[4] Due to these unique properties and the large number of structurally different chemicals, the assessment of PFAS bioaccumulative potential and toxicity is a very challenging task.[1] As more reports on their persistence and toxicity emerged, manufacturers began voluntarily phasing out production of certain PFAS products in the early 2000s. Some countries have also imposed regulations and guidelines on PFAS usage of several compounds.[5] Despite reduced use of legacy compounds, PFAS continue to be produced and detected worldwide and their long-range transport continues to raise concern even in remote locations.[3, 6]

The attention towards adverse impacts of PFAS has largely been related to human health hazards but the concern around their bioaccumulation in biota, and specifically marine biota, is rising as more studies report their prevalence in these habitats. PFAS have been shown to adversely affect several physiological processes and metabolic pathways[7] that are conserved across phyla. Maternal transfer of several PFAS, including emerging PFAS, to fetus has been documented.[8] Identification of trends related to occurrence, fate, behavior, and bioavailability of PFAS is critical to understanding the risks posed by this class of contaminants. Further, comparative evaluations of trends support selection of priority PFAS for monitoring programs which are relevant to risk assessments and implementation of management options. Selection and grouping of PFAS based on their bioaccumulative potential (focused on protein binding properties) coupled with toxicity

(focused on disruption of key metabolic pathways) can streamline management efforts.[9] For example, such efforts are useful in the derivation of protective criteria intended to identify concentrations below which an individual PFAS would not represent a significant toxic risk. Based on their high persistence, bioaccumulation and hazard potential, Kwiatkowski et al have proposed management of PFAS as a class, rather than individual chemicals.[3]

In this review, we focus on the occurrence and bioaccumulation of PFAS in marine organisms and present comparisons for taxonomic classes ranging from marine plankton to mammals. We have collected data from published studies across temporal and spatial scales to identify overall trends of PFAS bioaccumulation in the marine environment. For this review, temporal scales include individual years while spatial scales extend over large regions of marine systems (e.g., large sections of oceans). Bioaccumulation trends over spatial and temporal scales are valuable for identifying priority contaminants of concern and high-risk taxa. Additionally, region- and population-specific trend assessments are required to advance biomonitoring efforts in specific areas (e.g., bays, contaminant hotspots). Of course, the more highly resolved data across temporal and spatial scales are important to understand PFAS bioaccumulation trends in specific areas (e.g., bays).[10] Such localized data provide us insights into risks to local fauna and identification of hotspot regions. However, trends that hold over large spatial and temporal scales provide robust comparisons, assisting in prioritization of chemicals of highest concern and identification of most vulnerable species. In addition, trends that are observed in temporal studies (as discussed in this review) conducted in different regions further highlight the usefulness of our approach. Syntheses of bioaccumulation trends across taxa, as presented in this review, can help to better understand the management of this vast contaminant class.

In recent decades, PFOS (perfluorooctanesulfonic acid) and PFOA (perfluorooctanoic acid) have been the subject of numerous studies which have investigated their bioaccumulation and toxicity across different taxa.[11–13] PFOS biomagnification has also been observed in arctic food webs.[4, 12] The PFAS bioaccumulation trends and comparisons presented in this review include perfluoroalkyl sulfonic and carboxylic acids (PFSAs and PFCAs respectively, or simply sulfonic and carboxylic acids hereafter), as well as several precursor and replacement compounds. Replacement PFAS have been introduced as substitutes for more hazardous PFAS;[14] however, some of these replacements as well as precursor compounds are detected across species and are raising concern.[9, 14, 15] These comparisons across taxa also highlight good bioindicator species of PFAS bioaccumulation.

Advancement of our understanding of PFAS occurrence and bioaccumulation, and more specifically biomagnification, towards the goal of better risk management requires more information on uptake and elimination kinetics. Despite the ubiquity of PFAS in marine organisms, bioaccumulation data comparisons are challenging because of differences in reporting concentrations (use of wet versus dry weight) and data compilation metrics (arithmetic means, geometric means, ranges, medians).[16] This review also identifies such challenges and data gaps in PFAS bioaccumulation research as well as highlights the need for standardization in reporting PFAS concentrations in biota. While we summarize the presence of PFAS in seawater, marine sediments and organisms, reporting on the toxicity of PFAS to marine organisms is beyond this review’s scope.

2. METHODS

Web of Science and Google Scholar were utilized for conducting literature searches. Published studies were selected for data extraction using keywords as described below and filtered for publication time range 2000–2020. The majority of the selected studies were identified from Web of Science (all databases) searches using keywords (1) PFAS and marine organisms (73 results), (2) per and polyfluoroalkyl substances and marine organisms (24 results), (3) per and polyfluoroalkyl substances marine occurrence (21 results), (4) PFAS bioaccumulation in marine organisms (25 results), (5) perfluorinated alkyl acids and marine organisms (32 results), (6) “perfluoroalkyl acids” and “marine organisms” (17 results). Additionally, Google Scholar searches were conducted using keywords (1) “PFAS bioaccumulation” and “marine organisms” (11 results), (2) “perfluorinated alkyl acids” and “marine organisms” (65 results). After duplicate removal, a total of 143 manuscripts were selected for data extraction. Tables S1 and S2 list all the PFAS and organisms presented in this review, respectively. Table S3 lists the studies from which occurrence and bioaccumulation data were extracted.

Sampling sites include marine/coastal regions and natural saltwater locations. Details on locations, dates and tissue types utilized for current comparisons are available upon request. Studies that report either individual concentrations or arithmetic means were used for data extraction. Studies that report other statistical metrics such as geometric means, medians, ranges were not included in our analyses. Except for seawater, sediment and plankton data, only studies reporting concentrations based on wet weight (ww) were selected. Out of 143 studies used in this review, 20 (19 sediment studies and 1 planktonic study) present data based on dry weights (dw); these were included in the analysis.

Seawater data were divided into five major oceans of the world (i.e., Arctic, Atlantic, Pacific, Indian and Southern Oceans). Further, Atlantic and Pacific Ocean data were divided into northern and southern regions. Thirty-one studies were utilized for seawater and sediment data extraction and six for plankton. Our database searches revealed more published studies on PFAS occurrence and bioaccumulation for seawater and sediment samples from the northern hemisphere. Seawater samples include surface water and deep chlorophyll maximum samples from coastal and offshore sites. Several studies presented here report surface sediment data points (i.e., top 10 cm), but despite differences in sample collection depths across studies, these samples reflect the biologically active zone in the marine environment. These observations do not include suspended particulate data. Wherever required, seawater data were converted to pg/L and sediment data were expressed as ng/g dw. Given the limited number of published studies, zoo- and phytoplankton data were combined to obtain overall planktonic trends for a more inclusive assessment. Plankton data were also combined to reflect concentrations based on dry and wet weights as data on plankton PFAS levels are not always reported consistently. Seawater, sediment, and plankton data are shown as arithmetic means taken across temporal and spatial scales.

The focus of this review is on wild marine organisms and PFAS concentrations are presented across several tissue compartments. Studies reporting PFAS levels in supermarket/seafood-market shellfish and fish were not included. Along with plankton, classes of

marine organisms included are invertebrates, fish, reptiles, birds and mammals. Eighteen invertebrate studies including 68 species (taxonomic identification used to the genus level where species information wasn't available) were used for data extraction. The invertebrate data presented here reflect either whole body or soft tissue burdens, unless specified otherwise.

The fish dataset includes information on 104 species from 21 studies. Data from studies reporting whole fish and sagittal sections (representing whole fish) were combined to reflect fish burdens. Fillet and muscle data were also combined for fish muscle dataset.

To be inclusive, blood, plasma, and serum data were merged; these data, expressed as ng/g and ng/mL, were combined to generate means. Wherever applicable, these combined data are presented as ng/g ww. Limited information on PFAS levels in marine reptiles is available and data were extracted from three studies. Mammalian and avian datasets were the most data-rich and spanned several taxonomic families. Mammalian data include 36 species from 44 studies and avian data include 59 species from 35 manuscripts. Bird egg data were combined across laying sequence as well as part of the egg (i.e., yolk versus whole) analyzed.

Wherever possible, data were extracted to obtain individual datapoint measurements from the main body of the reviewed articles as well as their supplemental information. However, in order to obtain a more complete analyses, arithmetic means presented in published literature were also utilized wherever individual datapoint measurements were not available. PFAS bioaccumulation data are presented as box and whisker plots showing arithmetic means (x in the boxplot), medians (horizontal line within the box), the 75% quantile (top of box), 25% quantile (bottom of box), ranges of datapoints for each taxonomic grouping (the whiskers), and the raw data points including the outliers (the circles). These plots show either all PFCA or all PFSA values for trend comparisons across taxonomic groups. Further, sum of PFAS is also presented to identify trends in total PFAS levels across taxa. For further resolution within taxonomic and chemical classes, we also present means of all datapoints in column graphs in supplemental figures. Wherever applicable, considerations regarding arithmetically-averaged datapoints are discussed in reference to independent studies that report these data.

Non-detects or datapoints below detection limits (<MDL) were removed from the analyses and not used to calculate means. As analytical methods evolve over time, the detection limits for PFAS have changed. We present data combined across temporal and spatial scales that are extracted from manuscripts published over a 20-year period. Therefore, unlike site-specific studies, there are no valid substitutes for non-detects for this synthesis. It must be noted that we are only reporting measured concentrations above detection limits and omission of non-detects does bias our dataset towards higher values. However, the goal of this review is not to compare sites or populations, but to identify overall trends of reported PFAS concentrations. For this review, long-chain PFAS are defined as having ≥8 carbons (≥C8) unless otherwise noted. The data presented here reflect summed concentrations of branched and linear isomers. Age and sex-based differences have been reported to be unclear

across species (e.g., as described for fish in Hart, et al.[17] and for marine mammals in Bossi, et al.[18]), hence data were combined across gender and sex (if available) for completeness.

3. RESULTS AND DISCUSSION

3.1 Seawater, surface sediments and plankton

Seawater—Both short- and long-chain PFAS were detected in seawater across all five major oceans. PFAS in seawater include PFCAs ranging in chain length from PFBA (C4) to PFODA (C18), PFSAs ranging from PFBS (C4) to PFDS (C10), and several precursor and replacement compounds. Figure 1A shows percent contribution of individual PFAS in seawater. The most diverse PFAS profile was detected in the North Pacific with twenty-seven different compounds while Southern Ocean data only show two different PFAS types (Figure 1A). Such differences could be indicative of spatial variabilities characterized by differences in PFAS sources, distance from the source(s), and PFAS transport. It must be noted that targeted assessments are limited to a set of selected PFAS and the 'real world' total PFAS burdens and diversity are likely higher in the environment. Emerging non-targeted analytical approaches are valuable tools (Table 1) in PFAS monitoring aimed at capturing PFAS diversity across different matrices.[19] The sum of all PFAS in the seawater dataset was the highest in the Indian Ocean (41.1 ng/L) followed by the North Pacific (12.8 ng/L), the North Atlantic (4.0 ng/L), the South Atlantic (2.6 ng/L), the Arctic (1.1 ng/L), the South Pacific (0.5 ng/L) and the Southern (<0.1 ng/L) Oceans. PFAS profiles vary among oceans, but overall trends indicate that PFOA and PFOS are found globally in seawater (Figures 1A and S1, S2). PFCAs with ≥12 carbons (i.e., PFDoA, PFTrDA, PFTeDA, PFPeDA, PFHxDA, PFODA) contribute less than 2% to PFCA profiles in every major ocean (Figure S2A). In the Arctic Ocean, PFBA and PFBS are dominant contributors to carboxylic and sulfonic acid profiles, respectively (Figure S2). Additionally, FOSA (24.7%) and PFBA (23.9%) contribute the most to the total PFAS concentrations in the Arctic Ocean followed by PFPeA (12%), PFHpA (8.6%), and PFOA (6.6%). The North Atlantic data show PFUnA (55.1%) as the dominant PFAS followed by PFOS (11.5%), PFOA (10.5%) and PFHxA (6.1%) (Figure 1A). PFOS is the dominant sulfonic acid in the North Atlantic and the biggest contributor (43.4%) to the PFAS burden in the South Atlantic Ocean (Figure S2). Among the PFCAs, PFOA contributes the most and was also the second most dominant PFAS (30.1%) in the South Atlantic. PFOA also dominates the PFAS profile in the North Pacific (38.8%) followed by PFBA (16.5%), PFPeA (7.6%), and PFHxA (6.2%). PFAS profiles of the South Pacific, Indian and Southern oceans are dominated by PFOS with respective contributions of 29.7%, 32.3% and 70%. PFDA (21.8 %) and PFOA (30%) are the second largest contributors to total PFAS burdens in the South Pacific and Southern Oceans (Figure 1A). The PFAS profile of the Indian Ocean also includes PFHxS (16.1%), PFBA (13.9%), PFPeA (10.9%), and PFHxA (8%). Perfluoroalkane sulfonamide-based PFAS, particularly FOSA, were also detected in seawater (Figure S3). Continental discharges are proposed to be the main sources of PFAS pollution in the marine environment and there is evidence for inverse relationships between salinity and PFAS concentrations.[20] The differences in PFAS concentrations across various water bodies reflect the relative inputs of the nearest landmass over time. Based on the seawater data presented in this

review, Southern Ocean is underrepresented in the existing PFAS literature and requires further investigations.

Surface Sediments—Sediment profiles also include both short- and long-chain PFAS as well as precursor and replacement compounds across different geographical regions (Figure 1B). However, unlike seawater, long-chain PFCAs are detected frequently in sediments and contribute more to overall PFAS burden (Figures 1B and S2A). Studies suggest that PFOS tends to partition into the sediment phase and PFOA into the water phase.[21–23] Such differences in partitioning are important to consider for criteria development and assessment of bioavailability. As seen in Figure 1, in comparison to seawater data, the contribution of PFOS to overall PFAS burden is found to be higher than PFOA in sediments. However, both PFOA and PFOS are detected in sediments from all the regions presented in this review; greater contribution of PFOA to total PFAS burden in the northern hemisphere was also observed. Specifically, PFAS concentrations were the highest in the North Pacific Ocean (4.61 ng/g) followed by the Southern Ocean (4.56 ng/g), the South Pacific (3.16 ng/g), the North Atlantic (2.29 ng/g) and the Arctic (1.54 ng/g) Oceans as shown in Figure S1B. PFBA contributes 17.48%, 7.74% and 38.99% to the PFCA profiles of the sediments from the Arctic, North Pacific and Southern Oceans, respectively (Figure S2A). Long-chain PFCAs such as PFNA, PFDA, PFUnA and PFTrDA are detected in sediments from all regions presented in this review. Sediment PFSA profiles were dominated by PFOS in all regions. Further, PFHxS was detected in sediments from all regions as well; PFBS and PFDS were observed in four out of five reported regions in this review (Figure S2B). Compared to other precursor and replacement compounds detected in the sediments, 6:2 FTS was reported at relatively high concentration in the North Atlantic samples (i.e., 1.3 ng/g dry weight, Figures 1 and S3).[24] Upon calculation of arithmetic means for comparisons across regions, this precursor is found to contribute 56.7% to the total PFAS burden in the sediment from multiple sites in the North Atlantic. Interestingly, this same study also conducted seawater analyses and 6:2 FTS was below detection limits. Such findings reveal the need for further investigations into precursors and replacement PFAS across global oceans in seawater and sediment phases and the nature of their partitioning between phases.

Plankton—PFOA and PFOS were detected in plankton from all regions presented in this review (Figure 1C). The total PFAS concentrations in the plankton were the highest in the South Atlantic Ocean (28.3 ng/g) followed by the South Pacific (19.9 ng/g), Indian (18.3 ng/g), North Atlantic (13.9 ng/g), North Pacific (7.0 ng/g) and Arctic (5.7 ng/g) Oceans as shown in Figure S1C. Short-chain PFCAs including PFBA, PFPeA and PFHpA were detected in plankton from the Atlantic, Pacific and Indian Oceans. PFOA is the dominant PFCA in the plankton (Figure S2A). However, long-chain PFCAs (≥C9) contribute less than 10% of total PFAS burden in plankton (Figure 1C). Casal, et al.[25] suggested that PFPeA, PFHpA, and PFOA together account for ≥ 80% of the total PFCAs. This study also noted that although long-chain PFCAs (i.e., C10-C13) contribute less to total PFAS burden in plankton, they contribute more to the total PFAS burden in the northern hemisphere than in the southern. The presence of long-chain PFCAs in plankton has been attributed to their geographical location and site-specific seawater concentrations but further investigations are warranted to evaluate trends and relationships between water

and plankton PFAS concentrations. As noted above, some studies have also suggested short-chain PFAS are detected more frequently in the water phase and long-chain PFAS are generally found in sediments.[13, 26, 27] However, short-chain PFAS, such as PFBA, have also been detected in sediment samples from remote locations. Short-chain PFAS have high volatility and water solubility and their long-range atmospheric deposition has been suggested as a mechanism for their distribution globally.[28] It is likely that plankton reflect PFAS concentrations in the water column more closely than higher-trophic level organisms with more complex physiological processes. Most of the plankton reported here are exposed to surface waters and hence accumulate short-chain PFCAs from their surroundings (rather than from benthic sediments). Some of the trends reported in region-specific studies may not be evident in our combined assessments presented in this review due to the use of arithmetic means across spatial scales. Nevertheless, the trends that are detected in data combined across spatial and temporal scales emphasize the need for regulation of priority PFAS and future investigations. For example, prevalence of PFOA in plankton as well as in seawater,[12, 13] and its elevated relative contribution to PFAS burdens, as observed in Figures 1 and S2, are important patterns to consider for evaluating underlying mechanisms dictating the partitioning of these contaminants between environmental phases. As seen in Figure 1, the key PFSA in plankton from all regions is PFOS. Precursor and replacement compounds are also detected in plankton samples (Figure S3). Limited data are available on plankton PFAS bioaccumulation and further investigations are required to assess overall trends and relationships as well as comparison of bioaccumulation patterns between phyto- and zoo-plankton. PFAS bioaccumulation factors measured for oceanic plankton indicate that short-chain PFAS must not be ignored while assessing bioaccumulation and potential biomagnification risks.[25]

Perfluoroalkane sulfonamide-based PFAS were detected in seawater, sediment as well as plankton across different regions (Figure S3). Replacement PFAS, such as chlorinated polyfluoroalkyl ether sulfonic acids (Cl-PFESAs) and fluorotelomer sulfonates (FTS), have also been observed in these samples and are of rising concern due to their reported toxicity.[29] Despite their relatively low concentrations, their increased applications and persistence warrant further research into their bioaccumulative potential as well as identification of their degradation or terminal products.

3.2 Invertebrates

Limited information on invertebrate PFAS bioaccumulation is available. Most of the invertebrate data are focused on crustaceans and mollusks; however, some PFAS bioaccumulation trends were also observed in other invertebrates as well. A wide range of PFAS concentrations were reported in invertebrates (Figures 2 and 3). For example, PFOA and PFOS have been reported in cnidarian studies with giant green anemone at 4.6 and 0.1 ng/g ww, respectively (Figure S4). PFBA (0.26 ng/g ww) as well as long-chain PFAS (PFNA 0.05 ng/g ww, PFDA 0.05 ng/g ww, PFUnA 0.09 ng/g ww, PFDoA 0.02 ng/g ww) were also detected in giant green anemone at low concentrations (Figure S4). PFAS levels in cnidarians and most annelid polychaetes were detected at <5 ng/g ww (Figures 2 and 3). However, species-specific differences were detected and studies report high PFOA concentrations in lugworm and seaworm (82 and 167 ng/g ww, respectively) compared

to other PFAS (Figure S4B). Long-chain PFCAs have been detected more frequently in polychaetes, and PFOS was found in all polychaetes presented in this study. Short-chain PFBS and PFHxS were also detected in polychaetes (Figure S4).

In shrimps and crabs, the majority of PFCA concentrations are below 10 ng/g ww with median concentrations of 0.20 and 0.18 ng/g, respectively (Figure 2). Crustacean data, in both shrimps and crabs, (Figure S5), show that PFOA is detected at relatively high concentrations when compared to other PFCAs. The highest crustacean PFOA concentrations were detected in Chinese crab (65.2 ng/g ww), Blind pea crab (16.8 ng/g ww), Pacific mantis shrimp (16.2 ng/g ww), and Gazami crab (11.14 ng/g ww) (Figure S5). Despite these higher values, the overall PFAS concentrations were found to be similar in shrimp and crab datasets with long-chain PFCAs observed across several species (Figures 2 and S5). Although the detection frequency of short-chain PFCAs is not as high as long-chain compounds, PFBA was detected across multiple species of shrimps and crabs. Higher PFOA levels in some shrimp and crab species may represent region-specific seawater PFAS concentrations.[30] Species-specific differences in crustacean PFAS bioaccumulation reflect differences in diet and feeding behaviors[31] among benthic and pelagic invertebrates.[32, 33] Other factors that are likely to affect crustacean PFAS profiles include molt cycles, larval stages, growth rates, and reproduction.[34] PFSA profiles (Figure 3) show higher levels in shrimps than crabs (median values of 0.95 and 0.48 ng/g ww, respectively). These profiles were dominated by PFOS; PFBS and PFHxS were also detected in crabs and shrimps (Figure S5). Most of the crustacean samples show PFAS burdens in soft tissues and muscle but, as indicated in Figure S5B, PFAS were also detected in roe (e.g., Asian paddle crab) (Figure S5B). Although roe is not as widely studied as other biological compartments, it provides insights into developmental and ecological implications. Further, due to the consumption of crustacean soft tissues and roe by humans, such findings also raise human health concerns.

Despite broad concentration ranges for PFCAs (mean 9.58 ng/g ww; median 0.20 ng/g ww, Figure 2) and PFSAs (mean 17.61 ng/g ww; median 0.30 ng/g ww, Figure 3), the highest PFAS burdens amongst invertebrates are reported in bivalves. Both short- and long-chain PFCAs were detected in mollusks (Figure S6). Overall trends suggest PFOA is detected in most mollusks, and PFBA is also found in several species. Bioconcentration factors (BCFs, contaminant uptake and retention by the organism from the dissolved phase via respiration) for PFOA are reported to be higher in bivalves than in fish[11]. In a unique instance, PFOA levels in the fur clam were detected to be 642 ng/g ww (Figure S6A). This finding could be reflective of increased PFOA levels in the water column and large filtering capacities of bivalves. Further, selective uptake of PFAS could be related to differences in receptor binding and depuration processes as well as benthic feeding. Bivalve PFCA data showed a wide range of concentrations and species-specific differences where several species of clams generally presented higher burdens and the brown mussel had PFUnA levels of 109.3 ng/g ww (Figure S6A). In addition to feeding habits, some of these vast differences in concentrations may also be attributed to species-specific activity of transport proteins belonging to ATP-binding cassette (ABC) superfamily of efflux transporters.[35, 36] PFBA, PFHxA, and PFOA were the main PFCAs found in gastropods (Figure S6B) with the nassa

mud snail containing 12.8 ng/g ww PFOA. Although cephalopods accumulated low levels of PFCAs, several long-chain PFAS were detected across species (Figures 2 and S6C).

Mollusk PFSA profiles were dominated by PFOS(Figure S7). For example, mean and median values for PFOS in Mediterranean mussels were 60.03 ng/g ww and 69.39 ng/g ww, respectively (Figure S7A, n=12). Further, PFBS and PFHxS were also detected in several species (Figure S7). Although studies have reported high concentrations in some bivalves,[37, 38] most mollusk species have <5 ng/g ww concentrations of PFSAs (Figure 3).

Precursors and replacement PFAS were also detected in invertebrates. The most commonly reported precursor compound in invertebrates is FOSA with concentrations reported below 1 ng/g ww (Figure S8). Other PFAS detected in invertebrates are Et-FOSA, Et-FOSAA, L-FOSAA, L-EtFOSAA, L-CH_3FOSAA and 6:2 Cl-PFESA. Most invertebrate studies report <5 ng/g ww of precursor and replacement PFAS across different taxonomic classes (Figure S8); however, EtFOSA was reported to be relatively high in invertebrates from some regions of the Arctic.[12] Specifically, the blunt gaper, Arctic shrimp, and Greenland cockle had burdens ranging from 3.0 to 31.5 ng/g ww, concentrations far exceeding other precursor and replacement PFAS (Figure S8B and S8C).

Invertebrate laboratory studies have shown that PFAS bioaccumulation is concentration-dependent and compound chain length is positively related to the sensitivity of the bioaccumulation factor (BAF, contaminant uptake and retention by the organism from all exposure routes including dietary, water, dermal)[39]. Such findings suggest that changes in the exposure concentrations affect bioaccumulation of long-chain PFAS more than short-chain PFAS. For example, a 56-day long study with green mussels at 1–10 μg/L concentration range showed that PFDA and PFOS have high BAFs but PFOA is not as accumulative[39]. However, large variability in field-collected data emphasizes the need for further investigations into the relationships between exposure concentrations and BAFs. Further, effects of different exposure routes (e.g., aqueous, sediment contact, diet) on bioaccumulation must also be evaluated.[40]

3.3 Fish

PFAS levels in fish are often reported in muscle or fillet and are focused on seafood safety concerns. Several studies also report whole fish and liver PFAS burdens. In addition, along with the birds and mammals discussed below, information on fish is sufficiently large that trends in the data become more apparent compared to the organisms discussed previously.

In the current dataset, PFCA concentrations were found below 5 ng/g ww in muscle tissues of most bony fishes (Osteichthyes) (Figure 4A). In a few cases, such as spot (19 ng/g ww) and inshore lizardfish (23 ng/g ww), PFNA muscle burdens were found to be above 15 ng/g ww (Figure S9A). Long-chain PFCAs, particularly C8 to C13, were detected at higher concentrations than short-chain PFCAs in most of the fishes included in this review. In cartilaginous fishes (Chondrichthyes) such as sharks and rays, concentrations of PFCAs with ≤10 carbons were found to be less than 1 ng/g ww (Figure S9B) while this class of compounds with ≥11 carbons, particularly PFUnA and PFTrDA, were observed to be higher in muscles of this type of fishes (e.g., angular rough shark and bigeye

thresher) when compared to several bony fishes. Due to these higher concentrations, the mean and median values for cartilaginous fish in the PFCA dataset were slightly higher than bony fishes (Figure 4A, mean values: bony fish 0.47 ng/g ww, cartilaginous fish 0.95 ng/g ww; and median values: bony fish 0.10 ng/g ww, cartilaginous fish 0.33 ng/g ww). Many studies suggest dominance of long-chain PFAS with odd number of carbons in fish.[41–43] This pattern has been explained partly due to degradation of fluorotelomer alcohols upon their release into the environment.[17, 41] Atmospheric degradation[44] as well as microbial degradation of fluorotelomer alcohols during wastewater treatment[45] yield PFCAs. Following uptake, metabolic transformation of fluorotelomer alcohols can also result in the production of PFCAs, although its contribution is minor.[46] Further, PFTeDA was also detected in many cartilaginous fishes but not in most bony fishes (Figure S9).

Mean and median PFSA concentrations in the muscle tissues of bony fishes were 1.14 ng/g ww and 0.33 ng/g, respectively (Figure 4B). The mean and median values of cartilaginous fishes (1.70 ng/g ww and 0.70 ng/g ww, respectively) are comparable with bony fishes. However, unlike the cartilaginous fish muscle dataset, several bony fishes PFSA concentrations are above 1 ng/g ww (Figures 4B). These concentrations above 1 ng/g ww represent PFOS concentrations (Figures 4B, S10). In both bony and cartilaginous fishes, PFOS dominated the PFSA profiles (Figure S10). Several species demonstrated elevated PFOS bioaccumulation in various sampled tissues; for example, muscle of spotted seatrout (9.25 ng/g ww), spot (9.4 ng/g ww) and darkfin hind (10.78 ng/g ww), liver tissues of right eye flounder (65 ng/g ww), striped mullet (70 ng/g ww) and bluefin tuna (46.63 ng/g ww), and whole fish samples of spotted seatrout (39.83 ng/g ww), red drum (42.3 ng/g ww) and spot (55.9 ng/g ww). In some instances, PFOS levels were found to be exceptionally high, such as in the liver of dusky flathead (135 ng/g ww). For other PFSAs, PFHxS and PFDS were also detected in some bony fishes (Figure S9A). Whole fish analyses showed similar trends of prevalence of PFOS and long-chain PFCAs in bony fishes (Figures S10 and S11, respectively). For example, the pinfish and sheepshead accumulated high concentrations of PFDoA (22 ng/g ww and 16 ng/g ww, respectively). PFHxS and PFDS, and relatively low concentrations of PFBS, were also detected in whole bony fish analyses (Figure S11) with pigfish and pinfish showing relatively high bioaccumulation of PFHxS. As discussed under our Methods section, due to compilation of these datasets over broad temporal and spatial scales, non-detects are excluded from these comparisons resulting in high average concentrations in some cases. One such example is the pinfish where data reflect relatively short temporal (2002–2004) and smaller spatial scales (southeastern coast of the United States). This dataset includes high variability within the measured concentrations as well as samples below detection limits. Although there are inherent differences in the datasets presented in this review regarding number of years and regions over which the data are collected for each taxonomic grouping, the high reported concentrations do raise concerns. One of our goals is to note that such high concentrations are indeed observed in biota which suggests that further investigative studies into bioaccumulation potentials and variabilities must be conducted for certain taxonomic groups and biological compartments.

Liver data confirmed the differences between cartilaginous and bony fishes that was observed in the muscle comparisons. These differences show that long-chain PFCAs (particularly PFUnA and PFTrDA) were higher in concentration across several cartilaginous

fish livers than in bony fishes (Figure S12A). These differences could be attributed to feeding strategies (bottom versus pelagic feeders), trophic position, and physiological differences and warrant further investigations. Such trends are also affected by spatial differences in PFAS occurrence. Similar to the discussion in the invertebrate section of this review, fish assessments also require comparative studies across species to determine concentration dependence of PFAS bioaccumulation.

PFOS burdens were found to be higher in liver tissues versus muscle as shown in Figure 5. Such tissue-specific differences are also reflected in other PFAS for bony as well as cartilaginous fishes (Figures 5, S10 and S12). Further, increased whole body burdens of some PFAS, including PFOS (Figure 5), in certain fish species could be indicative of elevated liver PFAS levels and more studies are required to understand such tissue-specific contributions to whole body burdens of different PFAS. It has been reported that associations of perfluoroalkyl acids with proteins and phospholipids affect their tissue partitioning and differentiate them from other lipophilic POPs.[47, 48] Differences in protein levels across species and tissue compartments as well as specific protein-binding efficiencies could contribute to differences in uptake and bioaccumulation of PFAS. Additionally, maternal transfer and gestation differences also impact PFAS assessments across fish species.[41] These patterns of elevated liver PFAS burdens across several fish species (Figures 5, S10 and S12) are indicative of important tissue-specific differences in bioaccumulation that must be considered during risk assessments for marine biota. For example, in some species, lower muscle burdens may not characterize them as a risk to seafood safety and human health but elevated PFAS levels in the livers of those same species may be indicative of poor overall fish health and high biomagnification potential through food webs, ultimately leading to poor ecosystem health.

Although muscle and liver are the most studied tissues for PFAS bioaccumulation in fish, a few studies also report PFAS in other biological compartments such as gills, heart, kidney and gonads as shown in Figure S13.[49] Several of these compartments also accumulate PFOS (Figure S13B). The dominance of elevated long-chain PFCAs in these compartments (Figure S13A) confirm the trends observed in liver, muscle and whole fish. Some temporal studies also support these trends which increase the concern regarding the persistence and accumulative potential of long-chain PFAS (Figure S14). One of the perfluoroalkane sulfonamide-based precursors, FOSA, was also detected in muscle, liver, blood, and whole fish analyses (Figure S15). Similar to the tissue-specific trends of other PFAS discussed in this section, FOSA levels were generally higher in liver and whole fish analyses than in muscle tissues in many fish species. While muscle concentrations were below 1 ng/g ww, whole fish analyses in the spotted seatrout and Atlantic croaker report FOSA concentrations ≥ 5.0 ng/g ww. Further, liver concentrations of FOSA in shorthorn sculpin and Atlantic Herring were 9 and 13.9 ng/g ww, respectively (Figure S15). Other novel replacement PFAS, such as Cl-PFESAs, were also detected in fish muscle (Figure S15A). Despite the lack of data on fish blood compared to other compartments, it must be noted that fish can accumulate these contaminants in their blood at relatively high concentrations (Figures S13B and S15D). For example, PFOS and FOSA levels in bluefin tuna blood were 40 ng/g and 15 ng/mL, respectively. Although the importance of muscle PFAS analyses should not be ignored, other protein-rich compartments must also be examined. Tissue-specific

differences in uptake and elimination are key to understanding physiological implications as well as mechanisms of PFAS bioaccumulation. Yi et al demonstrated in a pharmacokinetic study with rainbow trout that Cl-PFESAs were retained longer in liver and kidneys than PFOS.[50] However, elimination rates of these compounds were found to be comparable in blood. To develop a more sophisticated understanding of the bioaccumulation of PFAS by fish, more information on protein-binding sites and partitioning in different compartments is required.

3.4 Reptiles

PFCAs with ≥8 carbons were detected in the plasma of loggerhead turtles and Kemp's ridley turtles (Figure S16). Turtle plasma data show PFOS as the dominant PFAS and it is detected at much higher concentrations than other PFSAs. PFBS, PFHxS and FOSA were also detected in turtle plasma. Temporal data collected between 2000 and 2008 from loggerhead turtles further support the trends of elevated long-chain PFCAs as well as PFHxS and PFOS in plasma (Figure S17).[51] These trends of PFAS bioaccumulation are particularly concerning due to the threatened and endangered status of these marine reptiles. Populations of both species of turtles shown in Figure S16 are at the risk of extinction.[52] Under the United States Endangered Species Act, Kemp's ridley turtle is listed as endangered throughout its range. Some distinct population segments of the loggerhead turtle are considered threatened while others are listed as endangered (NOAA https://www.fisheries.noaa.gov/species/loggerhead-turtle#overview). The loggerhead turtle is also a 'priority species' under European Union environmental protection directives.[53] Adverse impacts of PFAS bioaccumulation on endocrine and reproductive functions are identified in some studies, which could have fitness implications for these protected organisms.[7] Although it has been reported that sex does not significantly influence PFAS bioaccumulation, age and species-specific differences have been shown.[52] Complicating these investigations is that only limited data can be collected from such species due to their conservation status, and it is therefore critical to understand underlying mechanisms of PFAS bioavailability, bioaccumulation and biotransformation across taxa to identify risks to vulnerable populations. Further, information on PFAS interactions with conserved protein targets across taxonomic classes at molecular and biochemical levels of organization is important for prioritizing PFAS management strategies.

3.5 Birds

Most of the studies on PFAS occurrence and bioaccumulation in seabirds include eggs, liver and blood (or plasma) levels. As noted in Figure 6A for avian eggs, mean and median values for the PFCA dataset were lower than for the PFSA dataset (mean values: PFCA 3.03 ng/g ww, PFSA 39.01 ng/g ww; median values PFCA 1.65 ng/g ww, PFSA 18.70 ng/g ww). The elevated PFSA burdens reflect higher PFOS concentrations without which the PFSA mean and median values were only 1.39 and 0.50 ng/g ww, respectively. Tissue- and species-specific differences were observed in PFOS bioaccumulation. High PFOS concentrations were identified in the eggs of gulls, cormorants, auks and herons with some datapoints exceeding 100 ng/g ww for all four types of birds (Figure S18). Some studies have presented evidence for differences in PFOS egg concentrations based on laying sequence.[54–56] High trophic positions of seabirds make them good candidates

for biomagnification studies.[57] For example, gulls have a wide PFOS concentration range (8 to 608 ng/g ww) but overall, they present elevated burdens in eggs and tissues (Figure S18). It must be noted that most gulls are omnivores and opportunistic feeders, and are known for their high energy requirements and elevated feeding rates. Other members of family Laridae such as terns, kittiwakes and noddies also show PFOS bioaccumulation in eggs and tissues; however, more data are required to characterize tissue- and species-specific differences as well as dietary effects on PFAS burdens. Interestingly, terns appear to have higher PFOS concentrations in liver tissues compared to eggs (e.g., 98–280 ng/g ww versus 1–2 ng/g ww, respectively) (Figure S18). Elevated PFOS egg burdens were also seen in birds from the order Suliformes including benthic feeders such as shags, piscivorous cormorants and gannets as well as in auks and herons but with wide concentration ranges within taxonomic groups (e.g., 5–433 ng/g ww for Suliformes, 7–400 ng/g ww for auks, and 20–143 ng/g ww for herons) (Figure S18A). Such observations could be indicative of metabolic and physiological differences related to PFAS elimination.[58, 59] Further, tissue PFAS burdens could reflect differences in exposure such as duration of exposure and spatial differences as well as variations in binding affinities to specific proteins and phospholipids across species. It has also been noted that depuration rates may be dependent on exposure concentration and linked to age.[55] More information on species- and tissue-specificity will help determine target tissues for bioaccumulation (e.g., proteinaceous, lipoidal) and toxicological analyses. A tissue-specificity study reporting PFOS burdens in brown pelican showed highest concentration in bile and spleen followed by lung, kidney, brain, heart and muscle (0.8 to 66 ng/g ww) (Figure S21).[60] Interestingly, these data suggest the tissues most often sampled (e.g., muscle) may not be the optimal indicator of ‘worst-case’ bioaccumulation and further illustrate the need for tissue-specific characterization of PFAS burdens. Tissue-specific differences in FOSA levels were also reported (Figure S21).

In order to identify PFAS fate and transfer patterns in birds, it is important to determine links between egg and liver PFAS burdens. For example, it has been suggested PFOS can be maternally transferred to the egg at a high transfer rate via yolk proteins that are synthesized in the maternal liver. Further, transfer rates of PFCAs to eggs increase with the length of the carbon chain,[61] hence enhancing the bioaccumulative potential of long-chain PFCAs in avian eggs. Studies suggest the first egg reflects maximum pollutant transfer from females to eggs, particularly for long-chain PFCAs.[54–56] Maternal transfer of PFAS to eggs is concerning as it can adversely affect developmental stages which are known to be particularly susceptible to contaminant burdens.

Most studies that present PFCA levels in birds include egg data; however, liver and blood studies have also shown similar bioaccumulation patterns. Overall, studies report that long-chain PFCAs with odd number of carbons are highly bioaccumulative in seabirds[58, 62] as seen in Figure S19A. Temporal studies using seabird eggs (Figure S23) also show this pattern of elevated burdens of long-chain PFCAs over multiple decades.[57] For example, for the thick-billed murre eggs and fulmar eggs, the PFUnA and PFTrDA temporal patterns are particularly illustrative (Figure S23). Avian livers show similar trends of higher levels of long-chain PFCAs (Figures S22 and S24). Further, long-chain PFCAs are observed in bird liver and blood samples across species (Figures S20A and S22A). Notably, some gull species have higher egg PFOA (Audouin gull 23.53ng/g ww) and blood PFUnA

(Glaucous gull 74.4 ng/g ww) concentrations compared to other avian species (Figures S19A and S20A). Although PFOS is the dominant fluorinated contaminant reported in most studies, there is evidence for PFCA levels to exceed total PFSAs reflecting dominance of PFCA burden over total PFOS (livers of northern fulmar and thick-billed murre from the Canadian Arctic[58]). Long-carbon chain PFCAs, PFUnA and PFTrDA, are reported as comparable to (or exceeding) PFOS levels in muscle samples of the black-footed albatross from the northern Pacific.[63] Birds of prey, such as white-tailed eagles, that occupy higher trophic levels show similar trends of long-chain odd numbered carbon PFCAs in their eggs, reflecting bioaccumulation up across trophic levels, as seen in Figure S25.[64] Data from other lesser studied compartments, such as feathers, muscle and adipose, (Figure S21) also show PFUnA and PFTrDA as dominant PFCAs indicating their preferential bioaccumulation and likely poor elimination. The prevalence of long-chain PFCAs with odd number of carbons is linked to inputs from deposition of atmospheric precursors and their degradation products.[44] Volatile precursors such as fluorotelomer alcohols and their degradation products consisting of long-chain PFCAs have been measured in the atmospheric samples from the Canadian Arctic.[65] The air and water data in this study suggest atmospheric delivery of long-chain PFCAs to aquatic ecosystems.

Although, significantly lower than PFOS concentrations, other PFSAs were reported in bird eggs and other tissues. Despite species-specific differences and tissue accumulation patterns, PFHxS was detected in eggs, blood, and liver of multiple bird species (0.01 to 6 ng/g ww) (Panel B of Figures S19, S20, S22). Temporal studies also reflect persistence of PFOS at relatively high concentrations in the eggs collected over several years (Figures S23, S25).[57, 64] In an extreme example, in 2004, eggs of white-tailed sea eagles from the Baltic Sea approached a very unusually high 1514 ng/g ww. These studies have also reported bioaccumulation of PFHxS and PFDS across the temporal scale in eggs and liver tissues in some seabird species (Figures S23–S25). Avian studies report occurrence of FOSA (Figures S20C, S22C) as well as replacement PFAS (Figure S22 B-C) in some species. In one study, the common cormorant accumulated 89 ng/g ww of FOSA in liver tissue. In the laughing gulls, elevated liver concentrations of Nafion BP2 and PFO5DoDA were reported (112.82 and 16.27 ng/g ww, respectively) (Figure S22B). Sex-specific differences in PFAS bioaccumulation have been reported in some birds;[62] however, in many studies, no such differences between male and female seabirds have been noted.[58, 59, 61]

3.6 Mammals

Marine mammals are reported to accumulate PFAS at high concentrations, especially in liver and blood tissues. Similar to the avian egg dataset, mean and median values were higher for the PFSA (mean 139.33 ng/g ww, median 14.80 ng/g ww) dataset in comparison to PFCAs (mean 12.63 ng/g ww, median 3.81 ng/g ww) due to high PFOS contribution in the mammalian livers (Figure 6B). Excluding PFOS concentrations, the mean and median for the PFSA dataset were 3.28 ng/g ww and 1.32 ng/g ww, respectively. Elevated PFOS levels were reported in livers and blood of several marine mammals (Figures S26); highest average concentrations were observed in polar bear livers (mean 1735.67ng/g ww; median 1568 ng/g ww, n=6). High PFOS levels were also detected in the livers of harbor porpoises (mean 665.9 ng/g ww; median 461 ng/g ww, n=110). Other PFSAs detected in mammalian

liver and blood tissues are PFHxS, PFHpS, and PFDS (Figure S27). PFHxS levels in polar bear adipose tissues (2.2 ng/g ww) were found elevated in comparison to other mammalian species (Figure S28).

PFCAs are reported at high concentrations in mammalian livers (Figure S27A). Long-chain PFCAs have been detected in several marine mammals at higher concentrations than short-chain PFCAs (Figure S27A). Similar to the avian datasets, levels of PFUnA in livers were observed to be particularly elevated in several mammals. For example, mean PFUnA concentrations in the livers of Dall's porpoise and polar bear were 305 and 144.67 ng/g ww, respectively. Liver PFNA levels in polar bear, white-beaked dolphin and sperm whale were also elevated (264.67, 242.1, 240 ng/g ww, respectively) (Figure S27). Blood PFCA data show similar trends although had overall lower levels than liver data (Figure S27B). However, mean concentrations of both PFDA and PFUnA were elevated in the bottlenose dolphin blood (89.5 and 82.5 ng/g ww, respectively). Studies also showed long-chain PFCAs at higher concentrations in the adipose tissues of some marine mammal species (Figure S28).

Sulfonamide-based precursors, such as FOSA, have been detected in livers of several marine mammals as well as in blood, adipose and muscle tissues (Figure S29, S31). For example, liver FOSA concentration in the short-beaked common dolphin was 878 ng/g ww (Figure S29A). The next highest liver levels were observed in the white-beaked dolphin with 122 ng/g ww (Figure S29). Unlike other mammals, cetaceans are unable to biotransform FOSA to PFOS and such differences are critical to understanding the links between environmental prevalence of precursors and their potential elevated body burdens.[66] Novel PFAS such as perfluoro-4-ethylcyclohexane sulfonate (PFECHS) and Cl-PFESAs have also been detected in the livers of ringed seals and polar bears but at relatively low levels (0.05 to 3 ng/g ww) (Figure S29). Polar bears also bioaccumulated FOSA (7.83 ng/g ww), Et-FOSA (1.5 ng/g ww), FBSA (0.4 ng/g ww), and 6:2 Cl-PFESA (0.27 ng/g ww) in liver tissues (Figure S29A).

Although the majority of the PFAS studies in marine mammals present liver data, and blood and adipose to a lesser extent, a few studies reporting kidney, spleen, milk and muscle levels of PFCAs and PFSAs are also available (Figures S30 and S31). Together, these studies suggest trends similar to the ones observed in mammalian livers including higher concentrations of long-chain PFCAs and PFOS. For example, PFNA, PFDA and PFUnA in the harbor seal muscle were 69.82, 59.1, 30.23 ng/g ww, respectively, while PFOS concentrations in the kidney and spleen of this same species of seal exceeded 378.46 and 307.37 ng/g ww, respectively (Figures S30, S31). Placental and lactational transfer of PFAS have also been reported in several marine mammals.[67–70] It must be noted that tissue-specific differences observed in PFAS bioaccumulation are important to consider for understanding physiological effects and, as noted in previous sections, are likely related to binding to specific sites on proteins, associations with phospholipids and elimination kinetics. In the muscle tissues of short-beaked common dolphins and long-fined pilot whales, FOSA was reported at concentrations 142 and 48 ng/g ww, respectively. Chlorinated PFESAs were also reported in muscle tissues of the finless porpoise (6:2 Cl-PFESA 3.84 ng/g ww; 8:2 Cl-PFESA 0.056 ng/g ww) (Figure S31). Some sex- and

age-specific differences in PFAS bioaccumulation have also been reported but more data are required to better understand such patterns.[67, 71, 72]

Interestingly, temporal bioaccumulation patterns also showed elevated concentrations of long-chain PFCAs (Figure S32). For example, liver tissue analyses conducted between 1991 and 2008 in harbor porpoises in the Baltic and North seas showed elevated levels of PFCAs with >8 carbons.[73] These analyses also confirm bioaccumulation of PFOS and its precursor, FOSA, at relatively high concentrations in porpoise livers. For example, in 2005, liver PFOS concentrations in the Baltic harbor porpoises were 2425 ng/g ww. Liver FOSA concentrations in the harbor porpoises from the North Sea exceeded 100 ng/g ww in several temporal assessments between 1995 and 2006 (Figure S32). Further, this temporal assessment shows consistent bioaccumulation of PFHxS, PFHpS and PFDS in liver samples confirming PFAS trends from our dataset that has been averaged across geographical regions and collection times for several marine mammals.

4. CONCLUSIONS AND RESEARCH NEEDS

We present a synthesis of a vast dataset of PFAS occurrence and bioaccumulation in marine taxa ranging from plankton to mammals. This review provides opportunities to further examine trends within and across species and biological compartments as well as across different temporal scales. We have highlighted similarities and differences in trends of PFAS occurrence within and across environmental compartments and taxonomic groupings and presented research needs to address current data deficiencies (Table 1). Data from several studies across spatial and temporal scales, presented as sum PFCA and sum PFSA, show overall patterns of PFAS bioaccumulation (Figure 7). With increases in trophic level, elevated burdens of PFCAs and PFSAs are detected. The range of datapoints for total PFSA burdens is elevated, especially at higher trophic levels, due to increased contribution of PFOS. The total PFAS levels, as shown in Figure 8, also demonstrate a trend of elevated concentrations and wider range of datapoints with increase in trophic level.

Due to the vast number of compounds in this chemical class, it is imperative that we improve our understanding and predictions of PFAS bioavailability, bioaccumulation, and toxicity. One way to address this challenge is to identify, group and prioritize PFAS of concern based on their (i) transport, fate and partitioning into environmental compartments, (ii) bioavailability and bioaccumulation patterns in aquatic organisms, and (iii) mechanisms and magnitude of adverse effects. While not the focus of this review, along with bioaccumulation, the toxic effects of PFAS in marine organisms must be further investigated.

PFAS transport, fate and partitioning

Temporal, spatial and taxonomic patterns of bioaccumulation discussed in this review show long-chain carboxylic acids, especially the ones with odd number of carbons, are detected more often across different organisms.[41, 42, 49, 57, 73] These patterns are significant as convergence between spatial and temporal trends, such as bioaccumulation of PFUnA and PFTrDA across species, facilitate identification of priority PFAS of immediate concern to aquatic life. Transport of PFAS by ocean currents as well as long-range atmospheric

deposition are also a factor[74, 75] and must be investigated further to understand spatial patterns of bioaccumulation. Specifically, significant inputs of long-chain carboxylic acids are suggested to be from atmospheric sources via deposition and transformation of volatile fluorotelomer alcohols.[64, 76, 77] Another source of PFAS transfer from the ocean to the atmosphere is sea spray aerosol that can contribute to long-range transport of these contaminants.[78, 79] In the water column, vertical transport is affected by PFAS solubility wherein shorter-chain PFAS are thought to be transported vertically more efficiently which could increase their bioavailability to pelagic plankton, as seen in Figure 9. As shown in Table 1, except for plankton, PFCA profiles of all taxonomic groups are dominated by long-chain PFCAs (Figure 9). Identification of such bioaccumulation trends emphasizes the need for further investigations into partitioning and bioaccumulation of PFAS based on chain-length. Differences in solubility and depth of the water column are also important factors to consider for monitoring efforts as well as understanding PFAS bioavailability.

Elevated PFAS concentrations in sediments pose a risk to benthic organisms[22] and make them important sources of PFAS within foodwebs . Further assessments of PFAS partitioning in sediment and water phases, along with bioaccumulation potentials linked to multiple selective processes at the organismal level are important for understanding patterns observed across organisms and identifying vulnerable taxa. Crucially, biomagnification factors as well as trophic transfer are elevated with increasing numbers of fluorinated carbons in the perfluoroalkyl chains. Consequently, even in areas with low seawater PFAS concentrations, biomagnification of long-chain PFAS and their widespread bioaccumulation in aquatic organisms raises concern.[16, 77, 80] This review includes occurrence data for precursors and replacement PFAS across taxonomic groupings. Although there has been an increase in the availability of such data in recent years, our understanding of prevalence, fate and preferential bioaccumulation of precursors and novel replacement PFAS remains limited.[81] Future research must consider these data gaps and also identify contributions of the biotransformation of precursors, such as FOSA, and other PFAS to inflated PFOS burdens in biota at higher trophic levels as well as the potential biomagnification.[12, 18, 82] Replacement compounds, such as Cl-PFESAs, are of rising concern for their trophic transfer and biomagnification potential through food webs[15, 83] despite their relatively low concentrations compared to legacy PFAS in some regions.[31] With increasing usage of novel replacement PFAS and improvement in analytical methods for their assessments, more information about their occurrence and environmental fate is likely to emerge. Recent temporal studies have shown their tissue-specific prevalence in marine mammals indicating increased usage.[15] Further, future research must also include toxicokinetic assessments of sulfonic acids other than PFOS, such as PFHxS, that have been shown to accumulate and biomagnify.[28]

Factors affecting bioavailability and bioaccumulation

At the organismal level, exposure is affected by factors such as environmental concentrations, diet, feeding behavior, trophic level, and migration. For example, within a localized contaminated environment, PFAS profiles of benthic and pelagic organisms may reflect differences in bioavailability and environmental partitioning.[84, 85]. Following exposure, several factors play critical roles in PFAS bioaccumulation resulting

in differences across species within geographical regions.[10, 86] Bioaccumulation is determined by toxicokinetics which includes absorption, distribution, biotransformation and elimination.[10, 87–89] Adequate understanding of species-specific differences in PFAS bioaccumulation warrants evaluation of relationships between these processes. In most environments organisms are likely exposed to a mixture of several different PFAS. Therefore, it is critical to examine the effects of exposure concentration on toxicokinetics to adequately understand bioaccumulation patterns.

Most of the studies report PFAS burdens based on wet or dry weight of tissues; however, normalizing PFAS burdens to total protein levels has been suggested,[69] analogous to lipid normalization performed for hydrophobic organohalogens. Protein binding efficiencies of PFAS affect bioaccumulation patterns in organisms.[39] Livers contain specific proteins, such as albumin and liver fatty-acid binding proteins, that efficiently bind PFAS[50] as reflected by elevated hepatic burdens in several organisms presented in this review. It has been suggested that sulfonic acids have stronger protein binding affinities than carboxylic acids with the same chain length.[69] For example, the low bioaccumulation potential of PFOA is contrasted against high PFOS burdens in pelagic fish[17] and in green mussels.[39] Further, binding efficiencies to these proteins are reported to increase with their perfluorinated carbon number and hence, longer-chain PFAS are found to be elevated in liver.[50] Long-chain PFAS are also shown to be more strongly associated with tissue phospholipids.[48] Binding efficiencies are also affected by the presence of chemical linkages and functional groups. For example, ether linkages in PFESA are thought to increase bioaccumulation due to enhanced binding efficiencies.[50] Frequently observed bioaccumulation patterns such as lower PFAS levels in muscles compared to liver or plasma can be indicative of differences in protein binding efficiencies to specific proteins.[11, 80] Without more information on binding sites for different types of PFAS, normalizing to total protein across tissue compartments and taxa remains a challenge.

Factors linked to protein levels, such as, age, sex, and maternal transfer, could contribute to varying bioaccumulation patterns.[4, 90–92] Tissue-specific patterns in muscle, liver or blood that characterize compound-specific partitioning are very useful from a biomonitoring and seafood consumption point of view. However, whole organism burdens are also critical to identifying trophic transfer and biomagnification potential. As noted in Table 1, information on tissue-specific partitioning and PFAS-binding targets that are evolutionarily conserved will further assist in identification of vulnerable taxa. As discussed before, food web studies suggest short-chain perfluoroalkyl acids are found elevated in lower trophic level organisms and long-chain perfluoroalkyl acids are prevalent in organisms at higher trophic levels.[82] Increased risks of PFAS bioaccumulation in top predators such as seabirds and marine mammals could affect top-down ecosystem processes. Another research need includes advancing our understanding of biomagnification via differences in elimination kinetics between organisms that respire in water versus on land (Table 1). It has been suggested that due to high aqueous solubility and low volatility of perfluorinated acids, the respiratory elimination of these compounds is efficient in aquatic or piscivore food webs; in contrast, slow elimination of these compounds in marine mammalian food webs allows them to biomagnify.[93] Such assessments are based on protein-water (K_{pw}) and protein-air (K_{pa}) partition coefficients and reflect the need for further advances in protein-based

elimination kinetics, application of protein-normalized concentrations, and development of more sophisticated bioaccumulation models (e.g., AQUAWEB-type models).[94]

PFAS management

The management, and more specifically, the derivation of ecological criteria protective of marine organisms for a class of compounds as vast and complex as PFAS is daunting. This is especially true when considering realistically available resources; consequently, research efforts in several areas need to be focused on the selection and categorization of the most hazardous chemicals. Many convergent findings across temporal and spatial scales, and taxonomic patterns, as discussed throughout this review, can assist in further streamlining research and management efforts. With existing and emerging information, PFAS could be grouped into several priority categories for monitoring, remediation, and toxicity assessments. As summarized in Table 1, key research needs benefitting bioaccumulation predictions and advancing chemical categorization include 1) PFAS partitioning in seawater and sediment phases affecting bioavailability, 2) effects of PFAS concentration on toxicokinetics 3) effects of ecological parameters (e.g., diet, feeding behavior, migration) on bioavailability, 4) information on protein-binding sites, binding efficiencies, and partitioning across tissue types, and 5) biotransformation of precursors and replacement compounds.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS-

The authors would like to acknowledge J. Grundy, M. Hedgespeth and M. Morales-McDevitt for their contributions toward the review of the manuscript. We would also like to thank T. Langknecht and M. Stuart for their assistance towards the preparation of reference libraries. This article was completed while B. Khan was a Research Participant with the Oak Ridge Institute for Science and Education (ORISE) at the US Environmental Protection Agency (EPA), Office of Research and Development, Center for Environmental Measurement and Modeling, Atlantic Coastal Environmental Sciences Division. This research was supported in part by an appointment to the US EPA Research Participation Program administered by the ORISE through an interagency agreement between the U.S. Department of Energy (DOE) and the US EPA. ORISE is managed by ORAU under DOE contract number DE-SC0014664.

Data Availability Statement-

All associated data and metadata, in the form of Excel spreadsheets, are available upon request from the corresponding author.

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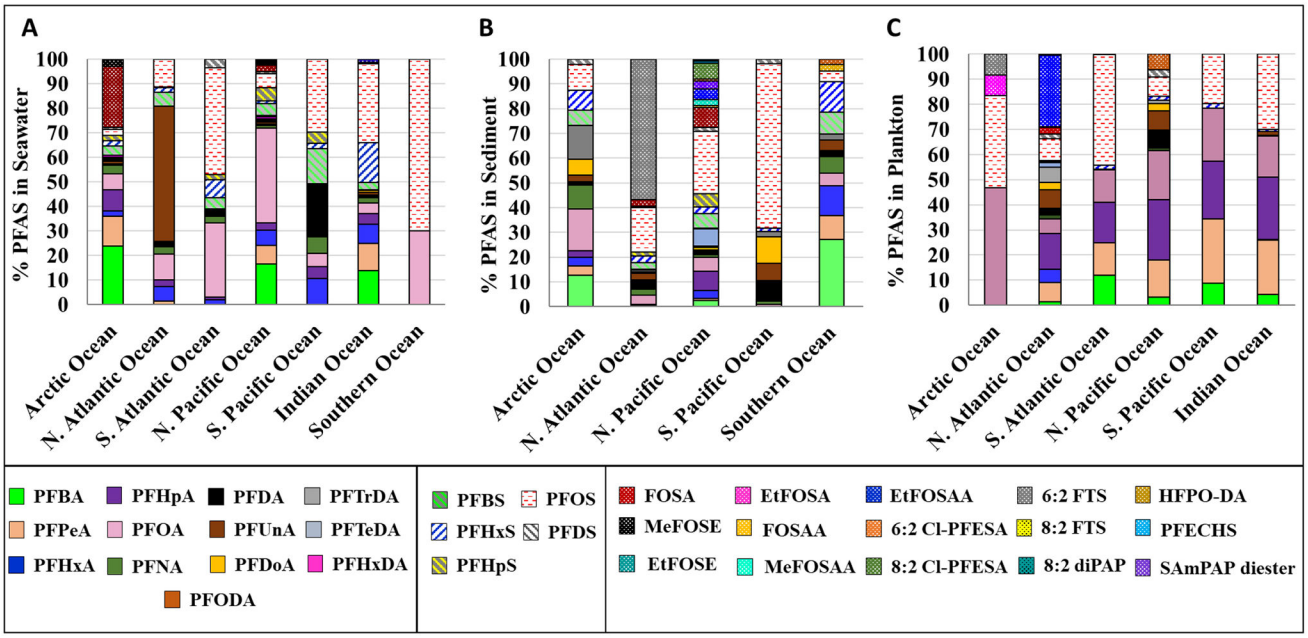

Figure 1.

PFAS % composition in seawater (A), sediment (B), and plankton (C) from five major oceans of the world. The legend is divided into three boxes (left to right) including, PFCAs, PFSAs, and precursors and replacement PFAS.

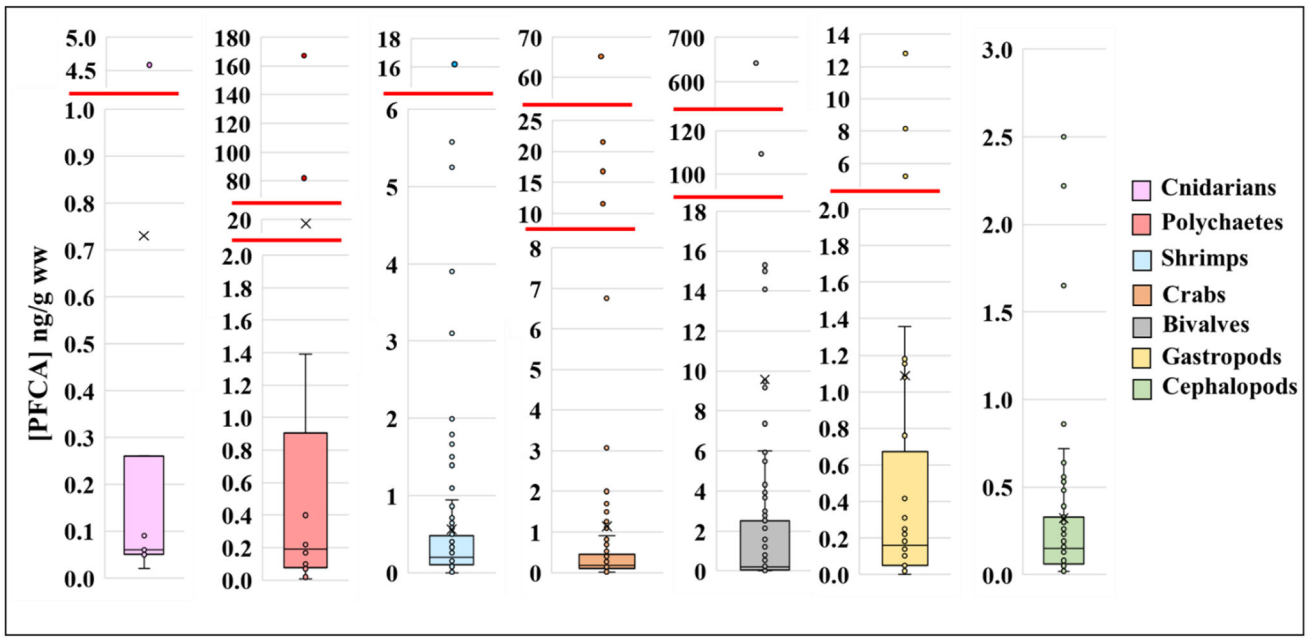

Figure 2.

PFCA concentrations in invertebrates. The red markers indicate changes in y-axis. Plots include PFAS concentrations ranging from PFBA (C4) to PFPA (C15).

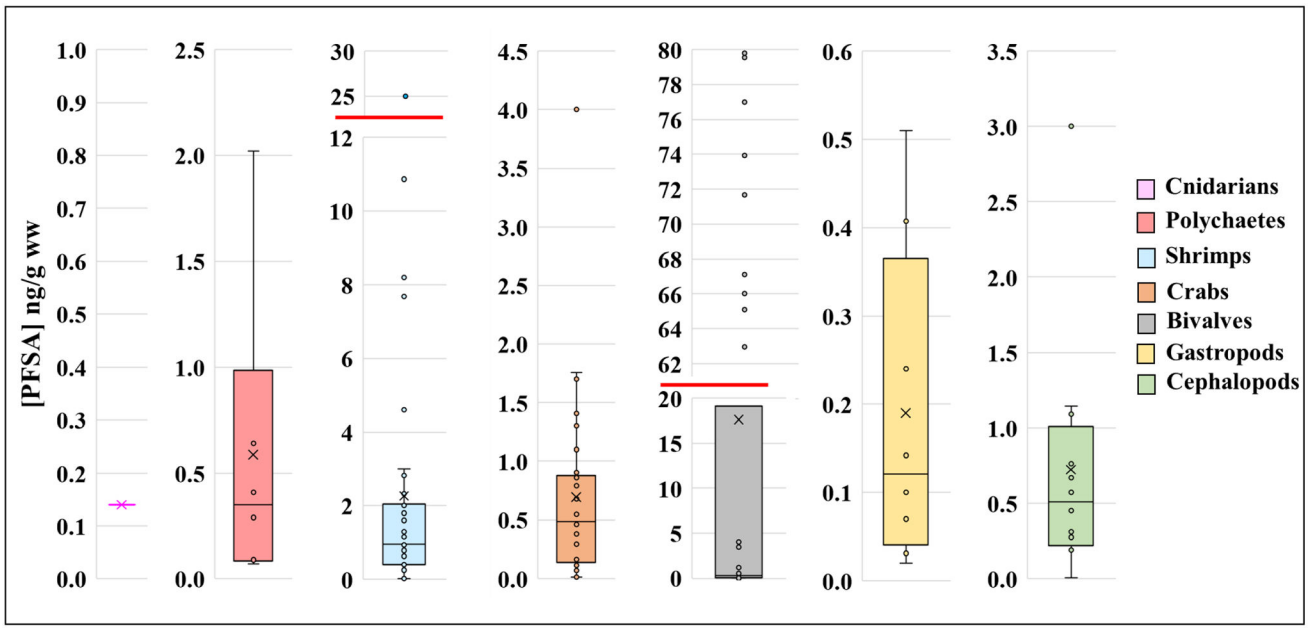

Figure 3.

PFSA concentrations in invertebrates. The red markers indicate changes in y-axis. Plots include PFAS concentrations ranging from PFBS (C4) to PFDS (C10).

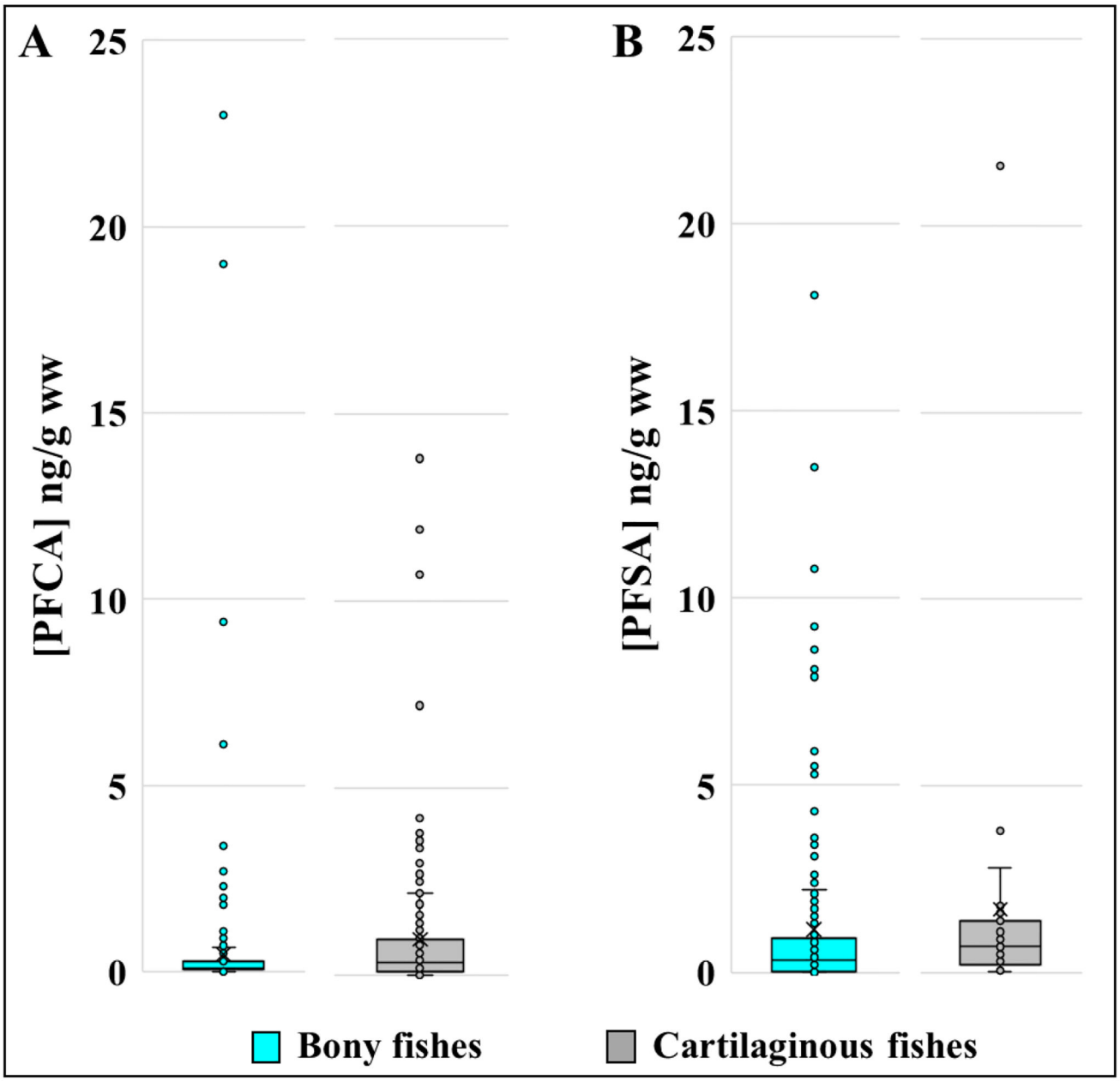

Figure 4.

PFCA (A) and PFSA (B) concentrations in the muscle tissues of bony and cartilaginous fishes. Plots include PFAS concentrations ranging from PFBA (C4) to PFTeDA (C14) and PFBS (C4) to PFDS (C10) for (A) and (B), respectively.

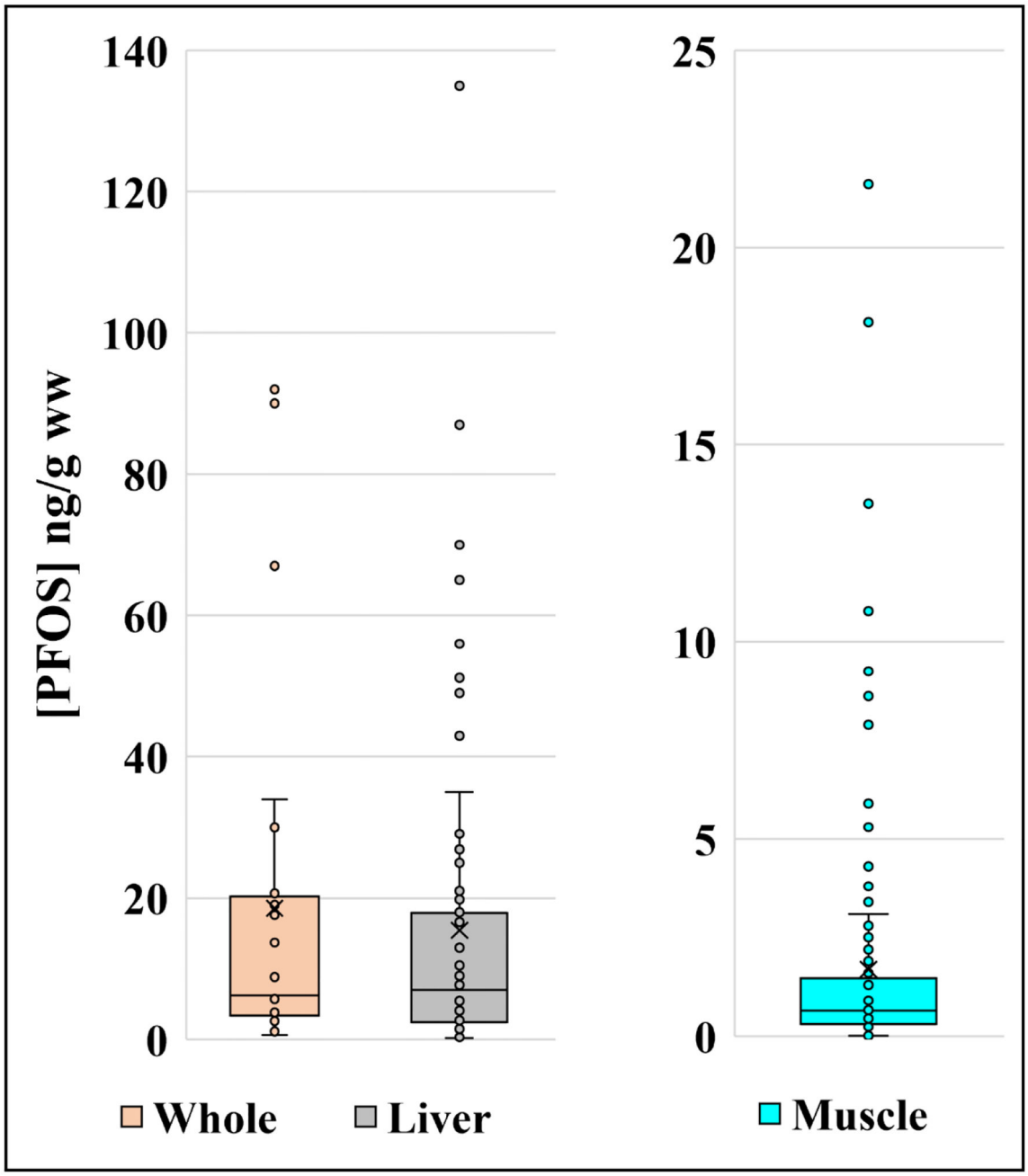

Figure 5.
Fish PFOS (C8) concentrations in whole fish, liver and muscle tissues.

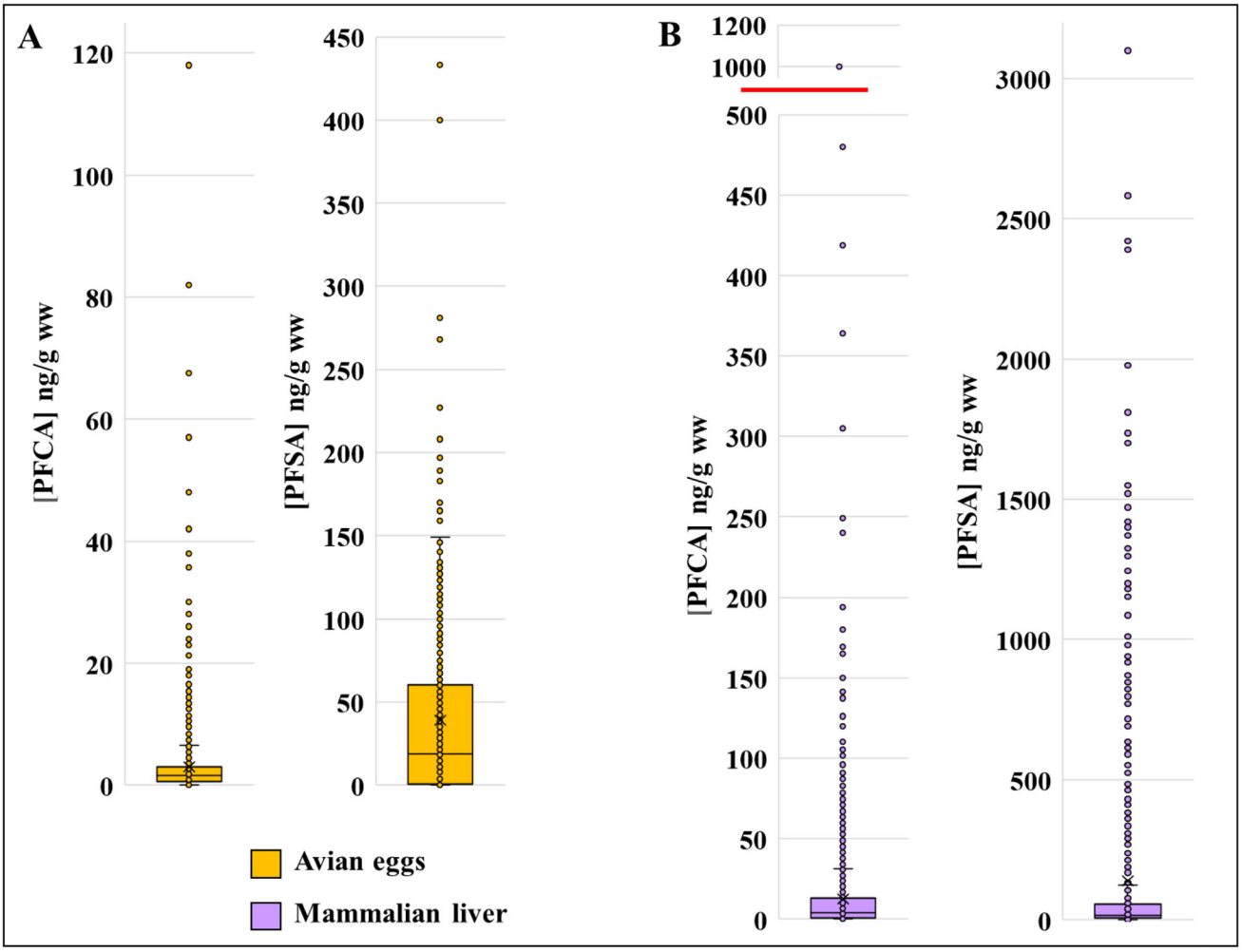

Figure 6.

PFCA and PFSA concentrations in avian eggs (A) and mammalian liver tissues (B). The red marker indicates change in y-axis. Plots include PFAS concentrations ranging from PFBA (C4) to PFPA (C15) and PFBS (C4) to PFDS (C10) for (A) and (B).

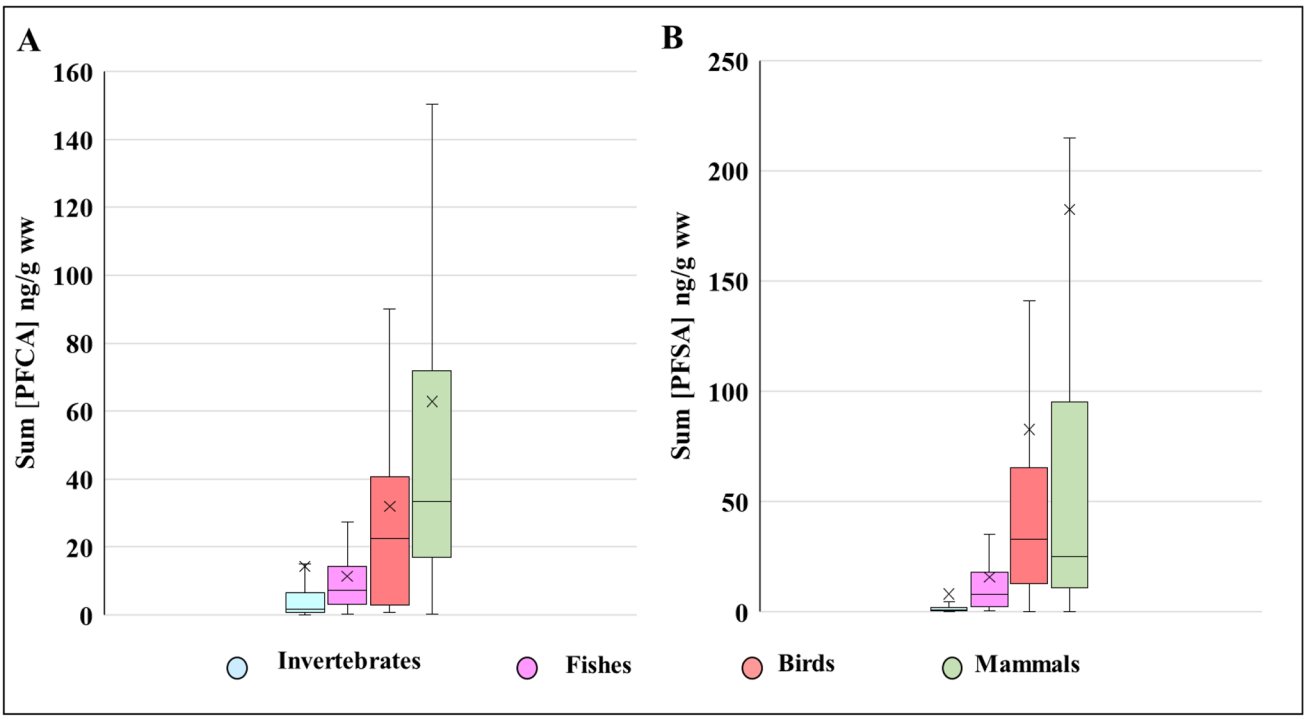

Figure 7.
Sum PFCA (A) and sum PFSA (B) in invertebrates and liver tissues of fishes, birds and mammals.

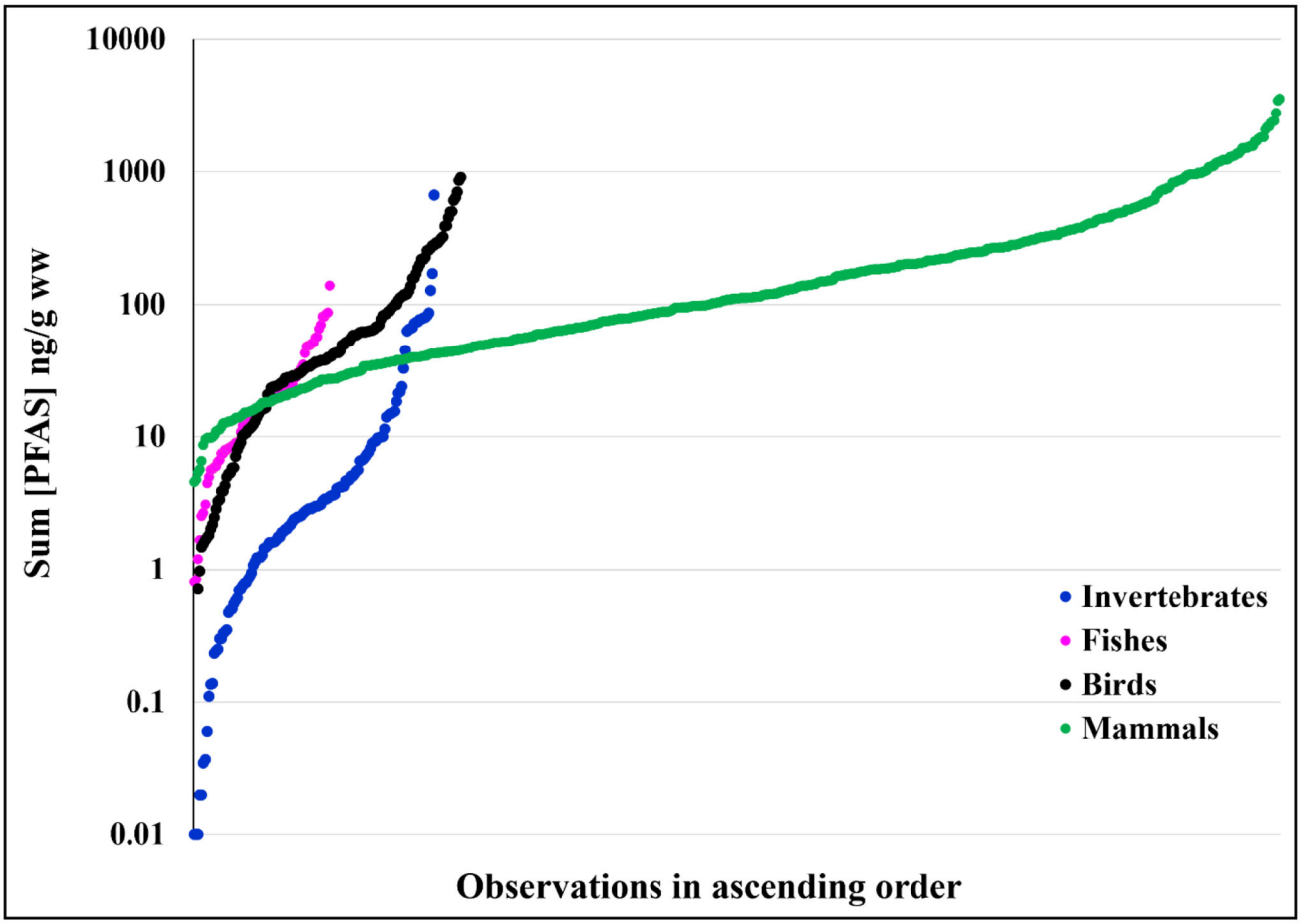

Figure 8.

Total PFAS burdens in invertebrates and liver tissues of fishes, birds and mammals. Each circle represents the sum of all PFAS compounds reported for each sample. Data are shown as concentrations on a logarithmic scale and sorted in ascending order.

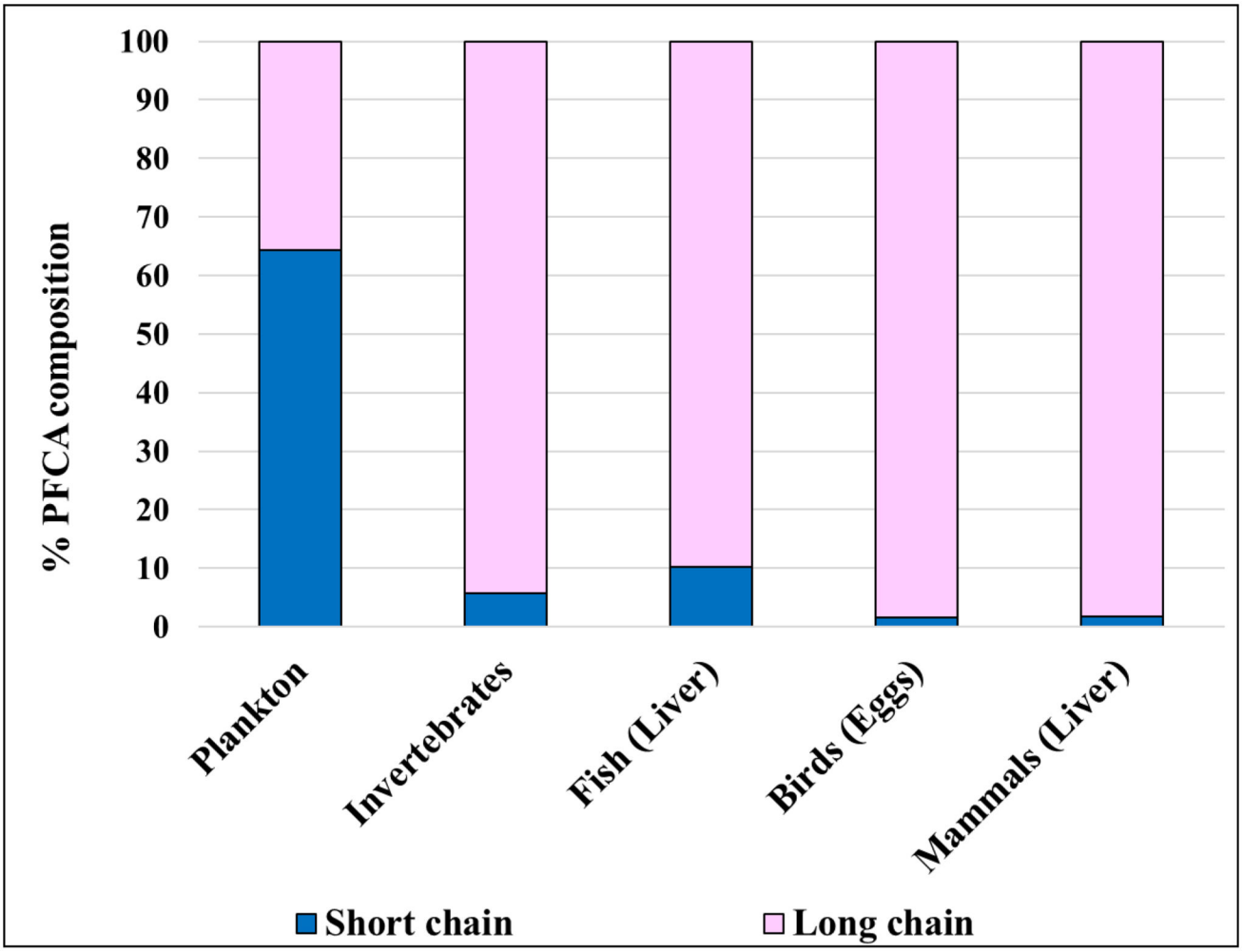

Figure 9.
Stacked column plots showing % composition of short- and long-chain compounds towards total PFCA burdens in plankton, invertebrates, fish livers, avian eggs and mammalian livers.

Table 1

Summary of notable trends in PFAS occurrence and bioaccumulation in the marine environment and research needs based on a review of peer-reviewed studies published between 2000 to 2020. The research needs listed below are applicable across compartments and must be considered in trophic studies as well.

Marine Compartment	Overall Notable Trends	Research Needs
Seawater	• Wide range of PFAS detected • Region-specific differences detected in PFAS profiles • PFOS and PFOA measured for and detected most frequently	• Application of non-targeted analyses to understand the diversity and distribution of legacy and novel PFAS in the oceans
Sediments	• PFOS abundance exceeds PFOA • Long-chain PFCAs detected frequently	• Evaluation of processes (e.g., partitioning, transformation and degradation) affecting PFAS distribution and bioavailability
Plankton	• Short-chain PFCAs higher than long-chain • PFOS and PFOA detected in plankton from every region	• Understanding relationships between water column and plankton PFAS concentrations
Invertebrates	• Broad concentration ranges of many PFAS • Diet and feeding behavior based differences	• Evaluation of factors affecting species-specific differences
Fish	• Liver concentrations higher than muscle • PFOS dominates PFSA profiles; long-chain PFCAs dominate PFCA profiles • Differences between bony and cartilaginous fishes	• Assessment of tissue-specificity of bioaccumulation and its ecological and human health implications
Reptiles	• Limited bioaccumulation data available • PFOS and long-chain PFCAs detected	• More bioaccumulation data needed to understand risks to endangered species
Birds	• Elevated bioaccumulation in eggs • PFOS, PFUnA and PFTrDA dominant	• Evaluation of binding efficiencies to proteins and phospholipids
Mammals	• Elevated bioaccumulation in liver • PFOS and long-chain PFCAs dominant	• Comparison of elimination kinetics in organisms respiring on land (such as mammals) versus in water (fishes)