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Specific profiles of perfluorinated compounds in surface and drinking waters and accumulation in mussels, fish, and dolphins from southeastern Brazil

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ABSTRACT

Despite the concern over widespread distribution of perfluorinated compounds (PFCs) even in sparsely populated regions of the world, few studies have reported their occurrence in South America. In this study, PFCs were measured in Rio de Janeiro State in southeast Brazil: in drinking water from various districts in the State, in river water and tucuxi dolphins from the Paraiba do Sul River, several species of fish from the State, and mussels from Guanabara Bay. Liver, kidney, and muscle from fishes were analyzed to enable an understanding of the tissue distribution of PFCs. PFOS, PFOA, and PFHxS were detected in all drinking water samples in concentration ranges of 0.58–6.70, 0.35–2.82, and 0.15–1.00 ng L^{-1}, respectively. The profiles of PFCs in drinking water from Brazil (with PFOS concentrations comparable to or higher than those of PFOA) were different from the profiles that have been reported for other countries. In fish, concentrations of PFOS were, in general, higher in liver than in muscle. Concentrations of PFOA in livers of fish were similar to or lower than fish muscle tissue concentrations. PFOS and PFOA were found in brown mussels from Guanabara Bay. Bioconcentration factors (BCFs) of PFOA calculated for mussels were higher than the BCFs calculated for fishes. Elevated concentrations of PFUnDA (mean: 109 ± 17.4 ng g^{-1} wet weight) were found in mussels from certain locations within Guanabara Bay. Although PFCs were detected in all types of samples analyzed, the concentrations were generally lower than the concentrations reported for Japan and the USA.

1. Introduction

Perfluorinated compounds (PFCs) are global environmental contaminants, and have been the subject of many recent investigations (Giesy and Kannan, 2001; Martin et al., 2003; Van de Vijver et al., 2005; So et al., 2006; Senthilkumar et al., 2007; Tao et al., 2008; Orata et al., 2009; Yeung et al., 2009). PFCs, typically epitomized by perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA), comprise a diverse class of chemicals that are used in a wide range of commercial and consumer products, as surfactants, water repellents, lubricants, adhesives, additives and coatings, and in fire fighting foams (Kissa, 2001). Despite the concern over widespread occurrence and toxicity of PFCs, even in sparsely populated regions of the world (Kannan et al., 2005a,b; Gonzalez-Barreiro et al., 2006; Schiavone et al., 2009), few studies have investigated the sources and profiles of PFCs in South America (Olivero-Verbel et al., 2006; Dorneles et al., 2008; Leonel et al., 2008). Previous investigations showed, however, notable concentrations of PFOS in dolphins from Brazil (Dorneles et al., 2008; Leonel et al., 2008), in fish and birds from Colombia (Olivero-Verbel et al., 2006), and in human blood from Brazil and Colombia (Kannan et al., 2004). Little is known on the environmental distribution of PFCs in Brazil. Rio de Janeiro, located in southeastern Brazil, is the second largest city in Brazil and third largest metropolitan area in South America, with a total population of approximately 15 million. The city is highly industrialized and urbanized. Guanabara Bay, which is located in the State of Rio de Janeiro (RIO), is bordered by 12 000 industries (including two refineries, several petrochemical plants, oil terminals, and shipyards that discharge their effluents directly into the bay) and four cities (including the Rio de Janeiro metropolitan area) (Azevedo et al., 2004). The aim of this study was to determine the concentrations and patterns of PFCs in a range of environmental and biological samples (drinking water, river water, seawater, mussels, fish, and dolphins) and to examine bioaccumulation profiles of PFCs in mussels, fish and dolphins. We determined concentrations of 10 PFCs, namely, PFOS, PFOA, perfluorohexanesulfonate (PFHxS), perfluorodecanesulfonate (PFDS), perfluorooctane sulfonamide

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(PFOSA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), and perfluorododecanoic acid (PFDoDA) in drinking water from various districts in RIO; river water, fish, and tucuxi dolphin from the Paraiba do Sul River; several species of fish and brown mussels from Guanabara Bay; and fish from Rodrigo de Freitas Lagoon. In addition to the liver tissue, we analyzed kidney and muscle tissues from fishes and dolphins to examine the relationship between muscle and liver concentrations of PFCs.

2. Materials and methods

2.1. Study area and sample collection

The Paraíba do Sul River, the largest river in southeastern Brazil, is 1145 km long, and flows through the most important urban and industrial centers in Brazil (Rio de Janeiro and Sao Paulo). Despite being the only source of drinking water for the Rio de Janeiro metropolitan area, the river is heavily contaminated by agricultural and highway runoff and discharges from untreated industrial and domestic wastes (Linde-Arias et al., 2008). Water samples were collected in the river near the river mouth (P1–P5) and upstream of a drinking water treatment plant (ETA-Guandu) (Fig. 1). Silver scabbardfish (*Lepidopus caudatus*) and whitemouth croaker (*Micropogonias furnieri*) were collected in the river near Campos dos Goytacases by local fishermen and transported on ice to the laboratory, where dissections were performed to separate organs and tissues (liver and muscle). Ten liver, two kidney and two muscle tissue samples were obtained from tucuxi dolphins (*Sotalia guianensis*), which were collected along the coast of RIO. The locations for sampling of water and brown mussel (*Perna perna*) within Guanabara Bay are shown in Fig. 1. Mussels were manually collected in August 2008 and stored in solvent-cleaned glass jars. Water samples were collected at each of the locations where mussels were collected in Guanabara Bay and near Urca beach (identified as Urca on the map; Fig. 1), using 1-L solvent-cleaned amber glass bottles. Various species of fish, such as silver scabbardfish, whitemouth croaker, and mullet (*Mugil liza*), were collected by local fishermen and transported on ice to the laboratory, where dissections were performed to separate organs and tissues (kidney, liver, and muscle).

The Rodrigo de Freitas lagoon is located within the densely populated region of Rio de Janeiro city (Fig. 1). Tilapia *(Tilapia rendalli)*, pearl cichlid (*Geophagus brasiliensis*), and mullet were collected from this lagoon by local fishermen; these are the fishes commonly consumed in this area. Tap water samples were collected from residents' homes and shopping centers in 12 districts (Jacarepaguá, Barra, Gávea, Leblon, Ipanema, Copacabana, Botafogo, Santa Teresa, Praça Mauá, Tijuca, Pavuna and São João de Meriti) within RIO. More details regarding samples and sampling locations are provided in Supporting Information.

2.2. Chemical analysis

Details regarding standards and chemicals and chemicals analysis are provided in Supporting Information. All fish and dolphin samples (liver, kidney, muscle) and mussels were freeze-dried and ground into a fine powder (for homogeneity) before analysis. Moisture content of the samples was recorded. PFCs in liver and kidney were analyzed according to the ion-pairing method

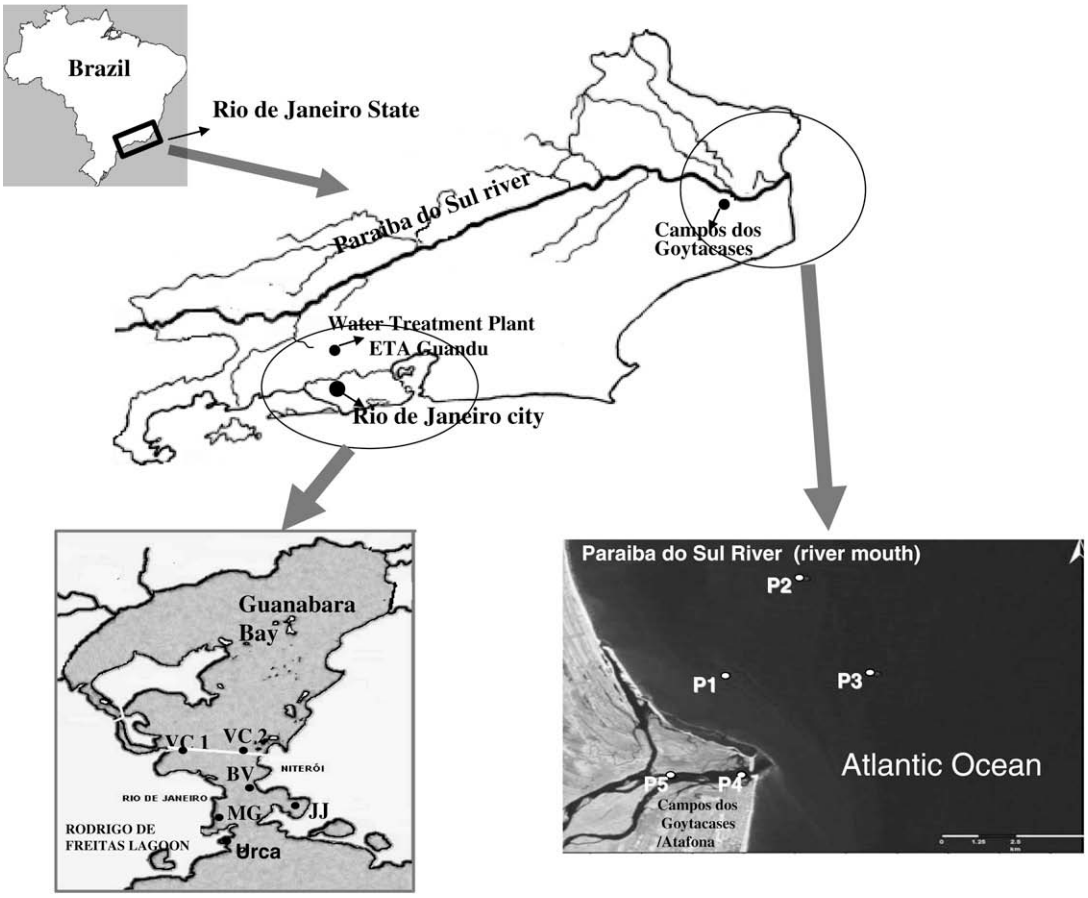

Fig. 1. Map of Brazil showing sampling locations in Rio de Janeiro State including the Paraíba do Sul River, and Guanabara Bay.

described elsewhere (Kannan et al., 2001). In order to validate the precision and accuracy of PFC determinations in muscle tissues, we employed three extraction methods: acetonitrile extraction, ion-pair extraction and alkali-digestion. Alkaline digestion followed by solid phase extraction (SPE) yielded the highest recoveries and precision for the muscle samples and was performed similarly to what has been described elsewhere (Taniyasu et al., 2005; So et al., 2006). Approximately 0.2 g of dry tissue (~1 g wet weight) was homogenized with 5 mL of Milli-Q water and an aliquot (2 mL) was transferred to a 15-mL PP tube, and 100 μL of a 50 ng mL^{-1} internal standards mixture ($^{13}C_4$-PFOS, $^{13}C_4$-PFOA, $^{13}C_2$-PFNA, $^{13}C_2$-PFDA) and 10 mL of 0.01 N KOH/methanol were added. The mixture was shaken at 250 rpm at room temperature for 1 h, centrifuged, and 3 mL of the solution were transferred into another PP tube; 100 mL of Milli-Q water were added, and the sample was shaken thoroughly. The extract was passed through an Oasis HLB cartridge (3 cc, 60 mg; Waters, Milford, MA) or Oasis WAX cartridge (6 cc, 150 mg; 30 μm, Waters). A few modifications to the previously reported method (So et al., 2006) were introduced. The analytical procedure for the extraction of water samples was similar to that described elsewhere (Orata et al., 2009). Water samples were analyzed in triplicate from each sampling location.

2.3. Instrumental analysis

Concentrations of 10 PFCs, PFHxS, PFOS, PFDS, PFOSA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, and PFDoDA, were detected and quantified on an Agilent 1100 Series high performance liquid chromatography (HPLC) coupled with an Applied Biosystems API 2000 electrospray triple-quadrupole mass spectrometer (ESI-MS/MS). Further details are given in Supporting Information. Details of analytical quality assurance and quality control are given in Supporting Information.

3. Results and discussion

This is the first comprehensive study of profiles and concentrations of PFCs in drinking and surface waters, mussel, fish, and dolphins from (river, bay and lagoon) RIO, Brazil. We also believe this to be the first study to measure and examine relationship of PFC concentrations among muscle, liver and kidney tissues of fish.

3.1. PFCs in water: specific profiles

PFOS, PFOA, and PFHxS were found in all drinking water samples in concentration ranges of 0.58–6.70, 0.35–2.82, and 0.15–1.00 ng L^{-1}, respectively (Table 1). PFHpA was detected in >90% of the samples at concentrations ranging from <0.1 to 2.21 ng L^{-1}. Other PFCs were rarely found. PFOS concentrations were slightly higher than the concentrations of PFOA in tap-water samples. This pattern is different from the patterns reported for water samples from many other countries, including the USA and Japan (Loos et al., 2007; Senthilkumar et al., 2007; Ericson et al., 2008; Takagi et al., 2008; Mak et al., 2009). Tap water collected from homes in RIO contained PFOS and PFOA at concentrations similar to the concentrations found in water collected after the treatment at ETA-Guandu, except for samples from Tijuca and Gavea, where the concentrations were higher (6.70 ± 0.2 and 3.56 ± 0.2 ng L^{-1}) for PFOS than (2.82 ± 0.1 and 1.58 ± 0.01 ng L^{-1}) for PFOA. The composition profiles of PFCs reported for tap water from China varied depending on the sampling location; PFOA accounted for more than 40% of the total PFCs in Shanghai, Beijing and Nanjing, whereas at least 50% of the total PFCs was PFOS, in samples from Shenzhen and Hong Kong (Mak et al., 2009). The distribution profiles of PFOA and PFOS from river water, drinking water treatment plant, and tap water are shown in Fig. S1. PFC concentrations have been reported in drinking water from others countries. Concentrations of PFOA and PFOS in tap water from Osaka, Japan, were in the ranges of 2.3–84 and 0.16–22 ng L^{-1} (Takagi et al., 2008), respectively; in Italy, 1.0–2.9 and 6.2–9.7 ng L^{-1}, respectively (Loos et al., 2007); in Spain, 0.32–6.28 and 0.39–0.87 ng L^{-1}, respectively (Ericson et al., 2008); in drinking water from a contaminated river in Germany (Arnsberg), PFOA was detected at 500–640 ng L^{-1} (Holzer et al., 2008). The concentrations of PFOA and PFOS found in water samples in our study are similar to the concentrations reported for Italy and Spain, but lower than the concentrations reported for Japan.

Water samples from Guanabara Bay contained PFOA, PFOS, and PFHxS at concentrations in the ranges of 0.7–3.25, 0.4–0.92, and 0.13–0.18 ng L^{-1}, respectively, while none of the other PFCs were detected. Concentrations of PFOA in water from the Paraiba do Sul River were similar to concentrations from Guanabara Bay.

The daily intake of PFOS, PFOA, PFHxS, and PFHpA through the consumption of tap water was estimated based on the mean concentration and a consumption rate of 2-L water d^{-1}. The daily intake values for PFOS, PFOA, PFHxS, and PFHpA were 3.4, 2.4, 0.74 and 0.96 ng $person^{-1}$ d^{-1}, respectively. The intake rate of PFOS from drinking water was 2-fold higher than the intake rates reported for Catalonia, Spain (Ericson et al., 2008), but within the acceptable daily intake, 0.3 and 3 μg kg^{-1} d^{-1} for PFOS and PFOA, respectively, set by of the Committee on Toxicity of Chemicals in Food, Consumer products and the Environment of the UK (COT, 2006a/09; COT, 2006b/10).

3.2. PFCs in biota: specific accumulation in muscle, liver and kidney

PFOS, PFOA, PFDS, and PFOSA were found in all of the biota samples from the Paraiba do Sul River (Table 2). PFOS was the most abundant compound in tucuxi dolphin liver (91 ± 42.4 ng g^{-1}, wet weight) and in scabbardfish liver (5.5 ± 2.4 ng g^{-1}, wet weight). The concentrations of PFOS in livers of scabbardfish, croaker, and mullet from Guanabara Bay were in the ranges of 3.36–28.9, 1.75–5.13, and 2.17–9.44 ng g^{-1}, wet weight, respectively (Table 2). In Rodrigo de Freitas Lagoon, PFOS concentrations in livers of pearl cichlid, tilapia, and mullet were in the ranges of 3.41–59.1, 11.5–45.3 and 11.4–49.7 ng g^{-1}, wet weight, respectively (Table S1, Supporting Information). The concentrations of PFOS in fish from this lagoon are higher than the concentrations found in Guanabara Bay and the Paraiba do Sul River. In this lagoon, concentrations of PFOA in fish livers were lower than concentrations of PFOS and ranged from <0.46 to 31.4 ng g^{-1}, wet weight; the highest concentration was found (31.4 ng g^{-1}, wet weight, mean: 17.6 ± 11.5 ng g^{-1}, wet weight) in pearl cichlid. PFUnDA, PFDoDA, PFDA, and PFNA were below the LOQ in most fish and dolphin liver samples, except for fish from this lagoon (<0.49–5.66 ng g^{-1}, wet weight for PFNA, 1.37–21.3 for PFDA, <3.12–13.2 for PFUnDA, and <2.51–14.5 for PFDoDA). Earlier studies have reported that fish liver (mullet, shad, and rockfish) from Lake Shihwa, Korea, contained a mean PFOS concentration of 81 ng g^{-1}, wet weight (Yoo et al., 2009), and fish livers from Michigan and New York State, respectively contained PFOS concentrations ranging from 32 to 173 ng g^{-1} (Kannan et al., 2005a,b) and 9 to 315 ng g^{-1} (Sinclair et al., 2006), wet weight; tilapia and Japanese perch from Taiwan contained mean PFOS concentrations of 310 and 260 ng g^{-1}, wet weight, respectively (Tseng et al., 2006). Our fish liver PFOS concentrations are one order of magnitude lower than those reported for Korea, the USA, and Taiwan, but similar to the values reported for fish samples from India (0.248–27.9 ng g^{-1}, wet weight) (Yeung et al., 2009). Concentrations of PFOS in livers of tucuxi dolphins in our study were similar to those reported for dolphins from other investigations (Kannan et al., 2001, 2002; Yeung et al., 2009).

Table 1
Perfluorochemical concentrations (ng L^{-1}; mean ± standard deviation and range) in drinking water, river water, and coastal water from southeastern Brazil.

Location	Sample type	*n*	PFHxS	PFOS	PFDS	PFHpA	PFOA	PFUnDA
Botafogo	Drinking water	2	0.21 ± 0.016	1.04 ± 0.083	0.12	0.20 ± 0.007	0.81 ± 0.017	<0.1
Gavea	Drinking water	2	0.6	3.56 ± 0.163	<0.09	0.60 ± 0.093	1.58 ± 0.007	<0.1
Ipanema	Drinking water	2	0.25 ± 0.018	1.24 ± 0.148	0.13 ± 0.031	0.25 ± 0.030	0.95 ± 0.121	<0.1
Copacabana	Drinking water	2	0.24 ± 0.008	1.09 ± 0.064	0.12	0.31 ± 0.117	1.03 ± 0.319	<0.1
Santa Teresa	Drinking water	2	0.25 ± 0.004	1.07 ± 0.120	0.12 ± 0.015	0.22 ± 0.084	0.93 ± 0.018	<0.1
Barra	Drinking water	2	0.26 ± 0.019	0.96 ± 0.075	<0.09	0.22 ± 0.087	1.03 ± 0.007	(<0.1–0.16)
SJ Meriti	Drinking water	2	0.24	1.30 ± 0.156	<0.09	0.27 ± 0.014	0.98 ± 0.063	<0.1–0.12
Jacarepagua	Drinking water	2	0.26 ± 0.019	1.11 ± 0.014	<0.09	0.29 ± 0.074	0.93 ± 0.018	<0.1
Pca Maua	Drinking water	2	0.24	1.07 ± 0.141	(<0.09–0.1)	0.12 ± 0.010	0.90 ± 0.071	(<0.1–0.12)
Pavuna	Drinking water	2	0.59 ± 0.005	0.58 ± 0.091	<0.09	2.21 ± 0.042	1.60 ± 0.099	<0.1
Tijuca	Drinking water	2	1.00 ± 0.047	6.70 ± 0.163	<0.09	0.86 ± 0.018	2.82 ± 0.092	<0.1
Leblon	Drinking water	2	0.28 ± 0.021	1.05 ± 0.074	0.09 ± 0.004	0.19 ± 0.091	0.89 ± 0.120	<0.1
ETA 2	Drinking water	2	0.15	1.30 ± 0.099	0.13	<0.1	0.35 ± 0.213	(<0.1–0.1)
ETA 1	River water	3	0.21 ± 0.033	1.32 ± 0.078	0.24 ± 0.055	(<0.1–0.11)	1.20 ± 0.083	(<0.1–0.1)
P1	River water	3	<0.1	0.17 ± 0.009	<0.09	<0.1	0.15 ± 0.021	(<0.1–0.12)
P2	River water	3	<0.1	(<0.1–0.14)	<0.09	<0.1	<0.09	<0.1
P3	River water	2	<0.1	<0.1	<0.09	<0.1	<0.09	<0.1
P4	River water	2	(<0.1–0.1)	0.64 ± 0.076	0.14	(<0.1–0.15)	1.22 ± 0.184	(<0.1–0.1)
P5	River water	2	<0.1	0.69 ± 0.003	0.11	(<0.1–0.26)	1.13 ± 0.724	<0.1
BV	Guanabara Bay	3	0.18 ± 0.028	0.92 ± 0.053	(<0.09–0.11)	<0.1	2.04 ± 1.497	<0.1
VC	Guanabara Bay	3	0.17 ± 0.037	0.40 ± 0.070	<0.09	<0.1	3.25 ± 3.162	<0.1
JJ	Guanabara Bay	2	0.13	0.40 ± 0.027	0.09 ± 0.007	<0.1	1.37 ± 0.205	<0.1
Urca beach	Guanabara Bay	2	0.14 ± 0.009	0.57 ± 0.187	(<0.09–0.17)	(<0.1–1.97)	0.77	<0.1
MG	Guanabara Bay	2	0.13 ± 0.009	0.53 ± 0.007	<0.09	(<0.1–0.11)	1.40 ± 0.774	<0.1
Recovery (%)	All water	6	94 ± 6	86 ± 10	73 ± 4	97 ± 8	100 ± 8	80 ± 14

ETA 1: sampling point before the water treatment plant ETA-Guandu; ETA 2: sampling point after the water treatment plant ETA-Guandu; BV, VC, JJ and MG are sampling locations in the Guanabara Bay; P1–P5 are sampling locations in the Paraiba do Sul River (see Fig.1); PFOSA, PFNA, PFDA, and PFDoDA were not detected in any samples at a detection limit of 0.09, 0.12, 0.12, and 0.12 ng L^{-1}, respectively.

Kidney samples were also analyzed for mullet from Guanabara Bay and for two tucuxi dolphins from the Paraiba do Sul River. PFOS and PFOA were found in all kidney samples at average concentrations of 3.86 ± 1.22 and 1.22 ± 0.28 ng g^{-1}, wet weight, respectively. In tucuxi dolphin kidney, six PFCs were detected; the most abundant compound was PFOS (mean: 31.1 ng g^{-1} wet weight), followed by PFOSA (mean: 16.0 ng g^{-1} wet weight), and PFUnDA (mean: 11.4 ng g^{-1} wet weight). PFOS and PFOSA concentrations were, respectively, 3- and 2-fold lower in kidney than in liver. Although PFHpA and PFUnDA had not been found in livers of dolphins, these compounds were found in kidneys. A few previous studies have measured PFCs in kidneys (Van de Vijver et al., 2005, 2007; Olivero-Verbel et al., 2006; Ahrens et al., 2009) of marine organisms. Concentrations of PFOS in kidney from our two tucuxi dolphins were 10-fold lower than concentrations reported for other marine mammals (harbor seals and porpoises).

Although consumption of fish could be a source of human exposure to PFCs, little is known about the partitioning and occurrence of PFCs in fish muscle tissue (Ye et al., 2008). In the present study, we analyzed muscle tissues from several species of fish. Nevertheless, muscle from mullet from Guanabara Bay contained PFOA and PFOS at respective mean concentrations of 3.4 and 3.49 ng g^{-1}, wet weight. PFOA was found in the muscle of scabbardfish at a mean concentration of 1.04 ng g^{-1}, wet weight, while PFOS was not detected in this fish species. Two previous studies have measured PFOS in fish fillets; fillets from common carp from the Upper Mississippi River (Ye et al., 2008), and from salmon, lake whitefish, and brown trout from Michigan (Giesy and Kannan, 2001), contained PFOS concentrations that were at least one order of magnitude higher than the concentrations in our fish muscle from RIO. It is interesting to note that PFOA is found at higher levels in muscle than in liver of fish. The liver to muscle ratios of PFC concentrations in mullet, scabbardfish, and croaker are shown in Table S2 (Supporting Information).

Bivalves, in particular mussels, are filter-feeding organisms and have been used as bioindicators for aquatic pollution monitoring. PFC concentrations in whole-body homogenates from brown mussels (mean concentration ± SD and range) from RIO are summarized in Table 3. PFOS, PFOA, and PFHpA were found in most of the mussel samples analyzed; the respective mean concentrations were in the ranges 3.5–4.5, 2.1–6.0, and 2.5–2.6 ng g^{-1} wet weight. Overall concentrations of PFOA (3.7 ng g^{-1}, wet weight) were slightly higher than the concentrations of PFOS (3.2 ng g^{-1}, wet weight) in these specimens. Mussels collected near the Rio-Niteroi Bridge contained elevated concentrations of PFNA, PFDA, and PFUnDA at 14.1 ± 15, 5.65 ± 0.49, and 109 ± 17.4 ng g^{-1}, wet weight, respectively, suggesting local sources of contamination. In South China and Japanese coast, concentrations of PFOS and PFOSA in mussels have been reported to range from 0.11 to 0.59 and from 0.04 to 2.9 ng g^{-1} wet weight, respectively (So et al., 2006), in Lake Shihwa from Korea, PFOS was detected at a mean concentration of 0.5 ± 0.2 ng g^{-1} wet weight (Yoo et al., 2009), in zebra mussels from the Great Lakes, PFOS concentration ranged from 2.4 to 3.1 ng g^{-1}, wet weight (Kannan et al., 2005a,b), PFOS concentrations in mussels from Danish coastal waters ranged from 0.11 to 0.58 ng g^{-1}, wet weight (Bossi et al., 2008); The above listed values are lower than the concentrations found in our study. However, high concentrations of PFOS have been reported (36.8–126 ng g^{-1}, wet weight) in mussels from north-central Portugal (Cunha et al., 2005).

3.3. Specific bioaccumulation and tissue distribution of PFCs: liver to muscle concentration ratios in fish

Biomagnification factors (BMFs) were estimated based on PFC concentrations measured in livers of predator and prey species. Bioconcentration factors (BCFs) were calculated based on PFC concentrations measured in water and livers of fish collected from the same area. The top predator, tucuxi dolphin, feeds mainly on scabbardfish and croaker. The estimated BMF of PFOS in tucuxi dolphin ranged from 7.7 to 63, while that for PFOA ranged from 1.3 to 2.6 (compared with hepatic concentrations in croaker and scabbardfish from the Paraíba do Sul River). PFOSA, like PFOS, showed high BMF values in dolphin livers, ranging from 5.6 to 35. The BMF for

Table 2
Concentrations (ng g^{-1} wet weight; mean ± standard deviation and range) of perfluorochemicals in liver, kidney, and muscle samples of fish and tucuxi dolphin from the Paraiba do Sul River (PS) and Guanabara Bay (GB), Brazil.

Tissue/PFC	Scabbardfish PS (n = 10)	Croaker PS (n = 10)	Dolphin PS (n = 10)	Scabbardfish GB (n = 12)	Croaker GB (n = 7)	Mullet GB (n = 15)
Liver						
PFHxS	<0.45	<0.45	0.69 ± 0.13 (0.55–0.91)	0.94 ± 0.68 (<0.45–2.25)	<0.45	<0.45
PFOS	5.54 ± 2.38 (3.36–9.90)	1.20 ± 0.53 (<0.62–2.35)	90.5 ± 42.4 (25.9–149)	9.83 ± 7.18 (3.36–28.9)	3.07 ± 1.14 (1.75–5.13)	4.30 ± 2.02 (2.17–9.44)
PFDS	1.31 ± 0.83 (<0.54–2.72)	2.05 ± 1.90 (<0.54–6.10)	2.87 ± 2.50 (<0.54–7.65)	<0.54	2.28 ± 2.03 (<0.54–5.65)	1.21 ± 0.70 (<0.54–2.18)
PFOSA	2.10 ± 1.08 (0.60–4.15)	0.79 ± 0.62 (<0.45–1.71)	25.9 ± 20.7 (3.38–60.5)	3.72 ± 1.63 (1.47–6.19)	0.83 ± 0.39 (0.51–1.67)	<0.45
PFHpA	<0.66	<0.66	<0.66	<0.66	<0.66	0.88 ± 0.19 (<0.66–1.16)
PFOA	0.58 ± 0.10 (<0.46–0.74)	0.47 ± 0.19 (<0.46–0.71)	1.12 ± 0.29 (0.70–1.86)	0.83 ± 0.13 (0.62–1.07)	0.52 ± 0.14 (<0.46–0.60)	0.87 ± 0.24 (0.6–1.42)
PFNA	<0.49	<0.49	1.02 ± 0.44 (<0.49–1.70)	<0.49	<0.49	<0.49
PFUnDA	<3.12	<3.12	<3.12	<3.12	<3.12	<3.12
PFDA	<0.58	<0.58	1.23 ± 0.74 (<0.58–2.55)	0.88 ± 0.22 (<0.58–1.15)	<0.58	1.03 ± 0.48 (<0.58–2.17)
PFDoDA	<2.51	<2.51	<2.51	<2.51	<2.51	<2.51
Muscle	Scabbardfish PS (n = 5)	Croaker PS (n = 4)	Dolphins (n = 2)	Scabbardfish GB (n = 4)	Croaker GB (n = 4)	Mullet GB (n = 8)
PFHxS	<0.55	<0.55	(<0.55–1.45)	<0.55	<0.55	<0.55
PFOS	<0.53	<0.53	95.8 ± 119	<0.53	<0.53	3.49 ± 1.31 (1.95–5.44)
PFDS	<0.49	<0.51	(<0.47–1.50)	<0.48	<0.50	<0.47
PFOSA	<0.63	<0.63	7.58 ± 4.77	<0.63	<0.63	<0.63
PFHpA	2.34 ± 0.93 (<1.54–3.0)	<1.54	<1.54	<1.54	<1.54	<1.54
PFOA	1.63 ± 1.10 (0.86–3.56)	<0.82	3.99 ± 1.04	1.04 ± 0.32 (<0.82–1.27)	<0.82	3.39 ± 0.95 (1.98–4.65)
PFNA	<1.41	<1.41	(<1.46–1.60)	<1.41	<1.41	<1.41
PFUnDA	<3.0	<3.0	(<3.0–3.70)	<3.0	<3.0	<3.0
PFDA	<1.19	<1.19	(<1.19–6.18)	<1.19	<1.19	<1.19
PFDoDA	<4.8	<4.8	<4.8	<4.8	<4.8	<4.8
Kidney	Scabbardfish PS	Croaker PS	Dolphins (n = 2)	Scabbardfish GB	Croaker GB	Mullet GB (n = 17)
PFHxS	NA	NA	2.27 ± 0.92	NA	NA	<0.83
PFOS	NA	NA	31.1 ± 13.1	NA	NA	3.86 ± 1.22 (1.64–5.46)
PFDS	NA	NA	3.14 ± 1.57	NA	NA	<1.48
PFOSA	NA	NA	16.0 ± 5.83	NA	NA	<0.81
PFHpA	NA	NA	<0.90	NA	NA	1.32 ± 0.38 (<0.9–2.03)
PFOA	NA	NA	1.68 ± 0.69	NA	NA	1.22 ± 0.28 (<0.6–1.76)
PFNA	NA	NA	<1.76	NA	NA	<1.76
PFUnDA	NA	NA	11.4 ± 1.53	NA	NA	13.4 ± 5.83 (<4.47–21.8)
PFDA	NA	NA	<1.26	NA	NA	<1.26
PFDoDA	NA	NA	<6.76	NA	NA	<6.76

NA = not analyzed.

Table 3
Concentrations (ng g^{-1} wet weight; mean ± standard deviation and range) of perfluorochemicals in brown mussels from Guanabara Bay, Brazil.

PFC	BV (n = 3)	VC1 (n = 4)	VC2 (n = 3)	JJ (n = 4)	MG (n = 3)
PFHxS	<0.80	<0.80	<0.80	<0.80	<0.80
PFOS	3.46 ± 0.70 (<0.95–3.95)	4.04 ± 0.93 (<0.95–4.70)	<0.95	4.46 ± 0.27 (<0.95–4.65)	<0.95
PFDS	<0.91	<0.91	<0.91	<0.91	<0.91
PFOSA	<0.73	<0.73	<0.73	<0.73	<0.73
PFHpA	2.52 ± 1.60 (<1.17–3.65)	2.64 ± 0.37 (<1.17–2.90)	<1.17	2.58 ± 1.95 (<1.17–3.97)	<1.17
PFOA	3.93 ± 1.76 (2.04–5.53)	6.02 ± 6.60 (0.84–14.9)	<0.84	2.76 ± 2.08 (<0.84–5.55)	2.13 ± 1.66 (<0.84–4.04)
PFNA	<1.06	<1.06	14.1 ± 14.9 (<1.06–24.6)	<1.06	<1.06
PFUnDA	<5.09	109.3 ± 17.4 (<5.09–121.6)	<5.09	<5.09	<5.09
PFDA	<1.17	5.65 ± 0.49 (<1.17–6.0)	<1.17	<1.17	<1.17
PFDoDA	<8.73	<8.73	<8.73	<8.73	<8.73

BV, VC1, VC2, JJ, and MG are sampling points in the Guanabara Bay (see Fig.1).

PFOS from fish liver to tucuxi dolphin liver were similar to that reported for Ganges river dolphins (12.1–33.7) from India (Yeung et al., 2009).

The estimated BCFs for PFOS in scabbardfish and croaker from the Paraíba do Sul River were 390–537 and 12–18, respectively, while the BCFs for PFOA in the two species were 2.2–11 and 18–96, respectively. In Guanabara Bay, the BCFs for PFOS in scabbardfish, croaker, and mullet were 46–172, 20–26, and 100–190, respectively. The BCFs for PFOA in scabbardfish, croaker, and mullet from Guanabara Bay were 1.8–4.4, 0.9–2.8, and 8.1–14, respectively. These results indicate that species-related differences exist in the BCF for PFOS and that the BCFs for PFOS in scabbardfish and mullet are 10-fold higher than the BCF in croaker. The BCF for PFOS in mussels from Guanabara Bay ranged from 138 to 297, while for PFOA, the BCF ranged from 63.5 to 266; this comparison indicates a higher BCF for PFOA in mussels than in fish. The BCF for PFOS in fish is 10–300-fold lower than the values that have been reported for fish in the Ganges River (5550) (Yeung et al., 2009) and for trout from the Lake Ontario (34 000) (Houde et al., 2008). Our BCF values for PFOA are similar to the values that have been reported for rainbow trout exposed to PFOA under laboratory conditions (Martin et al., 2003). A previous study has reported that the concentrations of PFOS in benthic invertebrates (such as mussels) were 1000-fold greater than the concentrations in surrounding water (Kannan et al., 2005a,b). In our study, PFOA was found to bioconcentrate in mussels to an extent of the same order of magnitude as the bioconcentration of PFOS.

The ratios of PFCs in liver, kidney, and muscle of fish and dolphins were determined. The ratio of concentrations of PFOS in liver and muscle was calculated for mullet (1.2) and for tucuxi dolphin (0.94) from Guanabara Bay. The liver/muscle concentration ratios for PFOA were 0.26 and 0.80 in mullet and scabbardfish (from Guanabara Bay), and 0.36 and 0.28 in scabbardfish and tucuxi dolphin (from the Paraíba do Sul River). The calculated ratios suggest that PFOA concentrations in muscle are higher than or similar to the concentrations in liver from the same species. This pattern is consistent with the pattern reported recently for edible fish species from the Mediterranean Sea (Nania et al., 2009). The liver/kidney concentration ratio for PFOS was 1:1 for mullet from Guanabara Bay and 3:1 for dolphins, while the ratio for PFOA was 0.71 in mullet, and 0.67 in dolphin. The concentration ratio for PFOS in kidney and muscle was 1 in mullet and 0.32 in tucuxi dolphin. For PFOA, the kidney to liver concentration ratio was 0.36 and 0.42 in mullet and dolphin, respectively. Overall, the distribution of PFCs in dolphin tissues followed the order liver > muscle > kidney. In our fish samples, while PFOS concentrations followed the order liver > muscle > kidney, PFOA concentrations decreased in the order muscle > kidney > liver.

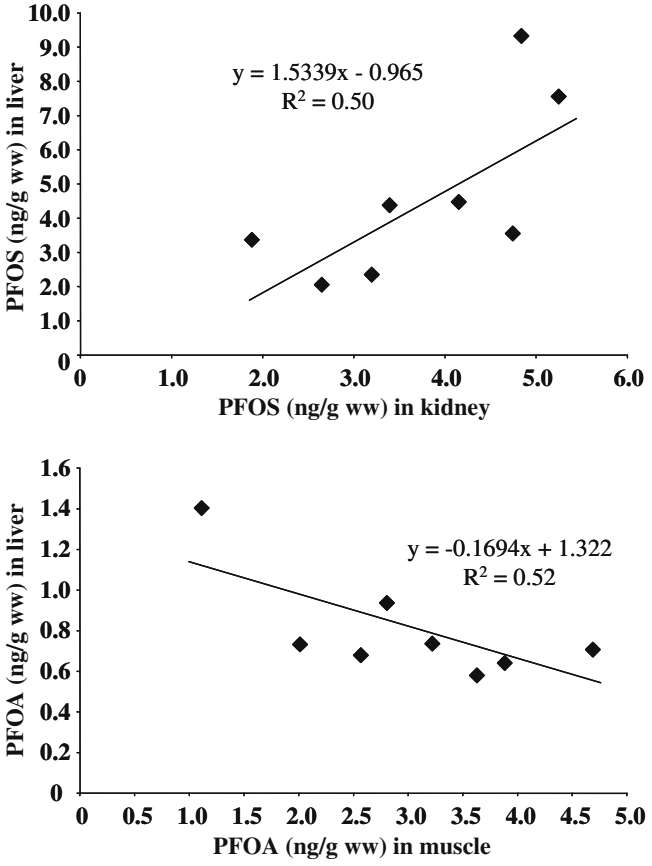

Fig. 2. Pair-wise correlations of PFOS and PFOA concentrations, for liver, kidney, and muscle tissues of mullet from Guanabara Bay, Brazil.

Most of the PFC concentrations measured in our fish and water samples did not follow a normal distribution. The non-parametric statistical analyses of concentrations indicated no significant correlations between PFC concentrations and total length or weight, in fish, dolphins, and mussels. A significant positive correlation was found for PFOS concentration between liver and kidney of mullet (Spearman's correlation coefficient = 0.833, $p = 0.01$, $n = 8$). For PFOA, a significant negative correlation was found, between liver and muscle (Pearson correlation coefficient = −0.717, $p < 0.05$, $n = 8$) of mullet from Guanabara Bay (Fig. 2). Similarly, concentrations of PFOS in mullet liver were negatively correlated with concentrations in muscle.

In summary, PFCs were detected in drinking and surface waters, in mussels and in liver, kidney, and muscle tissues of fish, and tucuxi dolphin from the southeastern coast of Brazil. The concentrations of PFCs in surface waters were approximately 10-fold lower than the concentrations reported for Japan and the USA. Concentrations of PFCs in fish and dolphins were an order of magnitude lower than the concentrations reported in previous studies of fish and dolphins from industrialized countries. The tissue distributions of PFOS and PFOA in fish showed some characteristic differences. Muscle tissue of fish contained concentrations of PFOA that were about the same or higher than the concentrations in livers, while PFOS concentrations were higher in livers than in muscle tissues. BCFs for PFOA in mussels were higher than the BCFs in fish species.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2009.07.079.

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