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Determination of inorganic trace elements in edible marine fish from Rio de Janeiro State, Brazil

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A B S T R A C T

Fish and seafood may represent risk for human health since they can accumulate contaminants from aquatic environment and magnify them up the food chain. The purpose of this study was to analyze and evaluate the levels of aluminum, zinc, iron, manganese, cobalt, copper, arsenics, selenium, cadmium, barium, lead and bismuth in 11 fish species (*Salmo salar*, *Sardinella brasiliensis*, *Pomatomus saltatrix*, *Micropogonias furnieri*, *Cynoscion leiarchus*, *Caranx crysos*, *Priacanthus arenatus*, *Mugil cephalus*, *Genypterus brasiliensis*, *Lopholatilus villarii* and *Pseudopercis numida*) captured at Rio de Janeiro State Coast, Brazil. Concentration ranges (mg kg^{-1} of wet weight) of the selected elements were compared with those reported in other studies. In some cases, comparison of certain elements in the same fish species was difficult due to the lack of data. Aluminum concentration was significantly high in all samples and only *M. cephalus*, *C. leiarchus* e *C. crysos* presented arsenic concentrations below 1 mg kg^{-1}, limit recommended by Brazilian legislation.

1. Introduction

In the last years, world consumption of fish and its products has increased mainly due to their health benefits such as preventing cardiovascular and other diseases (Cahu, Salen, & De Lorgeril, 2004). Fish and seafood are considered important sources of high-quality protein, minerals and essential polyunsaturated fatty acids (Guérin et al., 2011; Kris-Etherton, Harris, & Appel, 2003). In Brazil, fish consumption increased 39.8% between 2003 and2009, but the consumption level of 9.0 kg/habitant/year reached at the end of the period was still lower than that of 12 kg/habitant/year recommended by the World Health Organization (MPA, 2011).

Despite their recognized benefits, fish and seafood may represent a risk for human health since they can accumulate contaminants from aquatic environment and magnify them up the food chain (Türkmen, Türkmen, Tepe, Töre, & Ates, 2009; Tuzen, 2003; Matta, Milad, Manger, & Tosteson, 1999). Fish can contribute significantly to dietary human exposure to environmental pollutants (Guérin et al., 2003), and, in many studies, fish species have been employed as bioindicators of environmental contamination (Kasper, Botaro, Palermo, & Malm, 2007). However, factors such as time, catching place, habitat, gender and age may modify chemical constituents, and pollutant burden can diverge among different species and even among individuals of the same species (Maia, Oliveira, & Santiago, 1999). Moreover, fish metabolism may be harmed by some toxic trace elements that suppress essential trace elements such as copper, zinc, and selenium (Morgano, Rabonato, Milani, Miyagusku, & Balian, 2011).

The purpose of this study was to analyze and evaluate the levels of essential and toxic inorganic trace elements in edible fish species captured along the Rio de Janeiro State coast and ordinarily consumed by the population of Rio de Janeiro and Niterói.

2. Material and methods

2.1. Sample collection

Samples of 11 fish species were obtained from different sellers at St. Peter's Market, the largest supplier fresh fish of Rio de Janeiro, located in Niteroi, Brazil. For each species, five samples were collected on different dates between April and July 2009.

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The selected species were: *Salmo salar*, *Sardinella brasiliensis*, *Pomatomus saltatrix*, *Micropogonias furnieri*, *Cynoscion leiarchus*, *Caranx crysos*, *Priacanthus arenatus*, *Mugil cephalus*, *Genypterus brasiliensis*, *Lopholatilus villarii* and *Pseudopercis numida*. All fishes were caught along the coast of Rio de Janeiro State, except salmon that is imported from Chile. Although this species is not originally from Brazil, its consumption is high due to the nutritional qualities and the popularity of Japanese restaurants in several Brazilian cities (De Moura Filho et al., 2007; Morgano et al., 2011).

The fishes were selected by size and weight, including only adult animals. Minimum weights were 2.0 kg for *P. numida*, *M. cephalus*, *L. villarii* and *M. furnieri*, 1.5 kg for *P. arenatus*, *G. brasiliensis* and *P. saltatrix*, 0.5 kg for *C. leiarchus* and *C. crysos*, and 0.07 kg for *S. brasiliensis*.

2.2. Sample preparation

Immediately after collection, fish samples were transported to the laboratory in ice-cooled containers. Fishes were manually filleted and then the fillets homogenized. In case of smaller fishes (e.g. sardine), the fillets of various fishes were combined and then homogenized. The samples were freeze-dried and the water content was determined gravimetrically. All 55 freeze-dried samples were kept at −20 °C in airtight glass jars until analysis.

Approximately 0.5 g of each sample was analyzed for Al, Fe, Mn, Zn, Co, Cu, As, Se, Cd, Ba, Pb and Bi. The samples were digested by dry ashing in porcelain containers by adding 10 ml of concentrated HNO_3 and 5 ml $Mg(NO_3)_2$ (9% solution, w/v). The mixture was first maintained over a hot plate until dryness and then in muffle furnace at 450 °C for 12 h. The residue was dissolved in 0.5 ml of HNO_3 (10% solution, v/v) and transferred to a 14 ml volumetric polypropylene tube and completed with deionized water (Santos & Jacob, 2009).

2.3. Reagents

All glassware used was previously washed with Extran detergent (Merck, Darmstadt, Germany), decontaminated by immersion in a 10% (v/v) HNO3 solution for 12 h and rinsed with purified water. Water was deionized in a Milli-Q system (Millipore, Bedford, MA, USA) to a resistivity of 18.2 MΩ cm^{-1}. Nitric acid 65% and magnesium nitrate, both analytical grade, were obtained from F. Maia Industry and Trade Ltd. (São Paulo, Brazil) and Merck (Darmstadt, Germany) respectively. Multielement standard calibration solution of As, Co, Bi and Se (1000 mg L^{-1}) was purchased from SPEX CertiPrep (Greater London, UK), of Fe, Mn, Al, Zn, Cu, Ba and Pb (10,000 mg L^{-1}) from Ultra Scientific (Rhode Island, USA), and of Cd (1000 mg L^{-1}) from SpecSol (São Paulo, Brazil).

2.4. Inorganic contaminants determination

Al, Zn, Fe and Mn determination was performed on an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) model iCAP 6300, with dual configuration (axial and radial) and operational software iTEVA (Thermo Fisher Scientific, Cambridge, England).

Co, Cu, As, Se, Cd, Ba, Pb and Bi determination was achieved with an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) model X-Series II with operational software PlasmaLab (Thermo Fisher Scientific, Bremen, Germany). Details of the instrumental operating conditions are depicted in Table 1.

All samples were analyzed in batches, with method blanks and known standards. The accuracy of the analytical procedure was checked by analysis of certified reference material SRM 2976 – *Mussel Tissue* from National Institute of Standards (NIST). The results are presented in Table 2. Sensitivity, linearity, selectivity, accuracy, precision, limit of detection (LOD) and limit of quantification (LOQ) were determined by repeated analysis of reference material SRM 2976. The figures of merit for the elements analyzed are presented in Tables 3a and b.

Table 1
Experimental conditions used on ICP-MS and ICP-OES equipment to determine inorganic contaminants in fish samples.

	Experimental conditions
ICP-MS	
RF power	1400 W
Nebulizing flow rate	0.95 L min^{-1}
Auxiliary gas flow rate	0.70 L min^{-1}
Cold gas flow rate	13.0 L min^{-1}
Dwell time	10 ms
Extraction	−125
Resolution	300
Sample uptake rate	0.90 mL min^{-1}
Type of Nebulizer chamber	Conical
Nebulizer	Meinhard
ICP-OES	
RF power	1350 W
Auxiliary argon flow rate	1.5 L min^{-1}
Main argon flow rate	15 L min^{-1}
Integration and reading time	5 and 1sec
Nebulize	MiraMist
Type of Nebulizer chamber	Cyclonic

3. Results and discussion

Concentrations of essential trace elements and toxic trace elements are expressed in mg kg^{-1} wet weight basis (ww) and are given in Table 4. The mean value and standard deviation for water content for the species analyzed was 73.4 ± 4.6%.

3.1. Essential trace elements

3.1.1. Selenium

Selenium is a trace element that is essential for animal and human nutrition. It has been recognized as cellular antioxidant, and a protective agent against toxic trace elements, cancer and cardiovascular diseases. Selenium deficiency can cause several pathological conditions. However, depending on its concentration, this element can also be toxic to human, certain plants and animals (Al-Saleh, 2000). The Recommended Dietary Allowance (RDA) for men and women adults is 55 μg (0.7 μmol)/day (Institute of Medicine, 2001). In Brazil, there are no maximum levels established for Se in fish.

The lowest and the highest Se levels in fish species were 0.002 mg kg^{-1} in *P. arenatus* and 0.3 mg kg^{-1} in *S. salar*, respectively. In other studies, Se concentration range was 0.19–0.85 mg kg^{-1} (Tuzen, 2009) and 0.73–2.34 mg kg^{-1} (Lavilla, Vilas, & Bendicho, 2008) for different fish species. The mean concentration for

Table 2
Certified values of reference material NIST 2976 - Mussel Tissue and values experimentally obtained for trace elements. Data are mean ± SD ($n = 5$).

Elements	Certified values (mg kg^{-1})	Results obtained (mg kg^{-1})	Recovery (%)
As	13.3 ± 1.8	7.9 ± 1.4	70
Pb	1.19 ± 0.18	1.4 ± 0.1	119.8
Cd	0.82 ± 0.16	0.78 ± 0.03	94.6
Zn	137 ± 13	125.7 ± 11.0	91.7
Fe	171.0 ± 4.9	165.3 ± 31.9	103.5

Table 3a
Wavelength (λ), correlation coefficient (r), straight line equation, LOD and LOQ for trace elements analyzed by ICP-OES.

Element	λ (nm)	r	Straight line equation	LOD	LOQ
Al	167.079	0.9997	$y = 60.24 \times -1.68$	0.1 mg L^{-1}	10 mg L^{-1}
Fe	259.940	0.9999	$y = 397.5 \times -0.53$	0.05 mg L^{-1}	0.5 mg L^{-1}
Mn	257.610	0.9999	$y = 2581.93 \times +2.45$	0.025 mg L^{-1}	0.25 mg L^{-1}
Zn	213.856	0.9998	$y = 32536.75 \times +21.33$	0.05 mg L^{-1}	0.5 mg L^{-1}

M. cephalus was 0.01 mg kg^{-1}, for *P. saltatrix* 0.07 mg kg^{-1}, for *S. salar* 0.06 mg kg^{-1}, for *M. furnieri* 0.07 mg kg^{-1}, for *C. leiarchus* 0.02 mg kg^{-1} and for *S. brasiliensis* 0.09 mg kg^{-1}. The literature reports higher values for the same fish species such as 0.63 mg kg^{-1} for *M. cephalus* (Tuzen, 2009), 0.690 mg kg^{-1} for *P. saltatrix*, 0.123 mg kg^{-1} for *S. salar*, and 0.567 mg kg^{-1} for *S. brasiliensis* (Guérin et al., 2011). Tetuna Filho et al. (2010) also found higher values as 0.62 mg kg^{-1} for *M. furnieri*, 0.30 mg·kg−1 for *C. leiarchus*, and 0.64 mg kg^{-1} for *S. brasiliensis*.

3.1.2. Iron

Iron deficiency is frequently associated with anemia and, thus, with reduced working capacity and impaired intellectual development. The RDA for children (0.5–1 year old) and adults (male and female) is 11 and 18 mg/day, respectively (Schümann, Ettle, Szegner, Elsenhans, & Solomons, 2007).

The lowest and the highest Fe levels were 0.4 mg kg^{-1} and 26.1 mg kg^{-1} in *C. leiarchus*. Guérin et al. (2011) reported mean values for Fe of 11.7 mg kg^{-1} for *S. brasiliensis*, 19.0 mg kg^{-1} for *P. saltatrix*, and 1.87 mg kg^{-1} for *S. salar*. The levels found in this study are lower for *S. brasiliensis* (7.0 mg kg^{-1}) and *P. saltatrix* (3.5 mg kg^{-1}), and higher for *S. salar* (4.7 mg kg^{-1}). The mean Fe concentration in *M. cephalus* was 4.0 mg kg^{-1} that is lower than the average (125 mg kg^{-1}) described by Tuzen (2009). Other authors reported Fe level ranges of 36.2–110 mg kg^{-1} (Tuzen, 2009) and 6.5–70.1 mg kg^{-1} (Mendil, Ünal, Tüzen, & Soylak, 2010) in fishes from Turkey, of 27.2–218.0 mg kg^{-1} in fishes from Cambodian (Roos et al., 2007), and 8.8–19.0 mg kg^{-1} in fishes from Italy (Minganti, Drava, Pellegrini, & Siccardi, 2010).

3.1.3. Manganese

The essential trace metal Manganese is found in all tissues and is involved in the function of numerous organic systems. It is necessary for normal immune function, for regulation of blood sugar and cellular energy, reproduction, digestion, bone growth and even as cellular antioxidant (Aschner & Aschner, 2005). Although high concentrations of Mn may have toxic effects for human beings, no formal RDA has been established. The United States National Academy of Sciences (NAS, 2001) has established an adequate intake (AI) for Mn of 2.3 and 1.8 mg/day for adult men and women, respectively.

The lowest and the highest Mn levels found were 0.07 mg kg^{-1} in *M. cephalus* and 7.3 mg kg^{-1} in *S. brasiliensis*. Manganese concentrations reported by Tuzen (2009) and Mendil et al. (2010) varied respectively from 2.76 to 9.10 mg kg^{-1} and 1.0–9.4 mg kg^{-1} in fish samples, being higher than the levels found in this study. The mean level for *M. cephalus* was 0.1 mg kg^{-1}, that is lower than the value reported by Tuzen (2009) for the same species (8.18 mg kg^{-1}).

The mean Mn concentrations for *S. brasiliensis* (1.7 mg kg^{-1}) and *S. salar* (0.9 mg kg^{-1}) were higher than those reported by Guérin et al. (2011) of 0.648 mg kg^{-1} and 0.110 mg kg^{-1}, respectively. On the other hand, Guérin et al. (2011) found a higher mean Mn value for *P. saltatrix* (1.72 mg kg^{-1}) in comparison with this study (0.3 mg kg^{-1}).

3.1.4. Zinc

Zinc is an important trace element in human nutrition and fulfills many biochemical functions in human metabolism. A Zn deficiency in human organism leads to several disorders, but an excessive Zn intake can cause acute adverse effects (Scherz & Kirchhoff, 2006). The RDA for Zn is 11 mg/day and 8 mg/day for man and woman up to 19 years old, respectively, and the Tolerable Upper Intake Level (UL) is 40 mg/day for this age group (Institute of Medicine, 2001).

The lowest and the highest Zn levels found were 0.06 mg kg^{-1} for *C. leiarchus* and 39.3 mg kg^{-1} for *S. salar*. The mean value for *M. cephalus* of 3.9 mg kg^{-1} was lower than the 86.2 mg kg^{-1} informed by Tuzen (2009). The mean Zn concentrations obtained for *S. brasiliensis* (9.3 mg kg^{-1}) and *P. saltatrix* (5.6 mg kg^{-1}) were lower than those of 15.4 mg kg^{-1} and 16.0 mg kg^{-1}, respectively, reported by Guérin et al. (2011). The mean Zn concentration for *S. salar* (6.8 mg kg^{-1}) was higher than the 3.2 mg kg^{-1} found by the same authors. Other studies reported Zn contents of 4.83 mg kg^{-1} in fish samples from Australia (Jones, Mercurio, & Oliver, 2000) and 38.3 mg kg^{-1} in fish from Brazil (Costa & Hartz, 2009). Mendil et al. (2010) published Zn values in fish samples from Turkey in the range between 11.6 and 63.5 mg kg^{-1}.

3.1.5. Cobalt

Trace amounts of Cobalt are essential for humans and other mammals since it is an integral component of the vitamin B_{12} complex. Its deficiency in humans is similar to vitamin B_{12} deficiency, with symptoms such as anemia and disturbance of the nervous system (Gál, Hursthouse, Tatner, Stewart, & Welton, 2008; Nagpal, 2004). In higher concentrations, however, Co is toxic to humans, animals and plants (ATSDR, 2004).

The lowest and the highest Co levels found were 0.003 mg kg^{-1} for *M. cephalus* and 0.09 mg kg^{-1} for *C. crysos*. In comparison, Co levels ranged from $<$0.01 to 0.45 mg kg^{-1} in fish from Aegean Sea (Türkmen et al., 2009) and from 0.01 to 0.03 in fish from China (Onsanit, Ke, Wang, Wang, & Wang, 2010). Mean Co concentration

Table 3b
Isotopes, correlation coefficient (r), straight line equation, LOD and LOQ for trace elements analyzed by ICP-MS.

Element	Isotopes	r	Straight line equation	LOD	LOQ
Co	^{59}Co	0.9996	$Y = 126359.03 \times -26902.16$	0.05 μg L^{-1}	0.5 μg L^{-1}
Cu	^{65}Cu	0.9998	$Y = 12469.44 \times +4947.68$	1.0 μg L^{-1}	10.0 μg L^{-1}
As	^{75}As	0.9999	$y = 6370.21 \times +245.47$	1.0 μg L^{-1}	10.0 μg L^{-1}
Se	^{82}Se	0.9999	$y = 835.45 \times +14.31$	0.01 μg L^{-1}	1.0 μg L^{-1}
Cd	^{111}Cd	0.9999	$Y = 5401.23 \times +1656.98$	0.01 μg L^{-1}	1.0 μg L^{-1}
Ba	^{137}Ba	0.9999	$Y = 15329.46 \times +596.86$	0.05 μg L^{-1}	5.0 μg L^{-1}
Pb	^{208}Pb	0.9999	$Y = 90225.45 \times +14137.64$	0.05 μg L^{-1}	5.0 μg L^{-1}
Bi	^{209}Bi	0 0.9998	$Y = 74149.14 \times -11454$	0.05 μg L^{-1}	0.5 μg L^{-1}

y = absorbance and x = concentration of correspondent element

Table 4
Results obtained for essential trace elements and toxic trace elements in fish from Rio de Janeiro State (mg kg^{-1}, wet weight).

Species	Essential trace elements								Toxic trace elements					
	n		Se	Fe	Mn	Zn	Co	Cu	Bi	Al	Ba	As	Cd	Pb
C. crysos	Pool	Mean ± SD	0.05 ± 0.3	7.5 ± 2.6	1.1 ± 1.9	6.1 ± 1.6	0.02 ± 0.02	2.9 ± 1.3	0.006 ± 0.0006	64.7 ± 42.4	0.4 ± 0.07	0.6 ± 0.2	0.01 ± 0.02	0.3 ± 0.3
	(12)	Median	0.02	7.4	0.2	6.1	0.01	2.8	0.006	53.8	0.3	0.6	0.001	0.2
		Range	0.009–0.2	4.6–13.0	0.1–5.4	3.9–8.1	0.009–0.09	1.3–6.1	0.006–0.006	12.7–136.5	0.1–1.2	0.4–0.9	0.003–0.06	0.07–0.9
L. villarii	5	Mean ± SD	0.05 ± 0.06	1.9 ± 1.0	0.6 ± 0.6	3.6 ± 1.1	0.01 ± 0.008	2.6 ± 2.2	0.006 ± 0.001	77.3 ± 46.5	0.4 ± 0.3	6.1 ± 3.3	0.001 ± 0.007	0.2 ± 0.1
		Median	0.02	1.6	0.4	2.9	0.01	1.9	0.006	78.3	0.3	5.8	0.009	0.2
		Range	0.003–0.1	1.1–3.9	0.1–1.9	2.5–5.1	0.008–0.03	0.6–6.7	0.005–0.01	16.6–149.4	0.02–1.1	1.9–11.8	0.008–0.02	0.05–0.5
M. furnieri	5	Mean ± SD	0.07 ± 0.06	2.2 ± 0.8	0.3 ± 0.1	3.3 ± 0.5	0.01 ± 0.001	1.4 ± 0.6	0.01 ± 0.006	76.1 ± 46.8	0.2 ± 0.1	1.2 ± 0.5	0.007 ± 0.007	0.2 ± 0.1
		Median	0.05	1.9	0.2	3.3	0.01	1.3	0.01	70.8	0.2	1.2	0.006	0.1
		Range	0.02–0.1	1.4–3.8	0.1–0.4	2.5–4.2	0.009–0.01	0.7–2.6	0.007–0.03	10.1–163.3	0.1–0.5	0.5–1.9	0.002–0.02	0.09–0.3
P. arenatus	pool	Mean ± SD	0.05 ± 0.05	3.7 ± 4.4	1.4 ± 1.8	4.0 ± 4.7	0.02 ± 0.02	2.5 ± 1.7	0.005 ± 0.001	205.5 ± 228.3	0.5 ± 0.6	1.0 ± 0.3	0.06 ± 0.1	0.2 ± 0.1
	(6)	Median	0.03	2.3	0.4	2.4	0.01	2.0	0.005	86.6	0.4	1.0	0.01	0.2
		Range	0.002–0.2	1.0–15.9	0.2–4.4	2.0–17.3	0.008–0.06	0.6–5.1	0.004–0.006	15.0–638.1	0.1–2.1	0.7–1.6	0.002–0.3	0.06–0.4
P. saltatrix	pool	Mean ± SD	0.07 ± 0.05	3.5 ± 1.8	0.3 ± 0.3	5.6 ± 1.2	0.01 ± 0.002	2.3 ± 1.7	0.006 ± 0.001	103.2 ± 87.4	0.3 ± 0.3	0.4 ± 0.2	0.01 ± 0.02	0.2 ± 0.1
	(6)	Median	0.07	2.6	0.2	5.7	0.01	2.0	0.006	65.7	0.2	0.3	0.01	0.2
		Range	0.02–0.2	1.6–6.5	0.1–1.0	2.5–6.9	0.009–0.01	0.7–6.4	0.006–0.006	14.3–257.5	0.003–0.03	0.2–1.0	0.02–0.1	0.07–0.6
G. brasiliensis	Pool	Mean ± SD	0.05 ± 0.03	1.7 ± 0.7	0.6 ± 0.9	3.7 ± 0.6	0.01 ± 0.01	1.3 ± 0.9	0.005 ± 0.001	90.2 ± 53.0	0.2 ± 0.2	2.7 ± 1.8	0.008 ± 0.006	0.1 ± 0.08
	(6)	Median	0.05	1.8	0.1	3.6	0.008	1.1	0.005	92.2	0.2	1.6	0.01	0.1
		Range	0.02–0.1	0.7–2.7	0.1–2.4	2.9–4.8	0.006–0.04	0.4–23.5	0.004–0.006	28.3–209.1	0.1–0.9	1.1–5.5	0.006–0.02	0.05–0.3
S. salar	5	Mean ± SD	0.06 ± 0.1	4.7 ± 7.5	0.9 ± 1.5	6.8 ± 11.4	0.02 ± 0.02	2.4 ± 1.6	0.4 ± 0.3	394.2 ± 64.5	0.5 ± 0.4	0.5 ± 1.0	0.09 ± 0.2	0.04 ± 0.03
		Median	0.03	2.4	0.4	3.2	0.01	2.3	0.3	48.9	0.4	0.2	0.008	0.03
		Range	0.01–0.3	1.3–26.1	0.2–5.1	2.3–39.3	0.01–0.08	0.4–5.7	0.07–0.9	10.2–1934.3	0.05–1.4	0.1–3.4	0.004–0.2	0.01–0.09
M. cephalus	5	Mean ± SD	0.01 ± 0.02	4.0 ± 1.9	1.0 ± 1.8	3.9 ± 1.4	0.007 ± 0.01	1.2 ± 1.0	0.006 ± 0.002	70.4 ± 63.7	0.6 ± 0.9	0.4 ± 0.1	0.007 ± 0.005	0.2 ± 0.1
		Median	0.01	3.7	0.2	4.2	0.003	1.0	0.006	58.1	0.6	0.4	0.008	0.1
		Range	0.003–0.06	0.5–6.9	0.07–5.3	0.6–5.6	0.003–0.03	0.03–2.7	0.006–0.008	3.0–215.0	0.07–2.5	0.05–0.5	0.003–0.01	0.04–0.5
C. leiarchus	pool	Mean ± SD	0.02 ± 0.01	1.6 ± 0.7	0.3 ± 0.2	2.7 ± 0.9	0.009 ± 0.001	1.9 ± 1.5	0.005 ± 0.001	49.1 ± 38.3	0.3 ± 0.5	0.1 ± 0.04	0.01 ± 0.01	0.3 ± 0.5
	(15)	Median	0.01	1.5	0.2	2.9	0.009	1.6	0.005	43.7	0.2	0.1	0.01	0.1
		Range	0.008–0.05	0.4–26.1	0.9–0.1	0.06–3.3	0.007–0.01	0.5–5.1	0.005–0.007	9.4–135.5	0.03–1.6	0.002–0.15	0.002–0.02	0.05–1.7
S. brasiliensis	pool	Mean ± SD	0.1 ± 0.1	7.0 ± 2.4	1.7 ± 2.3	9.3 ± 1.4	0.02 ± 0.02	2.6 ± 1.2	0.007 ± 0.001	92.2 ± 69.3	0.7 ± 0.9	1.0 ± 0.2	0.02 ± 0.01	0.3 ± 0.3
	(74)	Median	0.05	6.5	0.5	9.4	0.02	2311	0.006	78.8	0.3	1.0	0.01	0.2
		Range	0.004–0.2	4.6–12.6	0.3–7.3	6.7–12.0	0.01–0.08	1.1–4.7	0.006–0.009	8.9–209.8	0.09–2.8	0.7–1.2	0.006–0.04	0.06–0.9
P. numida	5	Mean ± SD	0.04 ± 0.02	2.2 ± 1.5	0.3 ± 0.2	2.9 ± 0.5	0.01 ± 0.002	2.9 ± 3.8	0.006 ± 0.0005	215.5 ± 278.9	0.3 ± 0.3	2.9 ± 0.9	0.007 ± 0.008	0.1 ± 0.09
		Median	0.04	1.5	0.2	2.8	0.01	1.5	0.006	148.8	0.3	2.5	0.004	0.1
		Range	0.01–0.08	0.9–5.7	0.1–0.8	2.4–4.1	0.008–0.01	0.6–12.3	0.005–0.005	12.0–871.6	0.05–0.9	2.1–4.8	0.003–0.005	0.07–0.3

n = number of individuals analyzed and pooled samples followed by the number of individual components.

levels were <0.002 mg kg^{-1} in fish from Lebanon (Nasreddine et al., 2010) and 0.005 mg kg^{-1} in fish from a French market (Guérin et al., 2011). The mean values for *S. salar* (0.020 mg kg^{-1}) and *S. brasiliensis* (0.025 mg kg^{-1}) were higher than those of 0.004 mg kg^{-1} and 0.008 mg kg^{-1}, respectively, published by Guérin et al. (2011). However, the mean value in *P. saltatrix* was 0.01 mg kg^{-1}, slightly lower than 0.019 mg kg^{-1} reported by the same author (Guérin et al., 2011).

3.1.6. Copper

Copper is important in the process of biological transfer of electrons, and is vital for the synthesis of red blood cells and the maintenance of nervous system structure and function. Copper deficiency in adults can result in blood and nervous system disorders (Dabbaghmanesh, Salehi, Siadatan, & Omrani, 2011). The RDA is 900 μg/day and the UL is 10 μg/day for adults (Institute of Medicine, 2001).

The lowest and the highest Cu levels observed were 0.03 mg kg^{-1} for *M. cephalus* and 23.5 mg kg^{-1} for *G. brasiliensis.* In other fish species from Brazil, Cu values ranged from 0.56 to 1.64 mg kg^{-1} (Costa & Hartz, 2009) and, in fish from Aegean and Mediterranean seas, from 0.51 to 7.05 mg kg^{-1} (Türkmen et al., 2009). Other Cu concentration reported in the literature varied from 1.0 to 2.5 mg kg^{-1} in fishes from Turkey (Mendil et al., 2010) and from 0.06 to 0.22 mg kg^{-1} in fishes from China (Onsanit et al., 2010). The Cu mean concentrations found for *P. saltatrix* (2.3 mg kg^{-1}), *S. salar* (2.4 mg kg^{-1}) and *S. brasiliensis* (2.6 mg kg^{-1}), were higher than those of 2.01 mg kg^{-1}, 0.58 mg kg^{-1} and 1.15 mg kg^{-1} for the same species, respectively, reported by Guérin et al. (2011). Nasreddine et al. (2010) reported a mean value for Cu concentration of 0.255 mg kg^{-1} in fishes from Lebanon. In this study the mean value for Cu concentration in *M. cephalus* was 1.2 mg kg^{-1}, lower than 2.14 mg kg^{-1} reported for Tuzen (2009).

3.2. Toxic trace elements

3.2.1. Bismuth

Toxic effects of Bi are reported generally after exposure through therapeutic treatment affecting mainly liver and kidney (Fowler & Sexton, 2007). There is no maximum Bi level established for fish in the Brazilian legislation. However, in the literature, there is a lack of data on Bi in fish, only data on concentrations of the radioisotope ^{207}Bi in fish after nuclear tests is available.

The lowest and the highest Bi levels found were 0.004 mg kg^{-1} for *P. arenatus* and *G. brasiliensis*, and 0.9 mg kg^{-1} for *S. salar. S. salar* had the highest Bi mean concentration (0.3 mg kg^{-1}) followed in decreasing order by *M. furmieri* (0.01 mg kg^{-1}), *C. crysos, P. saltatrix, M. cephalus, S. brasiliensis, L. villarii, P. numida* (0.006 mg kg^{-1}), *P. arenatus, G. brasiliensis* and *C. leiarchus* (0.005 mg kg^{-1}).

3.2.2. Aluminum

Toxicity of Al in humans is mainly related to neurotoxicity and development of neurodegenerative diseases (Verstraeten, Aimo, & Oteiza, 2008). There is no maximum Al level established in Brazilian legislation.

The lowest and the highest Al levels observed were 3.0 mg kg^{-1} for *M. cephalus* and 1934.3 mg kg^{-1} for *S. salar.* Mean concentrations were 103.2 mg kg^{-1} in *P. saltatrix*, 394.2 mg kg^{-1} in *S. salar* and 92.2 mg kg^{-1} in *S. brasiliensis*. The same species captured in France showed much lower Al mean levels of 3.1 mg kg^{-1}, 0.53 mg kg^{-1} and 1.9 mg kg^{-1}, respectively (Guérin et al., 2011). There is only few data available about Al in fish, however, Yilmaz, Sangün, Yağlıoğlu, & Turan (2010) reported mean concentrations in the range between 2.23 and 4.93 mg kg^{-1} in fish from Turkey.

3.2.3. Barium

Exposure to soluble barium salts can cause various health disorders, such as hypertension, renal and cardiac malfunction (Oskarsson & Reeves, 2007). There is no maximum Ba level established for fish in the Brazilian legislation.

The lowest and highest Ba levels found were 0.003 mg kg^{-1} for *P. saltatrix* and 2.8 mg kg^{-1} for *S. brasiliensis. S. brasiliensis* (0.7 mg kg^{-1}) had the highest Ba mean concentration (0.7 mg kg^{-1}) followed by *M. cephalus, S. salar, P. arenatus, C. crysos, L. villarii,* , *P. numida, C. leiarchus, P. saltatrix, M. furmieri,* and *G. brasiliensis*, varying from 0.2 to 0.6 mg kg^{-1}. The average level for Ba in *P. saltatrix* (0.3 mg kg^{-1}) was also reported by Guérin et al. (2011), however, the Ba average levels found for *S. salar* (0.5 mg kg^{-1}) and *S. brasiliensis* (0.7 mg kg^{-1}) were higher than 0.02 mg kg^{-1} and 0.09 mg kg^{-1}, respectively, reported by the same author. Yilmaz et al. (2010) reported higher mean values for Ba concentrations in different fish species from Turkey (3.44–6.96 mg kg^{-1}).

3.2.4. Arsenic

Arsenic is an element present in nature that can be toxic to human, animals and plants; however, its toxicity varies with their different chemical forms (Devesa, Vélez, & Montoro, 2008). In Brazilian legislation, the maximum As level established for fish is 1.0 mg kg^{-1} (ANVISA, 1998).

The lowest and highest As levels observed were 0.002 mg kg^{-1} for *C. leiarchus* and 11.8 mg kg^{-1} for *L. villarii.* Tuzen (2009) reported As concentrations ranging from 0.11 mg kg^{-1} to 0.32 mg kg^{-1}, and Yilmaz et al. (2010) mean As concentrations ranging from 0.98 mg kg^{-1} to 1.74 mg kg^{-1}, both in fish from Turkey. Arsenic concentration ranges have been varied between 0.88 and 4.48 mg kg^{-1} in fishes from China (Onsanit et al., 2010), and between 0.156 and 0.834 mg kg^{-1} in fishes from Iran (Saei-Dehkordi, Fallah, & Nematollahi, 2010). For *S. salar*, As concentration ranged from 0.1 to 3.4 mg kg^{-1}, in contrast to the range of <0.004–1.53 mg kg^{-1} reported for the same species by Morgano et al. (2011). In another survey of different fish species from Brazil, As concentration ranged between <0.004 and 10.82 mg kg^{-1}, similar to the values of this study. For *S. brasiliensis,* As mean concentration (1.0 mg kg^{-1}) was similar to the mean value of 0.989 mg kg^{-1} reported by Vieira, Morais, Ramos, Delerue-Matos, and Oliveira (2011) for *Sardinella pilchardus.*

3.2.5. Cadmium

Cadmium is a toxic element that could be present in fish organism at high concentrations (Türkmen et al., 2009). The maximum Cd level for fish established by the Brazilian legislation is 1.0 mg kg^{-1} (ANVISA, 1998).

The lowest and the highest Cd levels found were 0.002 mg kg^{-1} for *C. leiarchus, P. arenatus* and *M. furnieri;* and 0.5 mg kg^{-1} for *S. salar*. In others species from Brazil, Cd concentration ranged from <0.003 to 0.047 mg kg^{-1} (Morgano et al., 2011). In three surveys of trace elements in fishes from Turkey, Cd concentration varied between <0.01 mg kg^{-1} and 0.75 mg kg^{-1} (Mendil et al., 2010; Türkmen et al., 2009; Tuzen, 2009). Cadmium levels in Chinese fishes ranged from 0.01 mg kg^{-1} to 0.04 mg kg^{-1} (Onsanit et al., 2010). Other Studies showed Cd mean level ranges in fish of 0.01–0.04 mg kg^{-1} (Yilmaz et al., 2010), 0.004–000.9 mg kg^{-1} (Nasreddine et al., 2010) and 0.024–0.111 mg kg^{-1} (Saei-Dehkordi & Fallah, 2011). Cd mean concentration for *M. cephalus* (0.007 mg kg^{-1}) was lower than 0.35 mg kg^{-1} reported by Tuzen (2009), and for *S. salar* (0.09 mg kg^{-1}) higher than 0.008 mg kg^{-1} published by Morgano et al. (2011). However, the values reported in the literature are generally lower than the values from this study.

3.2.6. Lead

Lead is one of environmental contaminants which can promote serious damage to human health. The main exposure route of non-occupationally exposed individuals is by food consumption (Liu, Wang, Song, & Wu, 2010). In the Brazilian legislation, maximum Pb level established for fish is 2.0 mg kg^{-1} (Saei-Dehkordi et al., 2010).

The lowest and the highest Pb levels found were 0.01 mg kg^{-1} for *S. salar* and 0.5 mg kg^{-1} for *C. leiarchus*. In comparison, Pb concentrations ranges were 0.28–0.87 mg kg^{-1} in fish from Black Sea (Tuzen, 2009), 0.21–1.28 mg kg^{-1} in fish from Aegean and Mediterranean Sea (Türkmen et al., 2009), and 0.10–0.56 mg kg^{-1} in fish from Turkey (Mendil et al., 2010). Lead mean concentration for *S. salar*, (0.038 mg kg^{-1}) was lower than 0.228 mg kg^{-1} reported by Morgano et al. (2011) and higher than 0.005 mg kg^{-1} reported by Guérin et al. (2011). Lead mean concentration for *P. saltatrix* (0.2 mg kg^{-1}) and for *S. brasiliensis*, (0.3 mg kg^{-1}) were higher than 0.047 mg kg^{-1} and 0.024 mg kg^{-1}, respectively, published by Guérin et al. (2011). Lead mean concentration for *M. cephalus* (0.2 mg kg^{-1}) was lower than 0.86 mg kg^{-1} informed by Tuzen (2009). In different fish species from Brazil, Pb mean concentrations ranged from 0.076 mg kg^{-1} to 0.195 mg kg^{-1} (Morgano et al., 2011). Other surveys reported Pb mean concentrations between 0.14 and 0.39 mg kg^{-1} in fish from Iskenderun Bay (Yilmaz et al, 2010), between 0.016 and 0.054 mg kg^{-1} in fish from Portugal (Vieira et al., 2011), and between 5.8 and 6.5 mg kg^{-1} in fish from Lebanon (Nasreddine et al., 2010).

4. Conclusions

This study was developed in order to provide information on metals concentrations in different fish species from Rio de Janeiro State, Brazil. Metal concentrations showed a great variability even within the same fish species that is in accordance with the findings of other studies. All fish samples presented cadmium and lead values below the Maximum Tolerable Limits established by the Brazilian legislation. Except of *M. cephalus*, *C. leiarchus* and *C. crysos*, all species showed arsenic concentrations higher than the maximum tolerable limit of 1 mg kg^{-1}, specified in the Brazilian regulations. Study of arsenic speciation is important once the toxicity level is dependent of its chemical form present in the sample. It is also important to assess some biological and environmental factors such as origin of the fish, sea environment, feeding habits of fish, age, among other factors can significantly influence on the concentration of this elements. More research of seafood quality is necessary to provide more data and help to ensure the quality of sea foods and safeguard of human health.

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