Toxicology Reports 1 (2014) 353–359

Contents lists available at ScienceDirect

Toxicology Reports

journal homepage: www.elsevier.com/locate/toxrep

Comparison of the nutritional and toxicological reference values of trace elements in edible marine fish species consumed by the population in Rio De Janeiro State, Brazil

Renata Jurema Medeiros [a,*], Lisia Maria Gobbo dos Santos [a], Jaylei Monteiro Gonçalves [a], Ana Maria Cheble Bahia Braga [b], Thomas Manfred Krauss [b], Silvana do Couto Jacob [a]

[a] *Instituto Nacional de Controle de Qualidade em Saúde (INCQS/FIOCRUZ), Av. Brasil, 4365, Manguinhos, Rio de Janeiro, RJ, CEP: 21.040-900, Brazil*
[b] *Centro de Estudos em Saúde do Trabalhador e Ecologia Humana (CESTEH/ENSP/FIOCRUZ), Av. Brasil, 4365, Manguinhos, Rio de Janeiro, RJ, CEP: 21.040-900, Brazil*

A R T I C L E I N F O

Article history:
Received 14 May 2014
Received in revised form 5 June 2014
Accepted 6 June 2014
Available online 28 June 2014

Keywords:
Inorganic elements
Health risk assessment
Fish
Seafood safety
Chemical contaminants
Essential elements

A B S T R A C T

The present study estimated the human daily and weekly intake of inorganic elements due to consumption of fish in Rio de Janeiro state and the associated potential health risks posed by some toxic elements. All samples analyzed had values of Cd and Pb below the Maximum Tolerable Limits of 3.0 mg kg^{-1} for Pb and 1.0 mg kg^{-1} for Cd; only *Mugil cephalus*, *Cynoscion leiarchus* and *Caranx crysos* had As concentrations below 1 mg kg^{-1}, maximum limit established by Brazilian legislation. The higher values of Cd and Pb correspond to 0.22% of PTWI and the higher value of As corresponds to 8.6% of PTWI. None of the studied species showed values higher than PTWI. The higher values of Cu EDI found in *Pomatomus numida* correspond to 33.3% of RDA; Fe in *Salmo salar* and *Genypterus brasiliensis* corresponds to 4.3% of EDI; Mn in *Sardinella brasiliensis* corresponds to 7.4% of EDI; Zn in *S. salar* corresponds to 13.2% of EDI and Se in *S. salar* corresponds to 20.6% of EDI. Some species can be a good source of inorganic elements. For risk assessment, it is important to assess specific eating habits of each region to avoid underestimating the data.

1. Introduction

Trace elements such as Zn, Fe, As, Pb, Cd, Co, Cu and Mn can be classified as essential and toxic [1]. Essential elements are micronutrients that need to be daily consumed in adequate amounts in order to sustain normal physiological functions [2], but when associated with adverse health effects by dietary exposure, they are considered toxic [3]. On that account, the assessment of inorganic trace elements plays an important role in the substance risk evaluation.

Levels of inorganic trace elements in fish can diverge among different species and even among individuals of the same species due to the influence of environmental and biological factors, such as origin of the fish, sea environment, feeding habits and age [4–6]. The accumulation of toxic elements in fish tissue can result in significant dietary human exposure to environmental pollutants and therefore fish needs to be monitored regularly [7,8].

However, edible fish represents a valuable source of long-chain polyunsaturated omega-3 fatty acids (e.g. eicosapentaenoic acid), high quality protein and important

* Corresponding author. Tel.: +55 21 3865 5258.
E-mail address: renata.medeiros@incqs.fiocruz.br (R.J. Medeiros).

http://dx.doi.org/10.1016/j.toxrep.2014.06.005
2214-7500/

organic and inorganic micronutrients (e.g. vitamin D, selenium) [9,10]. In order to balance the risk benefit, various health authorities recommend the ingestion of a certain amount of fish. The most common recommendation is one to two portions of a particularly oily fish per week, but more vulnerable groups, such as pregnant woman, should avoid fish from the top of the aquatic food chain, which could have higher levels of environmental pollutants [10–13].

According to the Food and Agriculture Organization [13] the world per capita food fish supply increased from an average of 18.1 kg (live weight equivalent) in 2009 to an amount estimated as 18.8 kg in 2011. Brazilian fish consumption also increased from 9.0 kg/per capita/year in 2009 [14] to 11.2 kg in 2011 [15]. Thus, we currently believe that the Brazilian population is already consuming fish near the minimum level recommended by the World Health Organization (WHO), 12 kg/per capita/year.

To ensure the safety of population health the Brazilian legislation determined the maximum tolerable levels, as 1.0 mg kg^{-1} for As and Cd and 3.0 mg kg^{-1} for Pb, for raw, frozen or chilled fish which are different from the values established by the European Community as maximum levels, 0.1 mg kg^{-1} for Cd and 0.4 mg kg^{-1} for Pb in muscle meat. However, there is a proposal for legislation of new food additives and contaminants in Brazil that aims to establish the same maximum tolerable values of the European Community legislation [16].

There is less data about the presence of inorganic trace elements in fish and sea food consumed in Brazil and consequently about their contribution to the dietary intake of the Brazilian population. The proposal of this study was to evaluate the levels of Fe, Mn, Zn, Co, Cu, As, Cd and Pb in 11 edible marine fish species commonly consumed by the population of Rio de Janeiro and Niterói cities and to compare them with appropriate nutritional and toxicological reference values and with data provided from other countries. The estimated daily intake (EDI) for these contaminants was calculated and the human risk assessment was evaluated by calculating the Hazard Quotient (HQ) which allows discussion about health risk due to fish consumption. Observed data can contribute for initiation of a broad discussion between nutritional benefits and the presence of contaminants in fish consumed in several Brazilian cities.

2. Materials and methods

2.1. Sampling

For this study, 11 edible marine fish species, widely consumed in the region (*Salmo salar*, *Sardinella brasiliensis*, *Pomatomus saltatrix*, *Micropogonias furnieri*, *Cynoscion leiarchus*, *Caranx crysos*, *Priacanthus arenatus*, *Mugil cephalus*, *Genypterus brasiliensis*, *Lopholatilus villarii* and *Pseudopercis numida*) were collected at Saint Peter Market from different suppliers. Saint Peter Market is a fresh fish market and distributor for the municipalities of Niterói, São Gonçalo and Rio de Janeiro, Brazil. Sampling extent was 5 samples for each species collected at different dates in the period from April to July 2009. Immediately after collection, the fish samples were transported to the laboratory in ice-cooled containers.

All fish were caught along the coast of Rio de Janeiro State, except *Salmo Salar* because it is imported from Chile and it was included in the study due to its high consumption in several Brazilian cities [17,18].

The fish were selected by size and weight. Every specimen was at least 2.0 kg in weight 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* which means it is an adult fish for this species.

Only *S. salar* was purchased as 2.0 kg fillets for each fish specimen studied. This is because these fish species are not naturally available in Brazil, being exported from Chile and arriving in Brazil without viscera and in some cases without the head hindering the correct measurement of weight and length.

2.2. Analytical determination of trace elements

For determination of Zn, Fe and Mn an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) of Thermo Scientific, model iCAP 6300 and operational software iTEVA was used and for determination of Co, Cu, As, Cd and Pb an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) of Thermo Fisher Scientific, model X-Series II with operational software PlasmaLab was used. 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 the National Institute of Standards (NIST). The results are shown in Table 1. The standard deviation was 18.2% for As, 9.8% for Pb, 0.4% for Cd, 8.75% for Zn and 19.2% for Fe. The parameters of sensitivity, linearity, selectivity, accuracy, precision, limit of detection and limit of quantification were established with tests from the reference material. The figures of merit for the elements analyzed are shown in Tables 2a and 2b. Details of sample preparation, analytical results and instrumental operating conditions are described by Medeiros et al. [19].

Table 1
Certified values of reference material NIST 2976 – *Mussel Tissue* and mean values experimentally obtained for trace elements ($n = 5$).

Elements	Certified values (mg kg^{-1})	Results obtained (mg kg^{-1})	Recovery (%)
As	13.3 ± 1.8	7.945 ± 1.45	70
Pb	1.19 ± 0.18	1.425 ± 0.14	119.8
Cd	0.82 ± 0.16	0.785 ± 0.03	94.6
Zn	137 ± 13	125.67 ± 11.0	91.7
Fe	171.0 ± 4.9	165.29 ± 31.9	103.5

Table 2a
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 ($mg\,L^{-1}$)	LOQ ($mg\,L^{-1}$)
Fe	259.940	0.9999	$y = 397.5x - 0.53$	0.05	0.5
Mn	257.610	0.9999	$y = 2581.93x + 2.45$	0.025	0.25
Zn	213.856	0.9998	$y = 32{,}536.75x + 21.33$	0.05	0.5

Table 2b
Isotopes, correlation coefficient (*r*), straight line equation, LOD and LOQ for trace elements analyzed by ICP-MS.

Element	Isotopes	*r*	Straight line equation	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)
Co	^{59}Co	0.9996	$y = 126{,}359.03x - 26{,}902.16$	0.05	0.5
Cu	^{65}Cu	0.9998	$y = 12{,}469.44x + 4947.68$	1.0	10.0
As	^{75}As	0.9999	$y = 6370.21x + 245.47$	1.0	10.0
Cd	^{111}Cd	0.9999	$y = 5401.23x + 1656.98$	0.01	1.0
Pb	^{208}Pb	0.9999	$y = 90{,}225.45x + 14{,}137.64$	0.05	5.0

The analytical results showed that all elements were detectable in samples. For Mn, 5 out of the 55 samples had levels below the limit of quantification (<LOQ), while for Zn and As one sample only had concentration below LOQ. The mean value and standard deviation for water content of the fish analyzed was (73.4 ± 4.6)%.

2.3. Human risk assessment analysis

The human risk assessment was based on calculation of Estimated Daily Intake (EDI) and Hazard Quotient (HQ) allowing the evaluation of health risk from fish consumption. The EDI ($mg\,kg^{-1}$ bw day^{-1}) was calculated using the following equation [20]:

$$EDI = C_{fish} \times \left[\frac{dc_{fish}}{bw}\right] \quad (1)$$

where C_{fish} = average or maximum value trace element concentration in fish muscle (mg/g wet weight); dc_{fish} = daily fish consumption ($g\,day^{-1}$) per capita [14]; bw = average body weight of Brazilian population (70 kg).

$$HQ = \frac{EDI}{RfD} \quad (2)$$

where EDI = estimated daily intake; RfD = reference dose.

There would be no obvious risk if the HQ was less than 1.

The human risk assessment for Rio de Janeiro state population was calculated using the provisional tolerance weekly intake (PTWI), average daily intake (ADI), and reference dose (RfD) previously established by the Joint FAO/WHO Expert Committee on Food Additives [20,21].

Concentrations of trace elements are expressed in $mg\,kg^{-1}$ wet weight (ww) basis and intakes in mg/day/70 kg person. For estimation of intake calculations we used 23.4 g fish/day and 70 kg body weight for adults. This is the last data on fish consumption by the Brazilian population survey conducted in 2009 [22].

For fish containing level of elements below the LOQ, a value equal to half the LOQ was assigned and used for calculation purposes [23]. For foods containing level of elements below the LOD, a value equal to half the LOD was assigned and used for calculation purposes [23].

3. Results and discussion

Medeiros et al. [19] data of highest muscle concentrations expressed in $mg\,kg^{-1}$ ww were used to conduct health risk assessments for human fish consumption of the studied species and they are described in Table 3.

3.1. Lead

The values for Pb ranged from 0.09 $mg\,kg^{-1}$ for *S. salar* to 1.66 $mg\,kg^{-1}$ for *C. leiarchus* which is close to the literature reported concentrations of 0.10–1.28 $mg\,kg^{-1}$ [18,24–29]. However, Nasreddine et al. [30] reported a high mean value of 6.13 (5.8–6.5) $mg\,kg^{-1}$ in fish from Lebanon. In others fish species from Brazil (*T. thynnus*, *P. pagrus* and *Centropomus* sp.) Pb mean concentrations ranged from 0.08 $mg\,kg^{-1}$ to 0.19 $mg\,kg^{-1}$ [18]. The Brazilian legislation [16,31] recommends a maximum Pb level of 3.0 $mg\,kg^{-1}$, and the European Community (EC) regulates 0.3 $mg\,kg^{-1}$ as the maximum limit [32]. Considering the limit value of Brazilian legislation, all samples except *S. salar* are below the maximum level accepted.

3.2. Cadmium

The values for Cd ranged from 0.013 $mg\,kg^{-1}$ for *S. salar* to 0.47 $mg\,kg^{-1}$ in *M. cephalus*. Tuzen [24] reported a lower value of 0.35 $mg\,kg^{-1}$ for *M. cephalus* and a higher value of 0.05 $mg\,kg^{-1}$ for *S. salar*. However, Morgano et al. [18] reported a lower value of 0.008 $mg\,kg^{-1}$ for these species. In others species from Brazil, Cd concentration ranged from <0.003 to 0.047 $mg\,kg^{-1}$ [18]. The European Community legislation [32] determines a maximum Cd level of 0.05 $mg\,kg^{-1}$, and the Codex Committee on Food Additives and Contaminants recommends 0.5 $mg\,kg^{-1}$ [33], whereas in Brazil the Cd limit is 1.0 $mg\,kg^{-1}$ for fish and fishery products [16,31]. Therefore, all results obtained are below those of the current legislations.

3.3. Arsenic

Seafood exists in two forms: inorganic and organic (arsenobetaine, arsenocholine and organoarsenicals). Although seafood contains a high concentration of organic

Table 3
Higher values for concentration of inorganic elements in fish from Rio de Janeiro State, Brazil (mg kg^{-1}, wet weight).

Fish species	Inorganic elements – higher concentration (mg kg^{-1} ww)								
	Se	Fe	Mn	Co	Zn	Cu	As[a]	Cd	Pb
C. crysos	0.21	13.02	5.36	0.09	8.09	6.07	0.09	0.06	0.92
L. villarii	0.17	3.88	1.91	0.03	5.09	6.71	1.18	0.02	0.50
M. furnieri	0.15	3.79	0.43	0.01	4.25	2.63	0.20	0.02	0.32
P. arenatus	0.16	15.98	4.46	0.06	17.35	4.44	0.16	0.31	0.45
P. saltatrix	0.14	6.54	1.00	0.02	6.87	6.39	0.10	0.03	0.59
G. brasiliensis	0.09	2.67	2.34	0.04	4.81	3.05	0.55	0.02	0.291
S. salar	0.31	26.07	5.07	0.08	39.30	2.60	0.34	0.47	0.088
M. cephalus	0.04	4.59	5.30	0.03	5.61	2.66	0.05	0.01	0.457
C. leiarchus	0.03	2.69	0.83	0.01	3.39	5.14	0.02	0.02	1.661
S. brasiliensis	0.23	12.62	7.35	0.08	12.05	4.72	0.12	0.03	0.904
P. numida	0.08	5.68	0.83	0.63	4.14	12.27	0.48	0.02	0.231

Modified from Medeiros et al. [19].
[a] Concentration of inorganic As was estimated as 10% of total As [40].

arsenic, it is much less toxic than inorganic arsenic [34] and can be efficiently and rapidly excreted in urine without transformation [35]. On the other hand, it is suspected that inorganic As present in fish consumed by humans is carcinogenic. As only about 10% of the As present in fish is in inorganic form only this percentage was used to calculate hazard [9,35,40]. The values for As ranged from 0.015 mg kg^{-1} for *L. villarii* to 1.18 mg kg^{-1} for *C. leiarchus* which showed values close to the maximum limit set by the Brazilian legislation of 1.0 mg kg^{-1} in fish and fishery products [16,31].

3.4. Copper

The values for Cu ranged from 2.60 mg kg^{-1} for *S. salar* to 12.27 mg kg^{-1} for *P. numida*. Guerin et al. [25] reported Cu mean value of 2.01 mg kg^{-1}, 0.58 mg kg^{-1} and 1.15 mg kg^{-1} for *P. saltatrix*, *S. salar* and *S. brasiliensis*, respectively. In other fish species from Brazil, Cu values ranged from 0.56 to 1.64 mg kg^{-1} [36].

3.5. Iron

The lowest Fe levels were 2.66 mg kg^{-1} for *S. salar* and the highest Fe levels were 26.07 mg kg^{-1} for *G. brasiliensis*. Guerin et al. [25] reported mean values for Fe in fish samples as 4.42 mg kg^{-1} and 11.7 mg kg^{-1} for *S. brasiliensis*, 1.87 mg kg^{-1} for *S. salar* and 19.0 mg kg^{-1} for *P. saltatrix*. These levels are higher than the Fe values of this study with 6.99 mg kg^{-1} for *S. brasiliensis* and 3.47 mg kg^{-1} for *P. saltatrix*, and lower for *S. salar* with 4.66 mg kg^{-1}. The mean Fe concentration in *M. cephalus* was 3.99 mg kg^{-1} that is lower than the average (125 mg kg^{-1}) described by Tuzen [24].

3.6. Manganese

The lowest and the highest Mn levels were found as 0.43 mg kg^{-1} in *M. furnieri* and 7.35 mg kg^{-1} in *S. brasiliensis*. The mean level for *M. cephalus* was 0.11 mg kg^{-1} lower than the value reported by Tuzen [24] for the same species (8.18 mg kg^{-1}). The mean Mn concentrations were 1.72 mg kg^{-1} for *S. brasiliensis* and 0.30 mg kg^{-1} for *P. saltatrix* that were lower than the mean values reported by Guerin et al. [25], 0.65 mg kg^{-1} and 1.72 mg kg^{-1} respectively. However, Guerin et al. [25] found lower mean Mn values for *S. salar* (0.11 mg kg^{-1}) in comparison with this study (0.86 mg kg^{-1}).

3.7. Zinc

The lowest and the highest Zn levels were found as 3.35 mg kg^{-1} for *C. leiarchus* and 39.32 mg kg^{-1} for *S. salar*. The mean value for *M. cephalus* was 3.90 mg kg^{-1} lower than 86.2 mg kg^{-1} reported in the literature [24]. Guerin et al. [25] reported mean values for Zn concentration as 15.4 mg kg^{-1} and 16.0 mg kg^{-1} for *S. brasiliensis* and *P. saltatrix* respectively higher than our values of 9.33 mg kg^{-1} and 5.62 mg kg^{-1} for the same species. For *S. salar* the mean value for Zn concentration was 3.20 mg kg^{-1} [25] lower than 6.82 mg kg^{-1} found in this study.

3.8. Cobalt

The values for Co ranged from 0.01 mg kg^{-1} for *M. furnieri* to 0.09 mg kg^{-1} for *C. leiarchus* and *C. crysos*. The mean value in *P. saltatrix* was 0.01 mg kg^{-1}, lower than 0.02 mg kg^{-1} reported by Guerin et al. [25]. However, the mean value for *S. salar* was 0.02 mg kg^{-1} and 0.02 mg kg^{-1} for *S. brasiliensis*, higher than 0.004 mg kg^{-1} and 0.008 mg kg^{-1}, respectively, published by the same author.

3.9. Selenium

The lowest and the highest Se levels were found as 0.03 mg kg^{-1} in *C. leiarchus* and 0.31 mg kg^{-1} in *S. salar*. The mean concentration for *M. cephalus* was 0.015 mg kg^{-1}, for *P. saltatrix* it was 0.075 mg kg^{-1}, for *S. salar* it was 0.06 mg kg^{-1}, for *M. furnieri* it was 0.07 mg kg^{-1}, for *C. leiarchus* it was 0.02 mg kg^{-1} and for *S. brasiliensis* it was 0.09 mg kg^{-1}. The literature reports higher values for the same fish species as 0.63 mg kg^{-1} for *M. cephalus* [24], 0.69 mg kg^{-1} for *P. saltatrix*, 0.12 mg kg^{-1} for *S. salar*, and 0.57 mg kg^{-1} for *S. brasiliensis* [25]. Tenuta Filho et al. [38] 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*.

Table 4
Estimated Weekly Intakes (EWI)[b] of Pb, Cd and As in fish from Rio de Janeiro State and internationally accepted safe levels of PTWI for the same elements.

Element	PTWI[a]	*C. crysos*	*L. villarii*	*M. furnieri*	*P. arenatus*	*P. saltatrix*	*G. brasiliensis*	*S. salar*	*M. cephalus*	*C. leiarchus*	*S. brasiliensis*	*P. numida*
Pb	1.75	0.0022	0.0028	0.0008	0.0011	0.0014	0.0007	0.0002	0.0011	0.0039	0.0021	0.0005
Cd	0.49	0.0001	0.00005	0.00004	0.0007	0.00006	0.00004	0.00110	0.00003	0.00004	0.00007	0.00004
As	0.015	0.0002	0.0012	0.0005	0.0004	0.0002	0.0013	0.0008	0.0001	0.00004	0.0003	0.0011

[a] Provisional Tolerable Weekly Intake (mg/week/70 kg body weight) [3,39].
[b] Estimated weekly intake (mg/week/70 kg body weight).

Table 5
Estimated Daily Intakes (EDI)[b] of Cu, Fe, Mn, Zn and Se in fish from Rio de Janeiro State and Recommended dietary allowance for the same elements.

Element	RDA[a]	*C. crysos*	*L. villarii*	*M. furnieri*	*P. arenatus*	*P. saltatrix*	*G. brasiliensis*	*S. salar*	*M. cephalus*	*C. leiarchus*	*S. brasiliensis*	*P. numida*
Cu	0.9	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3
Fe	14	0.3048	0.0907	0.0888	0.3739	0.1530	0.0624	0.6101	0.1074	0.0628	0.2954	0.0968
Mn	2.3	0.13	0.04	0.01	0.10	0.02	0.05	0.12	0.12	0.02	0.17	0.01
Zn	7	0.19	0.12	0.10	0.41	0.16	0.11	0.92	0.13	0.08	0.28	0.02
Se	0.034	0.005	0.004	0.004	0.004	0.003	0.002	0.007	0.001	0.001	0.005	0.002

[a] Recommended dietary allowance (mg/day) [37].
[b] Estimated daily intake (mg/day/70 kg body weight).

3.10. Risk assessment for health

Brazil is a country with great territorial extension; different values of fish consumption can be observed for different regions of the country. For example, in the northern region the average fish consumption is 95.0 g/person/day and in the southern region fish consumption is much lower 6.8 g/person/day [22]. These data indicate the importance of eating habits' evaluation of a population to assess the risk of ingestion of a toxic substance in humans. Nevertheless, according to IBGE, the average Brazilian seafood consumption (fresh fish and preparations) is 23.4 g/person/day [22].

To assist the evaluation of inorganic elements in food the Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives [21] set the reference dose (RfD). Values for the studied elements are Se = 0.005 mg kg^{-1} bw/day, Fe = 0.7 mg kg^{-1} bw/day, Mn = 0.14 mg kg^{-1} bw/day, Zn = 0.3 mg kg^{-1} bw/day, Cu = 0.4 mg kg^{-1} bw/day, As = 0.003 mg kg^{-1} bw/day, Cd = 0.001 mg kg^{-1} bw/day, and Pb = 0.002 mg kg^{-1} bw/day. Based on these values the EDI is lower than the RfD guidelines for most of the elements studied, thus strongly indicating no health risk due to trace elements in marine fish consumed by Rio de Janeiro state population. Estimated intake (daily and weekly) for an adult person with 70 kg body weight and the Hazard Quotient are presented in Tables 4–6. The Hazard Quotient for most elements studied was less than 1 and does not indicate risk for consumption of these fish species. The As presented the higher values of HQ, 1.31 for *L. villarri*, indicating an apparent risk for consumption of this fish species in relation to the presence of this element and its toxic form.

Based on population eating habits the Provisional Tolerable Weekly Intake (PTWI) value is an estimate amount of a contaminant that can be consumed by a human over a lifetime without appreciable risk. PTWI is established by the Joint Food and Agricultural Organization for the United Nations (FAO)/World Health Organization (WHO) Expert Committee on Food Additives [21]. PTWI values were used in the present study to serve as reference values for safe levels of 3 toxic metals: As, Cd and Pb. Estimated Weekly Intake (EWI) and Estimated Daily Intake (EDI) for a 70 kg body weight of an adult person on basis of the present study had results (Tables 4 and 5) that were comprised with standards values 5 for assessment of these elements. The values of EWI for Pb ranged from 0.0002 mg kg^{-1}/week for *S. salar* to 0.0039 mg kg^{-1}/week for *C. leiarchus*. For Cd the EWI values ranged from 0.00004 mg kg^{-1}/week for *M. furnieri*, *G. brasiliensis*, *C. leiarchus* and *P. numida* to 0.00110 mg kg^{-1}/week for *S. salar*. For As the EWI values ranged from 0.00004 mg kg^{-1}/week for *C. leiarchus* to 0.0013 mg kg^{-1}/week for *G. brasiliensis*. The higher values

Table 6
Values of Hazard Quotient for inorganic elements in fish from Rio de Janeiro State, Brazil.

Element	Fish species											Hazard Quotient
	C. crysos	*L. villarii*	*M. furnieri*	*P. arenatus*	*P. saltatrix*	*G. brasiliensis*	*S. salar*	*M. cephalus*	*C. leiarchus*	*S. brasiliensis*	*P. numida*	
Se	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.003	0.002	0.02	0.01	<1
Fe	0.01	0.002	0.002	0.01	0.00	0.00	0.01	0.002	0.001	0.006	0.003	<1
Mn	0.01	0.005	0.001	0.01	0.00	0.01	0.01	0.01	0.002	0.02	0.002	<1
Co	0.10	0.03	0.01	0.07	0.02	0.05	0.1	0.04	0.01	0.09	0.7	<1
Zn	0.01	0.006	0.005	0.02	0.01	0.01	0.04	0.01	0.004	0.01	0.005	<1
Cu	0.05	0.06	0.02	0.04	0.1	0.03	0.02	0.02	0.04	0.04	0.1	<1
As[a]	0.10	1.31	0.2	0.2	0.1	0.6	0.4	0.06	0.02	0.13	0.5	
Cd	0.02	0.007	0.01	0.10	0.01	0.01	0.2	0.004	0.01	0.01	0.01	<1

[a]Hazard Quotient = EDI/RfD. If the ratio is <1, there is no obvious risk.

of Cd and Pb correspond to 0.22% of PTWI and the higher value for As corresponds to 8.6% of PTWI. None of the studied species showed values higher than PTWI recommended for these elements.

For the essential trace elements, the Brazilian legislation set reference values for recommended dietary allowances (RDA) [37]. In the present study we calculated the value of estimated daily intake (EDI) for these elements and compared them with reference values (Table 5). The EDI values for Cu ranged from 0.1 mg/day for most of the species studied to 0.3 g/day for *P. numida*. For Fe the EDI values ranged from 0.062 mg/day for *G. brasiliensis* and *C. leiarchus* to 0.61 mg/day for *S. salar*. For Mn the EDI values ranged from 0.01 mg/day for *P. numida* and *M. furnieri* to 0.17 mg/day for *S. brasiliensis*. For Zn the EDI values ranged from 0.02 mg/day for *P. numida* to 0.92 mg/day for *S. salar*. For Se the EDI values ranged from 0.001 mg/day for *M. cephalus* and *C. leiarchus* to 0.007 mg/day for *S. salar*. For Co the EDI values ranged from 0.0002 mg/day for *C. leiarchus* to 0.1328 mg/day for *P. numida*. Nutritional and toxicological reference values have not been proposed for this element. The higher values of Cu EDI found in *P. numida* correspond to 33.3% of RDA; for Fe the higher value for EDI found in *S. salar* and *G. brasiliensis* corresponds to 4.3% of EDI; for Mn the higher value found in *S. brasiliensis* corresponds to 7.4% of EDI; for Zn the higher value of EDI found in *S. salar* corresponds to 13.2% of EDI and for Se the higher value found in *S. salar* corresponds to 20.6% of EDI. The present data indicate that these fish species can be a important source of nutrients for humans. It is important to note that these values were calculated for a portion of 23.4 g/day, much lower than usually eaten during a meal. These fish species appear to have greater nutritional importance due to their contribution to the intake of recommended daily allowances of nutritional elements.

4. Conclusions

This study was developed to provide information on trace elements concentration in different fish species from Rio de Janeiro State, Brazil. As expected, metal concentrations showed a great variability even within the same fish species. The total samples analyzed showed values of Cd and Pb below the Maximum Tolerable Limits of 3.0 mg kg^{-1} for Pb and 1.0 mg kg^{-1} for Cd; only *M. cephalus*, *C. leiarchus* and *C. crysos* had As concentrations below 1 mg kg^{-1}, maximum limits established by the Brazilian legislation. Study of speciation of arsenic is important once the toxicity level is dependent on its chemical form present in the sample. Fish species should be assessed for their nutritional contribution, as seen in this study; some species can be a good source of dietary inorganic elements that are part of a healthy diet.

Another important factor is that the calculations were made with data from Brazilian national food consumption habit and for fish the average of consumption was 23.4 g/person/day. This value underestimated the inorganic elements concentration found since it is well below a regular fish portion commonly consumed by a 70 kg adult. Besides it does not consider specific populations where fish consumption is even higher as it would make for disturbing data.

It is also important to assess some biological and environmental factors like origin of the fish, sea environment, feeding habits of fish, and age among others factors that can significantly influence the concentration of these elements.

Conflict of interest

None declared.

Acknowledgments

The authors are grateful for the financial support provided by CAPES and the laboratory support provided by INCQS/Fiocruz and CESTEH/Fiocruz.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.toxrep.2014.06.005.

References

[1] L.R. McDowell, Minerals in Animal and Human Nutrition, 2nd ed., Elsevier, 2003.
[2] S.B. Goldhaber, Trace elements risk assessment: essentiality vs. toxicity, Regul. Toxicol. Pharmacol. 38 (2003) 232–242.
[3] FAO/WHO, Summary of Evaluations Performed by the Joint FAO/WHO Expert Committee on Food Additives (JECFA 1956-2007) (first through 68th meetings), Food and Agriculture Organization of the United Nations and the World Health Organization, ILSI Press International Life Sciences Institute, Washington, DC, 2007, Available at: http://jecfa.ilsi.org/ (accessed June 2009).
[4] E.L. Maia, C.C.S. Oliveira, A.P. Santiago, Composição química e classes de lipídios em peixe de doce curimatã comum Prochilodus cearensis, Ciênc. Tecnol. Alim. 19 (3) (1999) 433–437.
[5] M. Pandelova, B. Henkelmann, O. Roots, M. Simm, L. Järv, E. Benfenati, K.-W. Schramm, Levels of PCDD/F and dioxin-like PCB in Baltic fish of different age and gender, Chemosphere 71 (2008) 369–378.
[6] H. Karl, A. Bladt, H. Rottler, R. Ludwigs, W. Mathar, Temporal trends of PCDD, PCDF and PCB levels in muscle meat of herring from different fishing grounds of the Baltic Sea and actual data of different fish species from the Western Baltic Sea, Chemosphere 78 (2010) 106–112.
[7] R. Zhou, L. Zhu, Y. Chen, Q. Kong, Concentrations and characteristics of organochlorine pesticides in aquatic biota from Qiantang River in China, Environ. Pollut. 151 (2008) 190–199.
[8] M. Davodi, A. Esmaili-Sari, N. Bahramifarr, Concentration of polychlorinated biphenyls and organochlorine pesticides in some edible fish species from the Shadegan Marshes (Iran), Ecotoxicol. Environ. Saf. 74 (2011) 294–300.
[9] C. Afonso, H.M. Lourenço, C. Cardoso, N.M. Bandarra, M.L. Carvalho, M. Castro, M.L. Nunes, From fish chemical characterization to the benefit-risk assessment – Part A, Food Chem. 137 (2013) 99–107.
[10] J. Hoekstra, Hart, A.H. Owenb, M. Zeilmaker, B. Bokkers, Thorgilsson, Björn, H. Gunnlaugsdottir, Fish, contaminants and human health: quantifying and weighing benefits and risks, Food Chem. Toxicol. 54 (2013) 18–29.
[11] EFSA, Guidance on human health risk-benefit assessment of foods, EFSA J. 8 (7) (2010) 1673.
[12] P.M. Kris-Etherton, W.S. Harris, L.J. Appel, Fish consumption, fish oil, omega-3 fatty acids, and cardiovascular disease, Arterioscler. Thromb. Vasc. Biol. 23 (2) (2003) 20–30.
[13] FAO, The State of World Fisheries and Aquaculture 2010 (SOFIA), Food and Agriculture Organization of the United Nations, Rome, 2010.
[14] MPA. Ministério da Pesca e Aquicultura, Consumo aparente de pescado no Brasil 1996–2009, 2009, Available at: http://www.mpa.gov.br/mpa/seap/Jonathan/mpa3/docs/folder%20consumo%20de%20pescado%202009%202.pdf (accessed April 2014).

[15] MPA, Consumo de pescado no Brasil aumenta 23.7% em dois anos, 2013, Available at: http://www.mpa.gov.br/index.php/imprensa/noticias/2226-consumo-de-pescado-no-brasil-aumenta-237-em-dois-anos (accessed April 2014).
[16] ANVISA. Agência Nacional de Vigilância Sanitária, RDC No 42, de 29 de agosto de 2013, Dispõe sobre o Regulamento Técnico MERCOSUL sobre Limites Máximos de Contaminantes Inorgânicos em Alimentos, 2013.
[17] L.G.M. De Moura Filho, E.S. Mendes, R.P.P. e Silva, L.M.N. de Barros Góes, K.P.B. de Araújo Vieira, P. de Paula Mendes, Enumeração e pesquisa de Vibrio spp. e coliformes totais e termotolerantes em sashimis de atum e vegetais comercializados na região metropolitana do Recife Estado de Pernambuco, Acta Sci. Technol. 29 (1) (2007) 85e90.
[18] M. Morgano, L.C. Rabonatoa, R.F. Milania, L. Miyaguskua, S.C. Balianb, Assessment of trace elements in fish of Japanese foods marketed in São Paulo (Brazil), Food Control 22 (2011) 778–785.
[19] R. Medeiros, L. Santos, A. Freire, R. Santelli, A. Braga, T. Krauss, S. Jacob, Determination of inorganic trace elements in edible marine fish from Rio de Janeiro State, Brazil, Food Control 23 (2012) 535–541, http://dx.doi.org/10.1016/j.foodcont.2011.08.027.
[20] S. Onsanit, C. Ke, X. Wang, K. Wang, W. Wang, Trace elements in two marine fish cultured in fish cages in Fujian province China, Environ. Pollut. 158 (2010) 1334–1342.
[21] JECFA. Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives, Summary and Conclusions of the 61st Meeting of the Joint FAO/WHO Expert Committee on Food Additives, JECFA/61/Sc, Rome, Italy, 2003, 10–19.06.03, 1–22.
[22] IBGE. Fundação Instituto Brasileiro de Geografia e Estatística (IBGE), Pesquisa de Orçamento Familiar – POF, 2009.
[23] GEMS/Food-Euro, Reliable Evaluation of Low-level Contamination of Food, Report on a Workshop in the Frame of GEMS/Food-Euro, Document EUR/ICP/EHAZ.94.12/WS04, Kulmbach, Federal Republic of Germany, 1995, 8pp.
[24] M. Tuzen, Toxic and essential trace elemental contents in fish species from the Black Sea, Turkey, Food Chem. Toxicol. 47 (2009) 1785–1790.
[25] T. Guerin, R. Chekri, C. Vastel, V. Sirot, J.L. Volatier, J.C. Leblanc, L. Noel, Determination of 20 trace elements in fish and other seafood from the French market, Food Chem. 127 (2011) 934–942.
[26] C. Vieira, S. Morais, S. Ramos, M. Delerue, P. Oliveira, Mercury, cadmium, lead and arsenic levels in three pelagic fish species from the Atlantic Ocean: intra- and inter-specific variability and human health risks for consumption, Food Chem. Toxicol. 49 (2011) 923–932.
[27] M. Turkmen, A. Turkmen, Y. Tepe, Y. Töre, A. Ates, Determination of metals in fish species from Aegean and Mediterranean Seas, Food Chem. 113 (2009) 233–237.
[28] F. Yilmaz, The comparison of heavy metal concentrations (Cd, Cu, Mn, Pb, and Zn) in tissues of three economically important fish (*Anguilla anguilla*, *Mugil cephalus* and *Oreochromis niloticus*) inhabiting Köycegiz Lake-Mugla (Turkey), Turk. J. Sci. Technol. 4 (1) (2009) 7–15.
[29] D. Mendil, Ö.F. Ünal, M. Tüzen, M. Soylak, Determination of trace metals in different fish species and sediments from the Yesilırmak in Tokat Turkey, Food Chem. Toxicol. 48 (2010) 1383–1392.
[30] L. Nasreddine, O. Nashalian, F. Naja, L. Itani, D. Parent-Massin, M. Nabhani-Zeidan, N. Hwalla, Dietary exposure to essential and toxic trace elements from a total diet study in an adult Lebanese urban population, Food Chem. Toxicol. 48 (2010) 1262–1269.
[31] MAPA. Ministério da Agricultura, Pecuária e Abastecimento. Instrução Normativa n° 24, de 14 de julho de 2009. Define os requisitos e critérios específicos para funcionamento dos Laboratórios de Análises de Resíduos e Contaminantes em Alimentos integrantes da Rede Nacional de Laboratórios Agropecuários, Seção 1, Diário Oficial da União, Brasília, DF.
[32] EU. European Union. Commission of the European Communities, 2001, Commission regulation (EC) n. 221/2002 of the 6 February 2002 amending regulation (EC) n. 466/2002 setting maximum levels for certain contaminants in foodstuffs, Official Journal of the European Communities, Brussels (2002), 6 February.
[33] A. Ikem, J. Egilla, Trace element content of fish feed and bluegill sunfish (*Lepomis macrochirus*) from aquaculture and wild source in Missouri, Food Chem. 110 (2008) 301–309.
[34] B.C. Han, W.L. Jeng, R.Y. Chen, G.T. Fang, T.C. Hung, R.J. Tseng, Estimation of target hazard quotients and potential health risks for metals by consumption of seafood in Taiwan, Arch. Environ. Contam. Toxicol. 35 (1998) 711–720.
[35] J.P. Buchet, D. Lison, M. Ruggeri, V. Foa, G. Elia, Assessment of exposure to inorganic arsenic, a human carcinogen, due to the consumption of seafood, Arch. Toxicol. 70 (1996) 773–778.
[36] S.deC. Costa, S.M. Hartz, Evaluation of trace metals (cadmium, chromium, copper and zinc) in tissues of a commercially important fish (*Leporinus obtusidens*) from Guaíba Lake, Southern Brazil, Braz. Arch. Biol. Technol. 52 (2009) 241–250.
[37] ANVISA. Agência Nacional de Vigilância Sanitária, Regulamento Técnico Sobre a Ingestão Diária Recomendada (IDR) de Proteína, Vitaminas E Minerais, 2005, RDC n° 269, de 22 de setembro de 2005.
[38] A. Tenuta Filho, L.L.F. Macedo, D.I.T. Favaro, Concentração e retenção do selênio em peixes marinhos, Ciência e Tecnologia de Alimentos (30) (2010) 210–214.
[39] Council of Europe, Partial Agreement in the Social and Public Field, The Guidelines on metals and alloys used as food contact materials are part of the Council of Europe's Policy Statements concerning materials and articles intented to come into contact with foodstuffs, Technical Document, Strasbourg, 2011.
[40] United States Food and Drug Administration, Guidance Documents for Trace Elements in Seafood, Center for Food Safety and Applied Nutrition, Washington DC, 1993.