Bioaccumulation of Per- and polyfluoroalkyl substances (PFASs) in a tropical estuarine food web

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HIGHLIGHTS

- Perfluoroalkyl substances (PFAS) were investigated in a tropical estuarine food web.
- Leaves, bivalves, polychaeta, crustaceans, and fish presented PFAS residues.
- PFOS, PFTrDA, and FOSA were the compounds most frequently detected in Subaé biota.
- The PFOS precursors FOSA and EtFOSA were also detected in Subaé estuarine biota.
- PFOS, PFNA and a C_8 PFOS precursor were observed to biomagnify in the food chain.

GRAPHICAL ABSTRACT
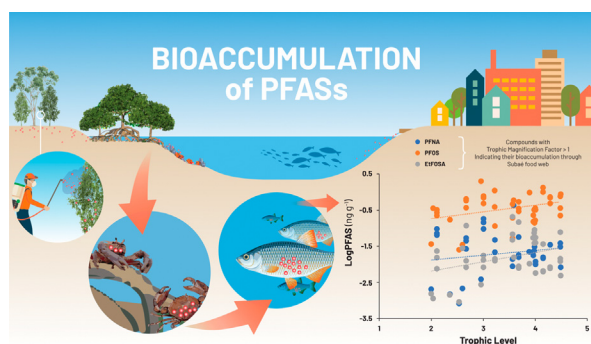
ARTICLE INFO

ABSTRACT

The biomagnification of per- and polyfluoroalkyl substances (PFASs) was investigated in a tropical mangrove food web from an estuary in Bahia, Brazil. Samples of 44 organisms (21 taxa), along with biofilm, leaves, sediment and suspended particulate matter were analyzed. Sum ($\sum$) PFAS concentrations in biota samples were dominated by perfluorooctane sulfonate (PFOS, 93% detection frequency in tissues; 0.05 to 1.97 ng g^{-1} ww whole-body (wb)), followed by perfluorotridecanoate (PFTrDA, 57%; 0.01 to 0.28 ng g^{-1} ww wb). PFOS precursors such as perfluorooctane sulfonamide (FOSA, 54%; 0.01 to 0.32 ng g^{-1} ww wb) and N-ethyl perfluorooctane sulfonamide (EtFOSA; 30%; 0.01 to 0.21 ng g^{-1} ww wb) were also detected. PFAS accumulation profiles revealed different routes of exposure among bivalve, crustacean and fish groups. Statistics for left-censored data were used in order to minimize bias on trophic magnification factors (TMFs) calculations. TMFs >1 were observed for PFOS (linear + branched isomers), EtFOSA (linear + branched isomers), and perfluorononanoate (PFNA), and in all cases, dissimilar accumulation patterns were observed among different trophic positions. The apparent biodilution of some long-chain PFCAs through the food chain (TMF < 1) may be due to exposure from multiple PFAS sources. This is the first study investigating bioaccumulation of PFASs in a tropical food web and provides new insight on the behavior of this ubiquitous class of contaminants.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) represent a diverse class of fluorinated anthropogenic chemicals with unique physical-chemical properties including combined hydrophobicity/lipophilicity (Buck et al., 2011), which make them desirable for a wide range of industrial processes and products. Notable applications of PFASs include firefighting foams (Dauchy et al., 2019), fluoropolymer manufacturing (Song et al., 2018), textiles (Wang et al., 2017), food packaging (Schaider et al., 2018; Schultes et al., 2019a), cosmetics (Schultes et al., 2018), and pesticides (Nascimento et al., 2018).

Since the early 2000s, there has been considerable concern over the widespread occurrence of PFASs, in particular the long-chain perfluoroalkyl acids (PFAAs), which display high persistence and have been found in the blood of humans (Giesy and Kannan, 2001; Lau et al., 2007; Wang et al., 2018) and biota (Dorneles et al., 2008; Giesy and Kannan, 2001; Hong et al., 2015; Houde et al., 2006b, 2011; Leonel et al., 2008; Quinete et al., 2009; Routti et al., 2017; Sanganyado et al., 2018). In 2009, one of the most widespread PFAAs, perfluorooctane sulfonate (PFOS), along with its salts and synthetic precursor perfluorooctane sulfonyl fluoride (POSF), were added to Annex B of the Stockholm Convention on Persistent Organic Pollutants (UNSCPOPs, 2009). Despite these regulatory initiatives, production of PFOS and other long-chain PFAAs continues in some parts of the world under regulatory exemptions.

In Brazil, manufacture and use exemptions have been obtained to continue producing and using Sulfluramid, which contains the active ingredient N-ethyl perfluorooctane sulfonamide (EtFOSA), a PFOS-precursor (Avendaño and Liu, 2015; Zabaleta et al., 2018). Sulfluramid is a formicide extensively introduced as a substitute for the organochlorine pesticide Mirex (Nagamoto et al., 2004), which is mostly used in eucalyptus and pine plantations to combat leaf-cutting ants (*Atta* sp. and *Acromyrmex* spp.). Brazil is among the largest consumers of Sulfluramid in the world (MMA, 2015a, 2015b). In the past five years, around 280 t year^{-1} of Sulfluramid (0.3% EtFOSA) was imported, but there are considerable uncertainties with this estimate since the quantities of Sulfluramid precursor (i.e. POSF) imported into Brazil are not available (MDIC, 2019). Based on increasing production of eucalyptus and pine-derived cellulose (Rossato et al., 2018), it is expected that the demand for Sulfluramid will continue in the next years. A recent study suggested an elevated contributions from a PFOS precursor (e.g. Sulfluramid) in Subaé river waters in the Northeast of Brazil (Gilljam et al., 2016), indicated by the presence of PFOS precursors (PreFOS) compounds in the region (i.e. perfluorooctane sulfonamide - FOSA/ PFOS ratio above 5:1).

While there are few data available on PFAS-based products beyond Sulfluramid in Brazil (MDIC, 2019), a recent ecotoxicological study suggested that PFAS-based aqueous film-forming foams (AFFFs) continue to be used (da Silva et al., 2019) while the National Implementation Plan for the Stockholm Convention in Brazil (MMA, 2015a, 2015b) highlights several PFAS-based consumer products which are permitted. Also, PFASs contamination in tropical areas has been associated with the AFFF use (Munoz et al., 2017b). Together with the use of Sulfluramid in forestry, PFAS-containing AFFF and consumer products (e.g., food packaging, cosmetics, etc.) may be important PFAS sources to the local environment.

The process of biomagnification is an important mechanism for micronutrient transfer through food chains (Barclay et al., 1994; Gribble et al., 2016), but it is also a mechanism that promotes accumulation of anthropogenic toxic compounds (Borga et al., 2012; Mackay and Boethling, 2000). Unlike the well-known lipophilic bioaccumulation mechanism of most of the POPs, the PFASs enter the food chain due to their proteinophilic characteristics (Goeritz et al., 2013). Despite studies reporting the occurrence of PFASs in organisms globally (Becker et al., 2010; Hong et al., 2015; Houde et al., 2006b, 2011; Martin et al., 2003; Munoz et al., 2017a; Sanganyado et al., 2018), few data are available

for South American ecosystems (Dorneles et al., 2008; Leonel et al., 2008; Olivero-Verbel et al., 2006; Quinete et al., 2009), and there is a lack of PFAS bioaccumulation data for tropical ecosystems. Coastal tropical environments concentrate the greatest extent of biodiversity and productivity (Brown, 2014). Additionally, numerous freshwater and marine species use these ecosystems (e.g., mangroves and estuaries) as a nursery, shelter and feeding area, highlighting the importance of those environments as providers of a myriad of ecosystem services.

Despite its ecological importance, the Subaé estuary, located in northeastern Brazil (Fig. 1), has been subject to a high load of domestic and industrial effluents for many years (Hatje et al., 2006; Hatje and Barros, 2012; Krull et al., 2014; Tavares et al., 1999). Seafood harvested in the Subaé estuary is still the main protein consumed by the local people and may also represent a source of contaminant exposure for the locals (Souza et al., 2011, 2014). Moreover, the consumption of contaminated fish and seafood may be a significant pathway of exposure for humans in several countries, including Brazil (Pérez et al., 2014).

The present study addresses the paucity of data on PFAS accumulation in tropical environments by examining the transfer of these compounds through an estuarine food web. Samples were obtained from the Subaé estuary, Brazil, and included several species of bivalves, crustaceans, polychaeta, and fish, along with Suspended Particulate Matter (SPM), sediment, leave of mangrove trees, and algal biofilm. To the best of our knowledge, this is the first study investigating the bioaccumulation of PFAS in a tropical food web.

2. Methodology

2.1. Standards and reagents

Authentic standards of 3 (N-alkyl substituted) perfluorooctane sulfonamides (*N*-methylperfluoro-1-octanesulfonamide (MeFOSA), EtFOSA, and FOSA), 3 perfluoroctane sulfonamidoacetates (*N*-methylperfluoro-1-octanesulfonamidoacetic acid (MeFOSAA), Perfluoro-1-octanesulfonamidoacetic acid (FOSAA), and N-ethylperfluoro-1-octanesulfonamidoacetic acid (EtFOSAA)), 9 perfluoroalkyl carboxylates (C_5-C_{14} PFCAs: Perfluoropentanoic acid (PFPeA), Perfluoroheptanoic acid (PFHpA), Perfluorooctanoic acid (PFOA), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), Perfluoroundecanoic acid (PFUnDA), Perfluorododecanoic acid (PFDoDA), Perfluorotridecanoic acid (PFTrDA), Perfluorotetradecanoic acid (PFTeDA), and 4 perfluoroalkyl sulfonates (PFSAs; Perfluorobutanesulfonic (PFBS), perfluorohexanesulfonic (PFHxS), PFOS, and Perfluorodecanesulfonic (PFDS)), as well as the isotopically-labelled standards $^{13}C_4$-PFHpA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFDoDA, $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_8$-FOSA, D_5-EtFOSA, D_3-MeFOSAA, D_5-EtFOSAA, and the recovery standards used to monitor internal standards performance $^{13}C_8$-PFOA and $^{13}C_8$-PFOS were purchased from Wellington Laboratories (Guelph, ON, Canada). Perfluoropentadecanoic acid (PFPeDA) was included in the target method as a qualitative analyte. A complete list of chemicals (Table S1) and reagents used for sample preparation is provided in the supporting information (SI).

2.2. Study area

The Todos os Santos Bay (BTS) (12°35′30″-13°07′30″S and 038°29′00″- 038°48′00″W) is characterized by a tropical humid climate, with an annual mean temperature around 25 °C and precipitation of 2100 mm, with mesotidal semidiurnal tides that control the currents inside the bay (Cirano and Lessa, 2007). The bay has three major tributaries: Paraguaçu River (56,300 km^2), Jaguaripe River (2200 km^2), and Subaé River (600 km^2). While Subaé is the smallest of the three rivers and has a low mean monthly discharge (9 m^3 s^{-1}), it is known to be a contamination hotspot, due to historically high anthropogenic pressure, especially regarding the introduction of trace elements to the estuarine
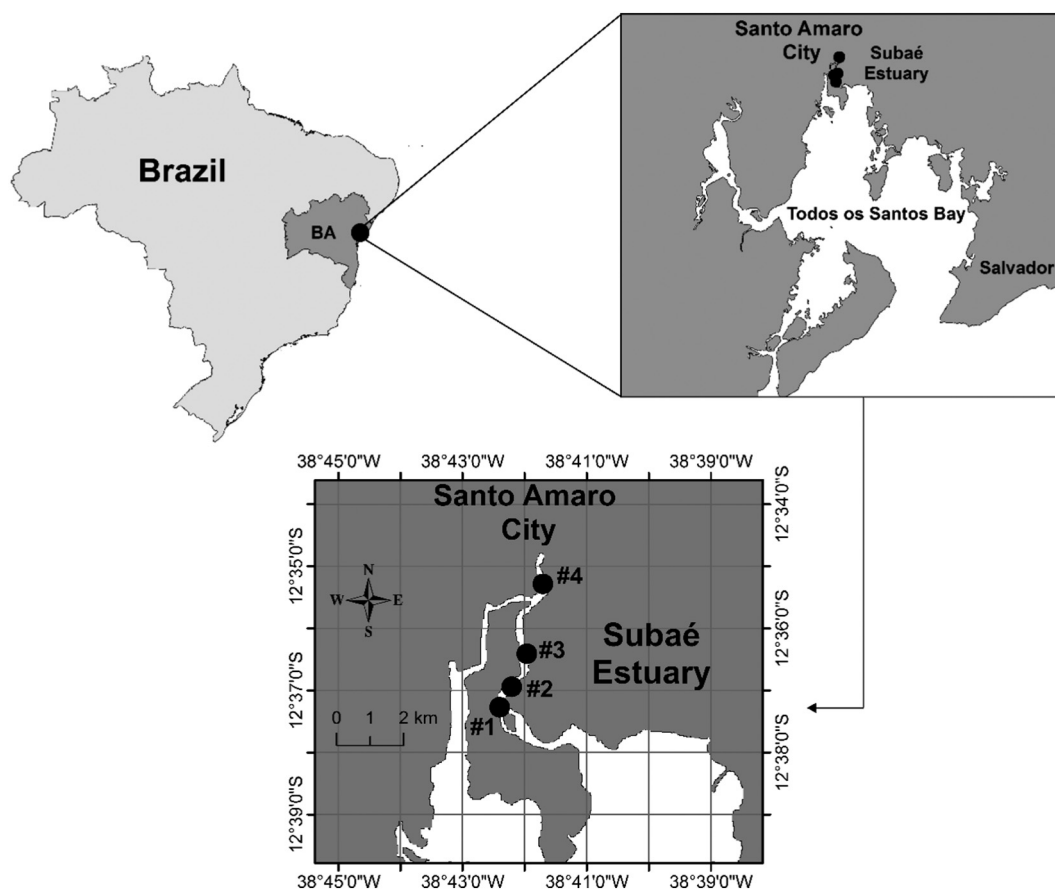
Fig. 1. Sediment and bivalve sampling stations of the Subaé, Todos os Santos Bay, BA, Brazil. Suspended particulate matter (SPM) was collected between sediment sampling stations (SPM#1 between #1 and #2, SPM#2 between #2 and #3, and SPM#3 between #3 and #4). Crustaceans and fishes were sampled between #1 and #4 sampling stations. Sampling point #1 is the closest station to the lower estuary area, while #4 (12° 35,451′S, 38° 41,672′ W) is the closest sampling point to Santo Amaro city.

system (Hatje et al., 2006; Krull et al., 2014). The anthropogenic activities over the last decade around Subaé river represent a risk to the biodiversity and ecological services in the estuary (Almeida et al., 2018; Gilljam et al., 2016; Hatje and Barros, 2012; Ribeiro et al., 2016). The literature regarding biocenosis in the BTS is scarce and is focused mostly on benthic assemblages (e.g. Alves et al., 2020; Magalhães and Barros, 2011; Silvany and Senna, 2019; Barros et al., 2012) and fish (e.g. Dias et al., 2011; Reis-Filho et al., 2019). Those studies show that estuaries of BTS are diverse (Alves et al., 2020; Loureiro et al., 2016; Reis-Filho et al., 2019), and present large variations in the distribution and abundance of assemblages among habitats and salinity gradients (Mariano and Barros, 2015). The presence of a diverse range of deposit feeder polychaeta connecting trophic levels is a remarkable characteristic of BTS food webs (Magalhães and Barros, 2011). Furthermore, the nesting activity of migratory high trophic level piscivorous birds was previously reported through the bay (Lunardi et al., 2012).

2.3. Sample collection

Twenty-one species of estuarine organisms were collected, including mangrove cupped oyster (*Crassostrea rhizophorae, n = 14*), mangrove shellfish (*Mytella guyanensis, n = 63*), blue crab (*Callinectes sapidus, n = 61*), clam (*Anomalocardia brasiliana, n = 5*), polychaeta (pooled), mangrove oyster (*Crassostrea brasiliana*, n = 5), stout tagelus (*Tagelus plebeius, n = 60*), crab (*Ucides cordatus*, n = 6), shrimp (*Litopenaeus* sp., n = 18), mangrove tree crab (*Goniopsis cruentata, n = 12*), mullet (*Mugil* sp., n = 3), torroto grunt (*Genyatremus luteus*, n = 3), mojarra (*Diapterus* sp., n = 9), silver jenny (*Eucinostomus* sp., n = 1), madamango sea catfish (*Cathorops spixii*, n = 5), fat snook

(*Centropomus parallelus*, n = 3), drum (*Stellifer* sp., n = 6), trevally (*Caranx* sp., n = 5), catfish (*Aspistor luniscutis*, n = 3), common snook (*Centropomus undecimalis*, n = 3), and barbel drum (*Ctenosciaena gracilicirrhus*, n = 1). Biofilm, mangrove tree leaves, bivalves, crabs, and polychaeta were manually collected, while shrimp, and fish were sampled using a fixed gill net (authorization SISBIO n. 61269–3/ 28885–4). Almost all sampled species (i.e. bivalves, crabs, shrimp, and fish) are marketed locally by fishermen (Soares et al., 2011), and none of them are listed on the IUCN red list as being in danger of extinction. Samples were collected along a transect and pooled (i.e. sample points from #1 to #4; Fig. 1). Composite samples of mangrove tree leaves (*Rhizophora mangle, Laguncularia racemosa*, and *Avicenia* sp.), biofilm (pool of species), and sediments (n = 4) were collected with a clean spoon at the same location as the benthic organisms (i.e. from site #1 to #4) during the low tide, when sediment was exposed. The SPM was sampled during the flood tide at three points (n = 3) between the location of the sediment sampling sites (SPM#1: between #1 and #2; SPM#2 between #2 and #3; and SPM#3 between #3 and #4) (Fig. 1). For each organism, biometry information was recorded (Table S2). Samples of muscle, liver/hepatopancreas, for fish and crustaceans, soft tissues for bivalves, and whole body for polychaeta were collected. After dissection, tissue wet weight was recorded and thereafter the samples were freeze-dried. More details on sampling and pre-treatment are provided in the Supplementary Information (SI).

2.4. Targeted PFAS analysis

Samples were processed using the method previously described in Zabaleta et al. (2018). Further details are provided in the SI. Briefly,

isotopically labelled internal standards (2 ng) were added to 0.5 g of freeze-dried sample (biota or sediment), which were extracted with acetonitrile (ACN) aided by sonication. The method was repeated for SPM samples, but with methanol as the extraction solvent. All extracts were stored in the freezer prior to instrumental analysis.

Instrumental analysis was carried out by ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS; Waters) operated in negative electrospray ionization mode. Further details on target PFASs analysis and the mobile phase gradient profile can be found in the Table S3. Two precursor/product ion transitions, one for quantification and the other for qualification, were monitored per analyte (Table S4). Either isotope dilution or an internal standard approach using a linear calibration curve with 1/x weighting was used for the quantitative determination of target compounds. Branched isomers were determined semi-quantitatively using the calibration curve for the linear isomer.

2.5. Organic carbon (TOC), total nitrogen (TN) and their stable isotope analysis

Total organic carbon (TOC), total nitrogen (TN), and stable isotopic composition of N and C ($\delta^{15}N$ and $\delta^{13}C$) were analyzed in sediment, muscle of fish and crustaceans, whole body of polychaeta, and soft tissues of bivalves. Samples were treated with 0.1 M HCl for removing carbonates prior to TOC and $\delta^{13}C$ analysis. Stable isotope ratios were measured using an isotope ratio mass spectrometer (IsoPrime100, Isoprime, Cheadle, UK) coupled in continuous flow to an elemental analyser (vario MICRO cube, Elementar Analysensysteme GmbH, Hanau, Germany). Carbon and nitrogen isotope ratios were expressed as δ values (‰) relative to the Vienna PeeDee Belemnite (vPDB) standard and to atmospheric N$_2$, respectively. We used International Atomic Energy Agency (IAEA, Vienna, Austria) certified reference materials sucrose (IAEA-C6, $\delta^{13}C = -10.8 \pm 0.5$‰; mean ± SD), and ammonium sulfate as primary standards (IAEA-N2, $\delta^{15}N = 20.3 \pm 0.2$‰; mean ± SD), and sulphanilic acid as secondary analytical standard ($\delta^{13}C = -25.6 \pm 0.4$‰; $\delta^{15}N = -0.1 \pm 0.5$‰; mean ± SD in each case).

2.6. Quality control

Each batch of 16 samples included blanks ($n = 2$), duplicates ($n = 1$), and spiked samples ($n = 3$; 2 ng of individual PFAS per replicate). Limits of detection (LODs) were estimated based on a signal-to-noise ratio (S/N) of 3 (Table S5). LODs ranged between 0.02 and 1.11 ng mL^{-1}, depending on the tissue and organism analyzed. Calibration curves (1/x weighting) were constructed using concentrations from LOD to 150 ng mL^{-1} and determination coefficients (R^2) were always in the range of 0.994–0.998. Solvent blanks were run between calibration curve points in order to monitor carryovers.

PFAS concentrations in blanks were below LOD in all instances. Spike/recovery experiments showed generally good results, with most compounds displaying recoveries from 80 to 115%. For a few target compounds (e.g. PFPeA, PFTrDA, PFTeDA, and EtFOSA), recoveries were below 60% or above 120% in specific batches. PFPeA was infrequently detected (i.e. < 30% of organisms) and was not subject to TMF determination. Concentrations of PFHpA, PFTrDA, PFTeDA, and L-EtFOSA, data were used as-is, but these concentrations should be considered underreported for some species (see Table S6), due to low spike recoveries for these compounds. In addition, L-EtFOSA was not reported in polychaeta and SPM due to elevated recoveries for these matrices. Perfluorohexanoic acid (PFHxA) was excluded from the set of data due to interferences with the main transition ion monitored.

2.7. Data handling and statistical analyses

$\delta^{13}C$ and $\delta^{15}N$ values were used to determine the trophic web structure and the trophic position (TP) of the organisms analyzed. The following equation (Eq. (1)) was subsequently used to estimate the trophic position (TP):

$$TP_{consumer} = 2 + \frac{\delta^{15}N_{consumer} - \delta^{15}N_{bivalve}}{2.3‰} \tag{1}$$

where 2.3‰ is assumed to be the $\delta^{15}N$ trophic fractionation factor, according to McCutchan Jr et al. (2003). TP of the organisms was achieved by subtracting $\delta^{15}N$ of bivalves which displayed the lowest $\delta^{15}N$ values among animal species (C. rhizophorae; $\delta^{15}N = 8.05$, secondary consumer) and are assumed to have a trophic position of 2 (i.e. first consumer level). $\delta^{13}C$ values without lipid correction were used to predict organic matter sources.

The Trophic Magnification Factor (TMF) was obtained as 10^{slope} by plotting the logarithm-transformed concentration of a given PFAS against the TP. TMF calculations were carried out using soft tissue PFAS concentrations for bivalves, polychaeta and shrimp, and estimated whole-body PFAS concentrations (C$_{wb}$) for fish and crab according to the follow equation:

$$C_{wb} = \sum_{n=1} C_{tissue_{PFAS}} \times f_{tissue_{PFAS}} \tag{2}$$

where C$_{tissue\_PFAS}$ is the concentration of a given PFAS in a specific tissue and f_{tissue_PFAS} is the mass fraction of this tissue in the whole body. A separate calculation was performed for each individual organism based on specific tissue concentration. When the liver concentration was not available, it was estimated that the concentrations in liver were a factor of 10 higher than those of muscle for each compound based on the findings of Nania et al. (2009) (further details are provided in the SI).

Concentrations below the LOD (i.e. non-detected data) were imputed as follows: after ln-transformation, the data were fit to a cumulative normal distribution using a Generalized Reduced Gradient algorithm in the Solver add-in feature of Microsoft Excel. Thereafter, the cumulative normal distribution curve was used to estimate the missing data at the tail of the distribution as previously described by Schultes et al. (2019a, 2019b). The imputation of missing data was previously suggested as a good practice in order to avoid bias introduced in environmental analyses (Helsel, 2006) arising from the use of either raw data or one-half LOD (Borga et al., 2012). However, there is no established threshold for the percentage of left-censored data that could be used without causing a negative effect (i.e. inflation) of TMFs. Detection frequencies of 20 (Munoz et al., 2017a) to 40% (Simmonet-Laprade et al., 2019) have been used in bioaccumulation studies. In the present study, a moderate threshold (30%) was chosen in order to include compounds previously detected in the present study area (Gilljam et al., 2016).

To compare the effect of imputation versus substitution on calculated TMFs, a linear regression of TL versus PFAS concentration was carried out, using the most frequently detected compounds (i.e. L-PFOS, 93% detection frequency [df]), a compound with a moderate detection frequency (PFDoDA, 46% df) and the compound with lowest detection frequency (L-EtFOSA, 30% df) (Fig. S1). In all cases (i.e. regardless of detection frequency), substitution using one-half LOD produced lower TMF estimates compared to imputation (1.19 and 1.53 for L-PFOS, respectively; 0.55 and 0.94 for PFDoDA, and 1.05 and 1.80 for EtFOSA). This is probably due to insertion of fixed values into the data set (i.e. one-half LOD), which tends to decrease the slope of the linear regression (Borga et al., 2012; Helsel, 2006). While we conclude that substitution will produce lower TMFs than imputation, overall, the differences were minimal and did not affect neither the observed biodilution (i.e. TMF < 1) nor bioaccumulation (i.e. TMF >1) for any compound.

BioEstat 5.0 (Informer Technologies, Inc.), and R statistical software (R version 3.5.2, 2018-12-20) were used for statistical analyses, with a critical level of significance of the tests set at ($\alpha = 0.05$). All PFAS concentrations in tissues were log-transformed in order to fit the assumptions of the statistical analyses. Significant relationships between TMF

and PFAS concentrations were determined with nonparametric Kendall's τ_b correlations (Munoz et al., 2017a). Kendall's τ_b correlations was used due to the slightly better fit of this method to outliers when compared to the other nonparametric option (i.e. Spearman correlation), besides their smaller gross error sensitivity (GES) and a smaller asymptotic variance (AV) (Croux and Dehon, 2010; Khamis, 2008). Non-detects and Data Analysis (NADA) and Linear Mixed-Effects Models with Censored Responses (LMEC) R-packages were used to perform the analyses (Helsel, 2005; Munoz et al., 2017a).

3. Results and discussion

3.1. Subaé estuary food web dynamics

Using the bi-plots of $\delta^{15}N$ versus $\delta^{13}C$, and the feeding habits of each species (obtained from the literature (Barletta et al., 2019; Ferreira et al., 2019; Lira et al., 2018; Matich et al., 2017; Souza et al., 2018; Wellens et al., 2015)), we projected the energy flow across the food web. $\delta^{15}N$ values increased from mangrove tree leaves to omnivore fish, ranging from 1.06 to 13.8‰ (Fig. 2) and all species connect to each other within the isotopic mixing space. As expected, $\delta^{13}C$ in mangroves was typical (−29.3 to −26.6‰) of terrestrial plants which the first product of photosynthesis is a 3-carbon molecule (C3 plants) (Minihan, 1983). A similar $\delta^{13}C$ composition was observed in sediment and SPM (−25.4 and − 26.9‰, respectively) indicating an influence of mangrove material in these matrices. $\delta^{13}C$ varied from −25.9‰ in bivalve (C. rhizophorae) to −17.4‰ in fish (Caranx sp.). Most bivalves displayed a close relationship with SPM (i.e. an average of 1.11‰ in $\delta^{13}C$ enrichment compared to SPM), except for M. guyanensis with an enrichment of 3.19‰, suggesting an additional source of carbon, probably from sediment (1.67‰ enrichment). Among crustaceans, U. cordatus displayed lower $\delta^{13}C$ values (−24.8‰) than other crustaceans, which agrees with their restricted leaf-feeder habit (Wellens et al., 2015), and sediment intake associated with leaves (average of 3.14‰ and 0.58‰, for carbon enrichment of leaves and sediment, respectively).

Litopenaeus sp. and G. cruentata displayed similar carbon isotopes ratios. These species display generalist feeding habits, but they are found in different locations within the mangrove forest. G. cruentata develop an important function in mangroves, recycling carbon in sediments in non-flooded areas (Wellens et al., 2015), while Litopenaeus sp. is an important link organism in this tropical food web (Lira et al., 2018; Vinagre et al., 2018), being the prey of several sampled fish in this study. Among fish, C. undecimalis showed distinctive low values of $\delta^{13}C$ (−23.8‰), even for a carnivore species showing a link to mangrove basal resource. In general, fish had $\delta^{15}N$ and $\delta^{13}C$ average values of 12.6 ± 0.84‰ and − 20.7 ± 1.91‰ (average ± SD), respectively. Polychaeta and shrimp represent the main food source for these fish species (Lira et al., 2018; Loureiro et al., 2016; Martins et al., 2017; Souza et al., 2018), which is aligned with C and N isotope results (Fig. 2). However, the large carbon variation between fish species may indicate an alternative source of food not considered in the present study and the fact they are not resident all the time in the studied region.

Bivalves represented the lowest TP of the food chain (TP = 2.0, C. rhizophorae; to TP = 2.6, T. plebeius), followed by crustaceans (TP = 2.1, C. sapidus to TP = 3.0, G. cruentata), polychaeta (TP = 3.6, pool of species) and fish (TP = 3.2, Mugil sp. to TP = 4.5, C. gracilicirrhus).

3.2. PFAS concentrations in biota

Sum ($\sum$) 22PFAS concentrations (and their isomers) above LOD in biota ranged from 0.28 ng g^{-1} ww wb (C. rhizophorae) to 3.72 ng g^{-1} ww wb (Litopenaeus sp.) (Fig. 3, Table S7) which is lower than the ranges reported for biota in subtropical ($\sum_{21}$PFASs; 0.50 to 17.5 ng g^{-1} ww wb) (Loi et al., 2011), temperate ($\sum_{23}$PFASs; 0.66 to 45.0 ng g^{-1} ww wb) (Munoz et al., 2017a) and polar areas ($\sum_5$PFASs 2.00 to 43.0 ng g^{-1} ww wb) (Tomy et al., 2009). PFOS was the most abundant PFAS among all species, with the exception of 3 bivalve samples (which were dominated by FOSA) and 1 fish (in which EtFOSA was dominant). Beyond the consistent observation of PFOS, the PFAS profile among individual species varied considerably. For example, most crustacean, polychaeta and bivalve samples contained relatively high levels of PFCAs compared to fish (Fig. 3). Also notable was that PFNA was the dominant PFCA among most crustacean, fish and polychaeta samples, but was generally not detected in bivalve. Differences in feed behavior, niche and protein contents of each group of organisms can help to explain this dissimilarity. Furthermore, more than one source of contaminants for those organisms could also play an important role in
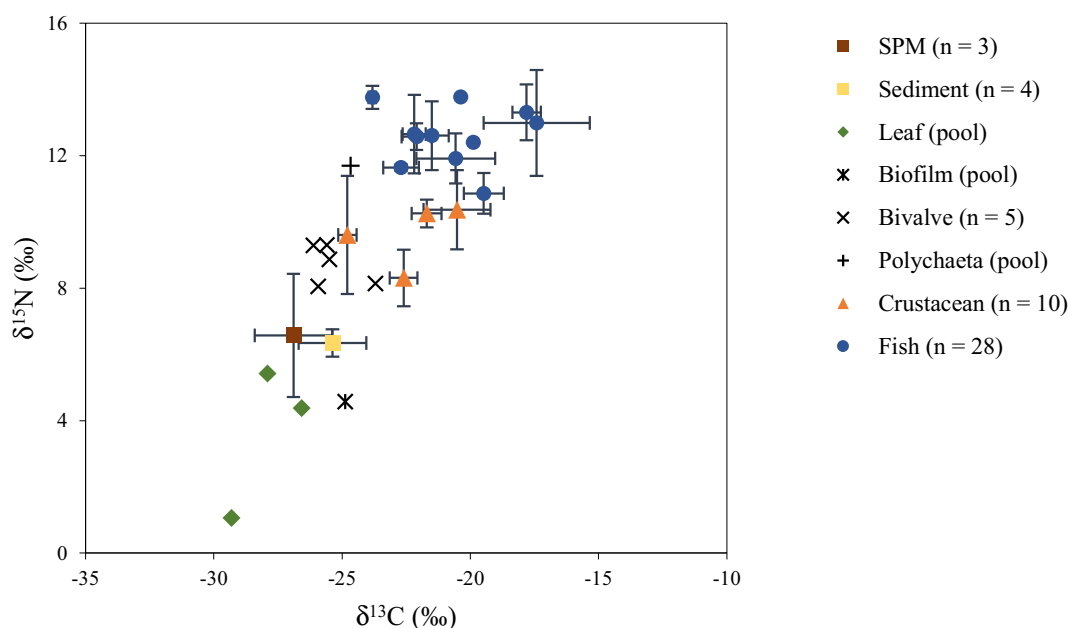

Fig. 2. Distribution of $\delta^{13}C$ and $\delta^{15}N$ in biotic and abiotic samples from the Subaé estuary, NE Brazil. Where SPM represents the suspended particulate matter and n the number of replicates analyzed.
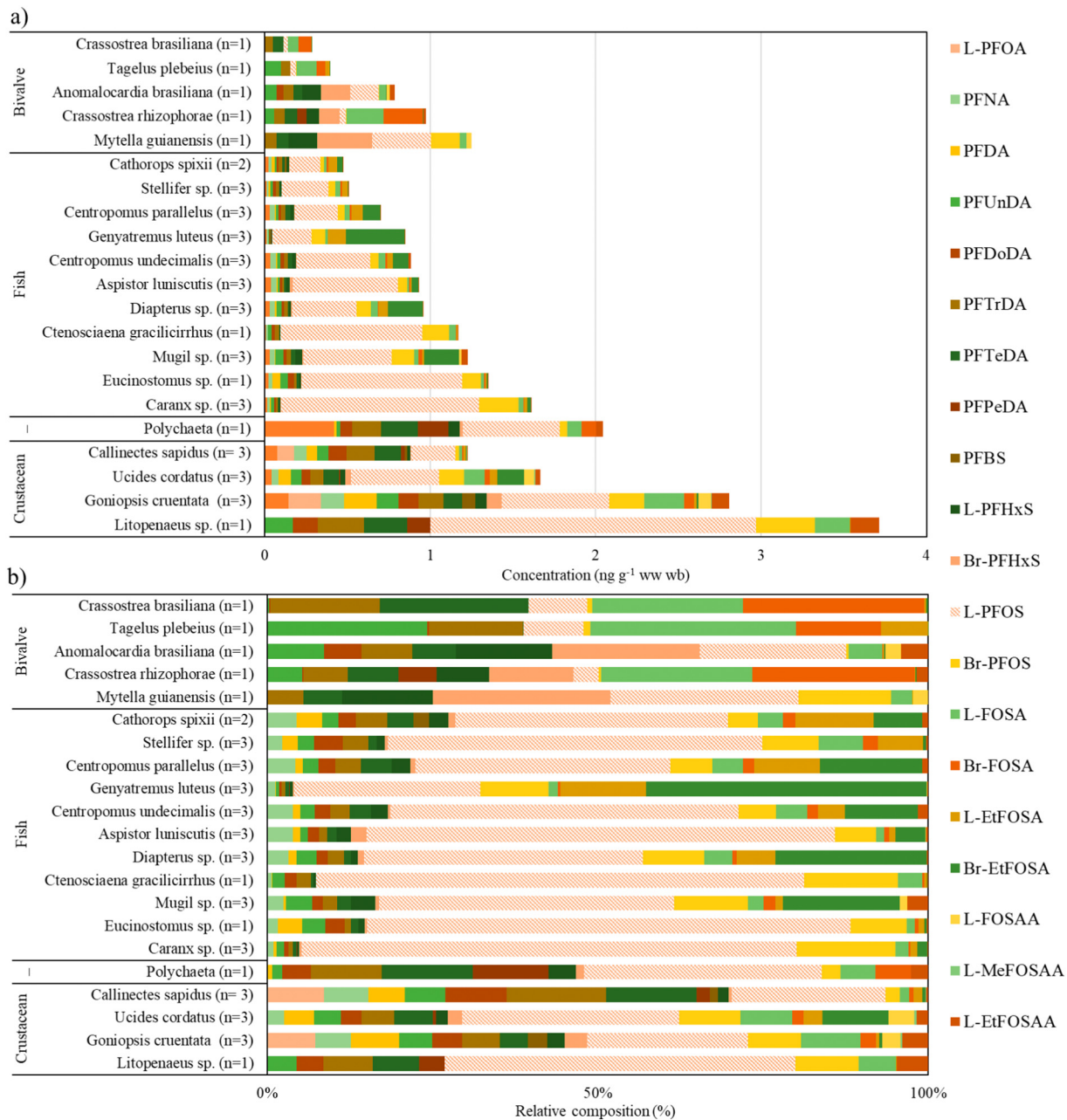
Fig. 3. Sum PFAS concentrations (ng g^{-1} wet weight (ww) for the whole body) measured in different organisms from the Subaé estuary (a); and relative PFAS profiles (normalized to 100%) (b). Number of organisms analyzed is shown in parentheses. EtFOSA was not reported for polychaeta. Br-PFOA, L-PFDS, Br-PFDS, L-MeFOSAA, Br-MeFOSAA, Br-FOSAA, MeFOSAA, and Me-EtFOSAA were not added to the figure due to either detection <LOD or low concentrations.

elucidating the PFASs accumulation patterns. While parts of the river can be under direct effect of sewage (consequently more exposed to AFFF and consumer products), other portions may be more affected by the leaching of forestry carrying Sulfluramid straight in the course of the river. Inputs of metals and nutrients have already been observed for different segments of the Subaé estuarine system (i.e. upper and lower estuary) (da Silva et al., 2017; Motta et al., 2018), but these data are unknown for PFASs. While most of the sampled specimens (i.e. bivalve, crustacean, and polychaeta) show either sessile behavior or limited mobility, fish can be exposed to a higher range of PFAS sources by swimming along the river and outside the estuary. Overall, the fish analyzed in the present study contained lower concentrations of the major PFCAs (PFNA, PFUnDA, PFDoDA, PFTrDA, PFTeDA) than other sampled organisms (Fig. 3). The reason for this is unclear but may indicate different exposure routes and/or PFAS accumulation in fish. Even though

most PFCAs were correlated with one another ($p < 0.05$; Table S8), correlations between PFCAs and PFOS were rare, suggesting a different source of contaminants for these organisms.

In *Laguncularia racemosa* (white mangrove) and *Rhizophora mangle* (red mangrove) leaves, only FOSAA was observed (0.16 and 0.07 ng g^{-1} ww, respectively) (Table S9). The PFASs were not detected in the biofilm sample (i.e. concentrations < LOD). The elevated concentrations of PFAS, and in particular L-PFOS in shrimps (1.97 ng g^{-1} ww wb) when compared to other organisms are consistent with the results of Carlsson et al. (2016), who proposed that the higher protein content in shrimp, compared to fish, may lead to higher PFAS concentrations in the former species. The detritivore habit of shrimp may also help to explain the observed profile, since the SPM showed detectable PFAS concentrations, and together with sediment it is an important route of uptake of organic compounds for aquatic epibenthic organisms (Liu

et al., 2018). For fish, L-PFOS concentrations were an order of magnitude lower than those reported for fish from a subtropical region (Loi et al., 2011), but similar to those reported for several species of fish from the Arctic (Butt et al., 2010; Tomy et al., 2004) and temperate (Munoz et al., 2018) zones. Fish and bivalve from the present work also contained lower ΣPFAS when compared with two highly industrialized areas in Rio de Janeiro (Σ_8PFAS, Guanabara Bay and Paraíba do Sul River) (Quinete et al., 2009). While PFAS profiles were similar among the sampled areas, the EtFOSA transformation product FOSA was absent in samples from the tributaries and coastal water from Rio de Janeiro, as well as bivalves and fish muscles, whereas it was present only in the liver of a few fish samples. This is perhaps unsurprising considering that sales of Sulfluramid in Rio de Janeiro were ~ 100 times lower than in Bahia state (i.e. between 2014 and 2017) (IBAMA, 2017) and there are no known records of Eucalyptus and Pine plantations in the area. These previous studies together with the present work may suggest that, although Sulfluramid is not the only source of PFASs for the Subaé River, the use of this pesticide in the region might contribute to greater detection of FOSA in different environmental matrices.

3.3. PFAS concentrations in abiotic samples

In SPM ($n = 3$), 16 PFASs were detected, including 11 linear and 5 branched isomers. Sum PFAS concentrations ranged from 1.85 ng g^{-1} dw (SPM#1) to 7.25 ng g^{-1} dw (SPM#2) (Fig. 4, Table S10). PFNA was the predominant PFAS in samples closer to the lower estuary (Fig. 1), while PFUnDA was the prevalent compound in the upper estuary. In comparison, 5 linear PFAS isomers were detected in sediments ($n = 4$), with sum PFAS concentrations in the range of 0.10 ng g^{-1} dw (#2) to 0.33 ng g^{-1} dw (#1) (Table S11). L-PFOS and L-PFOA were detected in all sediment samples at very low concentrations (L-PFOS: 0.07–0.34 ng g^{-1} ww and L-PFOA: 0.35–0.79 ng g^{-1} ww), while PFOS was detected in all SPM samples ranging from 0.48 to 1.56 ng g^{-1} dw. The presence of L-EtFOSA in sediments and its degradation products (e.g. L-FOSA) in SPM suggest that, even though the overall concentrations in Subaé estuary are low, there may be a source of Sulfluramid in

the region. The use of Sulfluramid in this area was previous suggested based on the high FOSA:PFOS detected in the Subaé river (Gilljam et al., 2016). The formicide can be mobilized from plantations to rivers and estuaries due to the leaching of contaminated soils. Stahl et al. (2013) and Zabaleta et al. (2018) suggested that leaching of soils caused by rainwater can promote the transport of EtFOSA and its degradation products to groundwater, rivers, and coastal zones. Sources other than Sulfluramid may also be important. For example, EtFOSAA, which was observed in SPM and sediment samples, does not form from EtFOSA, but rather from N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) a substance used widely in consumer products (e.g., food packaging) until 2002 (Benskin et al., 2013; Mejia Avendaño and Liu, 2015; USEPA, 2002).

Previous work indicated that sediments and soils can act as a sink for long chain PFASs, due to their sediment-water partitioning coefficient (Nascimento et al., 2018). Several species investigated in the present study display either benthic or demersal habits, which indicates that sediment exposure may represent a secondary source of PFASs for those organisms (Munoz et al., 2017a), in addition to bioaccumulation through the food chain. Nonetheless, estuarine areas are naturally dynamic and dilution of organic matter (and consequently PFASs) may occur at the site, thereby lowering observed concentrations in abiotic matrices.

3.4. Bioaccumulation of PFASs in the food chain

Bioaccumulation of PFASs in the present food web was evaluated for L- and Br-PFOS, PFTrDA, L-FOSA, PFUnDA, PFDoDA, PFTeDA, PFNA, and L- and Br-EtFOSA. TMFs and biomagnification factors (BMFs) greater than 1.0 are both considered reliable indicators of bioaccumulation (Borga et al., 2012). However, TMF is considered the most consistent way to characterize biomagnification of organic compounds over an entire food web (Franklin, 2016). TMFs were greater than 1 for L- and Br-PFOS, L- and Br-EtFOSA, and PFNA, indicating biomagnification across trophic levels. The concentration of four PFASs were significantly correlated with trophic level ($p < 0.05$; Table 1, Kendell's rank correlation;
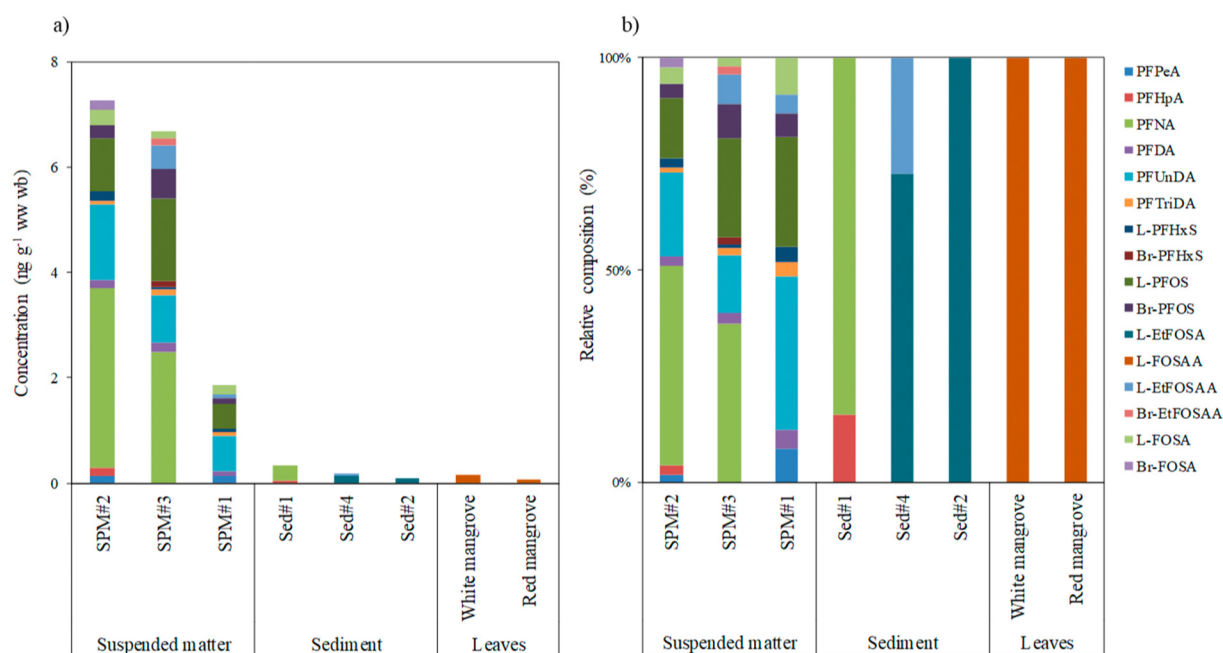

Fig. 4. Sum of PFAS concentrations in different samples from the Subaé estuary. (a) Concentrations are expressed in ng g^{-1} dry weight (dw) for sediment and SPM, and ng g^{-1} wet weight (ww) for leave and (b) corresponding composition profiles (relative abundance in % of Σ PFAS). Sed#3, Black mangrove and biofilm were excluded from this figure due no detected PFASs above LOD.

Table 1

Regressions of Log Concentration (concentrations expressed in ng g^{-1} ww whole body, min-max) vs TP (trophic position) in the whole food web, obtained with the NADA R-package [a], including the *p*-value of the regression, and Kendall's τ correlation coefficient (Helsel, 2005; Munoz et al., 2017a), compounds detection frequency[a], minimum and maximum whole-body wet weight concentrations, and Kendall's τ correlation coefficient[b]. EtFOSA was not reported for polychaeta.

Compound	Detection frequency (%)	Concentration average (min-max)	τ	TMF$_{FW}$ (min-max)
L-PFOS	93	0.49 (0.05–1.97)	0.215	**1.53** (1.49–1.57)
Br-PFOS	73	0.09 (0.01–0.35)	0.052	1.53 (1.45–1.61)
PFTrDA	57	0.06 (0.01–0.28)	−0.386	**0.39** (0.38–0.40)
L-FOSA	54	0.06 (0.01–0.32)	−0.177	0.64 (0.62–0.66)
Br-FOSA	27	0.02 (0.01–0.24)	−0.119	0.83 (0.78–0.88)
PFUnDA	48	0.04 (0.01–0.17)	−0.226	**0.41** (0.39–0.43)
PFDoDA	46	0.03 (0.01–0.15)	−0.075	0.94 (0.88–1.00)
PFTeDA	46	0.05 (0.01–0.26)	−0.329	**0.62** (0.48–0.80)
PFNA	41	0.03 (0.01–0.42)	0.029	1.34 (1.27–1.42)
L-EtFOSA	30	0.03 (0.01–0.21)	0.112	1.80 (1.72–1.89)
Br-EtFOSA	30	0.09 (0.01–0.58)	−0.021	1.60 (1.38–1.86)

[a] Note that for detection frequency percentage of individual tissue (muscle, liver, hepatopancreas and soft tissue of bivalves and shrimp, *n* = 56) was used;

[b] It was obtained with the NADA R-package, including Kendall's τ correlation coefficient, the resulting trophic magnification factor (TMF = 10^{slope}) with the confidence interval of 95% (min – max). Bold numbers indicate significant regressions (*p* < 0.05).

Figs. S2 and S3), showing bioaccumulation of L-PFOS (*n* = 44; τ = 0.215, *p* = 0.043) and biodilution of PFUnDA (*n* = 44; τ = −0.226, *p* = 0.034), PFTrDA (n = 44; τ = −0.386, *p* ≤0.001), PFTeDA (n = 44; τ = −0.329, *p* = 0.002). These data further highlight the potential of PFOS to be biomagnified through the tropical food web, which is consistent with prior studies in temperate and subtropical zones (Liu et al., 2018; Loi et al., 2011; Munoz et al., 2017a).

The absence of TMFs greater than 1 for most PFCAs was initially surprising, since bioaccumulation of C$_9$-C$_{12}$ PFCAs has been reported elsewhere (Houde et al., 2006a; Munoz et al., 2017a). However, biodilution has also been reported for C$_{13}$-C$_{14}$ PFCAs (Munoz et al., 2017a), which may be associated with the limitation of PFCAs with >10 fluorinated carbons to penetrate cell membranes due to their large molecular size (Conder et al., 2008; Hong et al., 2015). Alternatively, different sources of PFCAs for (1) bivalve, crustacean, and polychaeta, and (2) fish may also lead to an apparent lack of bioaccumulation. The low detection frequency of those compounds in organisms (i.e. from 41% (PFNA) to 57% (PFTrDA)) should also be considered.

The TMF determined here for PFOS was lower than previously reported for polar food webs, but similar to those in subtropical regions (Table S12) (Boisvert et al., 2019; Loi et al., 2011; Munoz et al., 2017a; Tomy et al., 2004). Variations in PFAS sources and/or proximity to sources may play a role in explaining these differences. For example, biota from the Northern Hemisphere tends to contain higher PFAS concentrations due to its proximity to point sources (Benskin et al., 2012). On the other hand, the ongoing use of EtFOSA in South America is unique, and exposure to this compound may cause PFOS accumulation in the Subaé estuarine wildlife due to its biotransformation (Gilljam et al., 2016; Nascimento et al., 2018). In addition, the upper trophic levels of polar food webs is occupied by top predator mammals, which means higher energy flow compared to tropical environments (Hobson et al., 2002). The lower TMFs in tropical aquatic ecosystems possibly reflects not only the lower input of

PFASs, but also the structure of food webs that generally larger number of organisms, which may dilute the energy flows (and by extension, contaminants) among them (Borga et al., 2012). Also, variances in protein content in the blood and tissues of distinct species can result in variability in the accumulation of proteinophilic contaminants (Goeritz et al., 2013). Finally, climatic factors cannot be excluded (e.g. water temperature) and water chemistry, which may also have an impact on PFAS accumulation at different trophic levels (Vidal et al., 2019; Xu et al., 2014).

Surprisingly, the TMF for L-EtFOSA was above 1 (1.80), suggesting that this compound is bioaccumulating in the Subaé estuarine food chain. However, since EtFOSA was rarely detected throughout the food chain and also in low concentrations (0.01 to 0.21 ng g^{-1} ww wb, 30% detection frequency), TMFs should be interpreted cautiously, and further studies are warranted to corroborate these results. To the best of our knowledge, TMFs for EtFOSA have not been previously reported, but Tomy et al. (2004) showed Trophic Position-adjusted BMFs above 1 for species from the Arctic web food and suggested that organisms from different TP will metabolize/accumulate EtFOSA in different proportions. It is well-known that EtFOSA is readily biotransformed into FOSA in a few types of soil under aerobic conditions (Avendaño and Liu, 2015; Yin et al., 2018; Zabaleta et al., 2018), and also in earthworms (Zhao et al., 2018) but no studies have been carried out in estuarine environments. The presence of PreFOS (i.e. L-EtFOSA, L-EtFOSAA, and FOSA) in the Subaé biota may contribute indirectly to the occurrence of PFOS in top-level organisms via biotransformation, which may in turn contribute to increasing the TMF of PFOS (Simonnet-Laprade et al., 2019). This is supported by the observed biodilution of FOSA through the food web. Nonetheless, an in-depth evaluation of a larger range of PreFOS (and long-chain PFCAs precursors) will be necessary to confirm if TMF inflation is occurring due to PFAS precursors biotransformation.

Interestingly, when EtFOSA TMFs were re-calculated after splitting the organisms into 2 groups based on their trophic level (i.e. group 1: *n* = 18, TP 2.00 to 3.22; and group 2: *n* = 26, TP 3.56 to 4.49), a much higher TMF was observed for group 1 (2.65) compared to group 2 (0.22), suggesting that dilution of this compound is occurring in top organisms (Table S13). Besides the differences related to habitats and trophic level between the aforementioned groups, the first group (TP 2.00 to 3.22) is composed mainly by filter-feeding organisms, while the second group (TP 3.56 to 4.49) comprises mostly omnivorous organisms. The different feeding habits of those organisms can imply dissimilar contaminant exposure and hence uptake. Higher TMFs for bottom species were previously reported for other PFASs (Munoz et al., 2017a), and may point to greater efficiency in metabolizing and/or excreting xenobiotics in higher trophic level organisms. This metabolic difference in the accumulation/depuration of PFAA precursors between fish and invertebrates has been previously reported (Langberg et al., 2019).

The divergence in TMFs observed for EtFOSA upon splitting the food web into two groups was not observed for PFNA, L-PFOS, or Br-PFOS (Table S13). These substances all displayed TMFs >1 regardless of whether the food web was split into two groups or considered together, suggesting a linear trend in bioaccumulation among the sampled organisms. However, this was not the case for L-FOSA and C$_{11}$-C$_{14}$ PFCAs. These substances all displayed apparent biodilution (i.e. TMF < 1) when the entire food web was considered but upon splitting the food web into two groups, L-FOSA, PFUnDA, and PFDoDA displayed bioaccumulation (i.e. TMFs>1) for both groups, while PFTrDA and PFTeDA displayed biodilution (i.e. TMF < 1) in the first group and bioaccumulation (i.e. TMF > 1) in the second group, which was the opposite of what was observed for EtFOSA. The factors controlling these phenomena are currently unclear and warrant further investigation, once the metabolization of PFASs by different organisms can help to explain the bioaccumulation pattern of these compounds through the food chain.

4. Conclusions

The bioaccumulation of PFASs was accessed in a tropical estuary in northeastern Brazil. PFASs were detected in all organisms analyzed, alongside with abiotic matrices (SPM and sediment). Unique accumulation profiles and low levels of PFASs were generally found in biotic and abiotic matrices when compared to subtropical, temperate and polar environments. Different patterns of bioaccumulation were observed through the sampled group of organisms (i.e. bivalve, crustacean, polychaeta, and fish), suggesting a set of factors (physical, chemical, biological and spatial) must be influencing on the PFAS assimilation. Moreover, PFOS, PFNA and EtFOSA were found to be bioaccumulating in this food chain, even though the bioaccumulation of the latter compound should be considered cautiously due to the low detection of EtFOSA in organisms. Nonetheless, the occurrence of PFASs in coastal marine biota is particularly concerning due to the potential for human exposure via consumption of these organisms. Further investigations into the sources of PFASs to Subaé estuary are warranted.

CRediT authorship contribution statement

Daniele A. de Miranda: Conceptualization, Investigation, Writing - original draft, Writing - review & editing. **Jonathan P. Benskin:** Writing - review & editing, Visualization, Resources. **Raed Awad:** Investigation, Writing - review & editing. **Gilles Lepoint:** Formal analysis. **Juliana Leonel:** Writing - review & editing, Visualization. **Vanessa Hatje:** Conceptualization, Writing - review & editing, Resources, Visualization, Supervision.

Declaration of competing interest

There are no conflicts of interest to declare.

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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.2020.142146.

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