

Contribution to food safety assurance of fish consumed at São Paulo city by means of trace element determination

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Abstract Controlling seafood quality is essential to ensure its safety for human consumption. Nevertheless, scarce information is available about seafood contaminant status in complex metropolitan markets in Latin America. Essential and toxic elements were determined in some of the most consumed fish species in São Paulo city, Brazil. Instrumental Neutron Activation Analysis was applied for the determination of As, Br, Co, Cs, Fe, K, Na, Rb, Se and Zn while Cd, Pb and Hg were determined by Atomic Absorption Spectrometry. Mass fraction results were higher than allowed values for some elements in some fish species, especially As. However, it was not possible to affirm that the fish consumed in São Paulo city presents risk to human health.

Keywords Food safety · Fish · Toxic element · Neutron activation analysis · Atomic Absorption Spectrometry

Introduction

The minimum recommended fish intake determined by the World Health Organization (WHO) is 12 kg of fish per capita per year [1]. According to the Brazilian Ministry of Fisheries and Aquaculture (MPA), fish consumption doubled in one decade in Brazil in 2013 due to the growing

acknowledgement of its nutritional importance as source of proteins and polyunsaturated fatty acids, basically achieving WHO recommendation [2]. Along with this increase in demand for fish is the increasing concern of the Brazilian Health Surveillance Agency (ANVISA) towards the quality of fish sold in terms of the presence of threats to human health, mainly in the form of pathogenic microorganisms [3].

A variety of substances with different uses and chemical stabilities which allows them to accumulate and persist in the environment may be present in seafood with a potential to cause adverse health effects [4, 5]. Organic compounds such as polychlorinated biphenyls (PCBs), dioxins and agrochemical residues are important classes of chemicals to be surveilled. In the case of inorganic compounds, they may be present due to natural biogeochemical processes but also be enhanced due to anthropogenic activities. As for toxic element levels such as As, Cd and Hg, they must be below the maximum permissible mass fraction limits for toxic elements in foodstuffs allowed for human consumption, in order not to pose health safety concerns [6, 7].

The purpose of this study was the application of Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectrometry (AAS) to assess the levels of As, Cd, Hg, Pb, Se and Zn in samples of fish species currently consumed in São Paulo city, Brazil. By the Brazilian law enforcement, the presence of these elements in fish must be monitored and below stated values prior to human consumption. However, little is known about actual dietary fish intake in Brazil as it may be a very regionalized issue. Then, it is still difficult to directly correlate fish consumption in Brazil to the hazard effects of elements to the Brazilian population. Due to the multielement character of INAA, other elements such as Br, Co, Cs, Fe, K, Na, and Rb were simultaneously determined.

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This initiative was taken under the framework of a Technical Cooperation Project of the International Atomic Energy Agency (IAEA) for Latin American and Caribbean countries aiming to ensure food quality and biomonitoring of contaminants in shellfish and fish (Project Number RLA/5/054, ARCAL CIII) [8].

Experimental

Fish sampling

Individuals of the species whitemouth croaker (*Micropogonias furnieri*), smooth weakfish (*Cynoscion leiarchus*), common snook (*Centropomus undecimalis*) and Brazilian sardine (*Sardinella brasiliensis*) were purchased in October 2009, at the Central Warehouse Company of the State of São Paulo (CEAGESP), main supply center for the population of the metropolitan area of São Paulo city. For each fish species ten specimens were sampled.

After collection, samples were washed with purified water (Milli-Q) and cleaned. White and red muscle tissues, usually considered the edible tissues in fish by the Brazilian population, were freeze-dried (Modulyo D, Thermo Electron), ground in a blender with titanium blades to prevent sample contamination (Performa Magiclean, Arno) and sieved to ensure sample homogeneity. Samples were kept under refrigeration until analysis.

In order to check method validation, the following certified reference materials (CRM) were analyzed along with fish samples: Mussel Tissue (NIST SRM 2976), Oyster Tissue (NIST SRM 1566b) and Dogfish Muscle (NRCC DORM-2).

Instrumental Neutron Activation Analysis

The comparative method of INAA was used to determine the elements As, Br, Co, Cs, Fe, K, Na, Rb, Se e Zn. Test portions of 0.200 g of each specimen and 0.150 g of each CRM were weighed on a calibrated Shimadzu AEM 5200 analytical balance. Elemental standards were prepared by pipetting aliquots of certified standard solutions (Spex Certiprep) into strips of Whatman 40 filter paper, using Eppendorf pipettes with previously checked nominal volumes. For some elements, stock solutions were diluted before being pipetted. After drying at room temperature in a laminar flow hood, the strips of filter paper were folded and placed in polyethylene bags, so as to obtain the same geometry of the samples. Each irradiation batch consisting of three test portions, one CRM portion and elemental standards was simultaneously irradiated for 8 h under a thermal neutron flux of about $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ in the IEA-R1 reactor of IPEN – CNEN/SP.

Measurements were performed in a Canberra high purity germanium (HPGe) detector model GC2018 coupled to the Canberra DSA 1000 digital spectral analyzer. Gamma ray spectra were collected and processed using the Canberra Genie 2000 software, version 3.1. After a seven-day decay period, induced gamma activities were measured for ^{76}As , ^{82}Br , ^{24}Na , and ^{42}K radionuclides for a period of 5400 s, while ^{60}Co , ^{134}Cs , ^{59}Fe , ^{86}Rb , ^{75}Se and ^{65}Zn radionuclides were measured for a period of 36,000 s after a 20-day decay period. Element mass fraction calculations were carried out using a Microsoft Excel spreadsheet for suitable radionuclide photopeak energies.

Atomic Absorption Spectrometry

Prior to analysis, samples and CRMs were acid digested, according to an adapted IAEA digestion procedure [9]. About 350 mg test portions were weighed in perfluoroalkoxy vials (Savillex) and 5.0 mL of concentrated HNO_3 (Merck) and 1.0 mL of 30 % (v/v) H_2O_2 (Merck) were added. Closed vials were left to rest for about 15 h. In order to complete digestion, vials were put in an aluminum block at 90 °C, for 3 h. Digests were cooled to room temperature and diluted to a final volume of 25.3 mL with Milli-Q water.

Cold Vapor Atomic Absorption Spectrometry (CV AAS) was used for Hg determination, using a Perkin Elmer FIMS spectrometer. Analytical curve solutions (0.5, 1.5, 2.5, 3.5 and 4.0 ng mL^{-1}) as well as reagent blanks were also digested as samples. The sample injection volume was 500 μL , argon was used as carrier gas at 50 mL min^{-1} flow rate, 0.2 % (v/v) HNO_3 (Merck) was used as the sample carrier solution at 10 mL min^{-1} flow rate while a 3% (m/v) stannous chloride (Merck) solution was used as reducing agent at 6 mL min^{-1} flow rate. After the atomization step, the Hg mass fraction was calculated by the spectrometer software after two replicate measurements.

Electrothermal Atomic Absorption Spectrometry (ET AAS) was employed for Cd and Pb determination, in the Perkin Elmer AAnalyst 800 spectrometer with Zeeman background correction at wavelengths of 228.8 nm and 283.3 nm, respectively. Analytical curve solutions for the determination of Cd were 1.4, 2.7, 4.0, 5.3 and 6.7 ng mL^{-1} and for the determination of Pb they were 2.9, 6.0, 9.0, 11.8 and 15.0 ng mL^{-1} . Analytical curves coefficients were obtained by a linear regression fit with least-squares method performed by the spectrometer software. 20 μL aliquots of the sample solution and 10 μL of matrix modifier [0.5 % (m/v) $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.03 % (m/v) $\text{Mg}(\text{NO}_3)_2$] were introduced to the furnace tube by the autosampler. After the atomization step, Cd and Pb mass fractions were calculated by the spectrometer software after two replicate measurements.

Results and discussion

Quality assurance

Table 1 shows experimental values obtained for the CRMs using the INAA and AAS methods, certified values as well as calculated *z*-scores. In this study, *z*-scores were calculated using the modified Horwitz equation as criterium to estimate the reproducibility standard deviations of the methods [10–12]. Cs was not certified in any of the reference materials and hence it was not possible to estimate *z*-scores and investigate the INAA method performance for this element. Concerning Br, only NIST SRM 2976 certificate gives information about this element, but it is a reference value. Anyway INAA results were consistent to it. Aside from K and Zn results in NIST SRM 2976, it was observed that *z*-scores were in the range ± 2 for all the other elements, indicating that the INAA and AAS methods are adequate for the purpose of determining these elements in the fish samples.

Element determination in fish samples

Obtained mean results and ranges for 10 specimens of each fish species are presented in Table 2 with comparison with national and international legislations [13–17]. All results

are presented at wet weight basis, in order to allow comparison to the legal limits. Wet weight results were calculated taking into account water loss during the freeze-drying process and the residual humidity calculated using a humidity determination balance (Ohaus MB45). Biometric measurements and whole fish to edible tissue mass ratios are presented in Table 3.

From nutritional and toxicological points of view, Cd, Hg and Pb do not have any known essential function in living organisms and their presence is always considered to cause chronic or acute toxic effects while the element As may play some essential role for some microorganisms, yet to be completely proved. On the other hand, Se, Zn, Co, Fe, K and Na are essential elements but may become toxic if the maximum tolerable daily intake values are exceeded. According to Table 2, only for Se and Zn maximum values in seafood were established for some of the consulted legislations for this group of elements. Little is known about nutritional functions or toxicity of Br, Cs and Rb in living organisms. In this study mass fraction results on these elements are presented as they were readily available to the INAA method used and may be useful for future investigations [14].

As a general trend *Sardinella brasiliensis* presented the higher levels of elements while *Centropomus undecimalis* presented the lower ones, even though for Hg this relation

Table 1 Element mass fractions in mg kg⁻¹ (mean values and expanded uncertainties, *k* = 2, dry weight) obtained for selected certified reference materials in comparison to certified values

Element	CRM					
	NRCC DORM-2		NIST SRM 2976		NIST SRM 1566b	
	This study (certified value)	<i>z</i> -score	This study (certified value)	<i>z</i> -score	This study (certified value)	<i>z</i> -score
As	16.0 ± 0.63 (18.0 ± 1.1)	-1.1	13.1 ± 3.7 (13.3 ± 1.8)	-0.14	7.63 ± 0.14 (7.65 ± 0.65)	-0.02
Br	27.0 ± 1.5 NC	-	329 ± 45 (329 ± 15) ^R	0	50 ± 1.2 NC	-
Cd (µg kg ⁻¹)	NA (43 ± 8)	-	822 ± 32 (820 ± 160)	0.02	2554 ± 82 (2480 ± 80)	0.21
Co	0.185 ± 0.020 (0.182 ± 0.031)	0.080	0.72 ± 0.04 (0.61 ± 0.02) ^R	1.0	0.35 ± 0.010 (0.371 ± 0.09)	-0.30
Cs	0.23 ± 0.01 NC	-	<0.015 (0.027 ± 0.001) ^R	-	<0.015 NC	-
Fe	137 ± 24 (142 ± 10)	-0.46	158.2 ± 2.3 (171.0 ± 4.9)	-1.0	198.6 ± 8.8 (205.8 ± 6.8)	-0.49
Hg (µg kg ⁻¹)	NA (4640 ± 260)	-	60.3 ± 3.4 (61.0 ± 3.6)	-0.05	35.4 ± 1.7 (37.1 ± 1.3)	-0.21
K (%)	1.25 ± 0.11 NC	-	1.06 ± 0.42 (0.97 ± 0.05) ^R	2.3	0.623 ± 0.05 (0.652 ± 0.009)	-1.0
Na (%)	0.39 ± 0.044 NC	-	3.61 ± 0.63 (3.5 ± 0.1) ^R	0.95	0.3056 ± 0.0036 (0.3297 ± 0.0053)	-1.5
Pb (µg kg ⁻¹)	NA (65 ± 7)	-	957 ± 40 (1190 ± 180)	-1.3	294 ± 15 (308 ± 9)	-0.24
Rb	5.01 ± 0.55 NC	-	4.1 ± 2.4 (4.14 ± 0.09) ^R	-0.08	2.87 ± 0.27 (3.26 ± 0.14)	-0.89
Se	1.38 ± 0.080 (1.40 ± 0.09)	-0.094	1.74 ± 0.14 (1.80 ± 0.15)	-0.23	1.83 ± 0.10 (2.06 ± 0.15)	-0.78
Zn	24.5 ± 2.3 (25.6 ± 2.3)	-0.44	159 ± 10 (137 ± 13)	2.1	1468 ± 69 (1424 ± 46)	0.58

NC not certified, NA not analyzed, < denotes below detection limit for a 0.150 g test portion, *R* reference value (non-certified)

Table 2 Element mass fractions in wet weight obtained for 10 specimens of selected fish consumed at São Paulo city and comparison to several legislations (mean values \pm SD and range in parenthesis)

Element	Species		Legislation						
	<i>Micropogonias furnieri</i>	<i>Cynoscion leiarchus</i>	<i>Centropomus undecimalis</i>	<i>Sardinella brasiliensis</i>	Brazilian [13]	Codex [14]	FSANZ [15]	Mercosul [16]	EU [17]
As, mg kg ⁻¹	2.7 \pm 1.0 (0.83–4.1)	1.1 \pm 0.1 (0.91–1.3)	0.18 \pm 0.17 (0.02–0.61)	1.7 \pm 0.4 (1.0–2.3)	1.0	0.1	2.0	1.0	2.0
Cd, μ g kg ⁻¹	<0.30	2.9 \pm 2.2 (1.3–8.6)	<0.30	10.6 \pm 4.7 (<0.30–17.3)	1000	–	–	50/100 ^a	500
Hg, μ g kg ⁻¹	19 \pm 10 (8.7–39)	10.1 \pm 1.9 (6.6–13)	20 \pm 14 (5.4–46)	5.0 \pm 3.8 (0.38–12)	1000/500 ^b	500	1000/500 ^b	1000/500 ^b	500
Pb, μ g kg ⁻¹	<7.6	42 \pm 20 (<7.6–59)	<7.6	<7.6	2000	300	500	300	5000
Se, mg kg ⁻¹	0.77 \pm 0.10 (0.60–0.90)	0.43 \pm 0.11 (0.27–0.63)	0.29 \pm 0.17 (0.15–0.63)	0.65 \pm 0.23 (0.28–0.92)	0.3	–	1.1	–	–
Zn, mg kg ⁻¹	3.15 \pm 0.44 (2.59–3.97)	3.9 \pm 1.1 (2.5–5.8)	3.92 \pm 0.62 (2.88–4.78)	7.6 \pm 1.0 (6.4–9.0)	50	–	–	–	–
Br, mg kg ⁻¹	4.4 \pm 0.5 (3.4–5.1)	7.3 \pm 1.6 (5.0–9.6)	5.5 \pm 1.0 (3.9–7.3)	4.3 \pm 0.4 (3.8–5.0)	–	–	–	–	–
Co, μ g kg ⁻¹	10.4 \pm 2.1 (5.7–12)	9.6 \pm 3.4 (4.5–15)	7.2 \pm 2.8 (3.5–12)	18.0 \pm 8.5 (9.7–39)	–	–	–	–	–
Cs, μ g kg ⁻¹	10.9 \pm 1.7 (9.0–14)	11.2 \pm 1.8 (9.6–16)	9.3 \pm 6.0 (3.2–23)	17.2 \pm 5.8 (10–26)	–	–	–	–	–
Fe, mg kg ⁻¹	<7.6	2.95 \pm 0.70 (1.97–4.49)	1.41 \pm 0.35 (1.11–2.20)	16.3 \pm 7.3 (9.8–35)	–	–	–	–	–
K, g kg ⁻¹	<0.29	3.16 \pm 0.43 (2.62–3.79)	3.27 \pm 0.29 (2.66–3.68)	4.36 \pm 0.47 (3.58–5.24)	–	–	–	–	–
Na, g kg ⁻¹	0.64 \pm 0.10 (0.49–0.79)	1.08 \pm 0.26 (0.74–1.45)	1.44 \pm 1.35 (0.54–3.67)	1.85 \pm 1.95 (0.56–5.24)	–	–	–	–	–
Rb, mg kg ⁻¹	0.62 \pm 0.05 (0.57–0.73)	0.57 \pm 0.10 (0.45–0.76)	0.57 \pm 0.46 (0.07–1.50)	0.94 \pm 0.15 (0.73–1.26)	–	–	–	–	–

^a Sardine limit, ^b predatory fish (as tuna) and other fishes, respectively; < denotes below detection limit for a 0.150 g test portion

is inverted. It was observed that most of the element mass fractions in the fish species are under the international and national maximum established limits for the elements treated by the legislations.

As for the essential element Se, mean mass fractions in all fish species are below the maximum level allowed by the Australia/New Zealand legislation, but only *Centropomus undecimalis* presented mean values below the allowed value by the Brazilian legislation [13]. It seems that Brazilian legislations are quite strict considering also the presence of Zn in fish tissues.

In the case of Cd, Hg and Pb, important elements form the toxicological point of view, element content in all species were below the limits for the legislations and in some cases were below the detection limits of the AAS methods used. The presence of Pb in *Cynoscion leiarchus* might be associated to its habitat and feeding behavior as it is found over mud and sand bottoms in river estuaries, feeding mainly on crustacean such as crabs, which might be impacted by industrial activities [18, 19].

Among the toxic elements, As was the element whose results imposed the higher concern as the four species presented mass fractions values above all the legislations. Similar situation was observed in a previous study with Brazilian species where approximately 90 % of the *M. furnieri* samples in winter and 70% in summer presented values above the Brazilian legislation and for *Sardinella brasiliensis* all the samples were above the Brazilian legislation [20]. In the present study, relatively lower As mean mass fractions were obtained for *Centropomus undecimalis* samples, but mean results were above the Codex legislation [14]. For another investigation, quite equivalent mean As results were obtained for *Cynoscion leiarchus* (1.10 mg kg⁻¹) and *Sardinella brasiliensis* (1.10 mg kg⁻¹) from a clean area of São Paulo state seashore while lower results were obtained for *M. furnieri* (1.85 mg kg⁻¹) [21]. The observed toxic element variation might be related to the origin site of the fish used in the different studies. *M. furnieri* specimens commercialized in the present study were caught in southern Brazil. Mass fraction values for As in Brazilian and São Paulo State marine sediments are considered high when compared to crust values and this might be associated to the observed high As values obtained in the fish samples in the present study [22, 23]. However, more information on the catching sites should be available for a proper evaluation of such influence.

The element As has a complex chemistry, especially in marine environments, where more than 50 compounds occur naturally [24]. Its presence in aquatic systems can be of natural origin, from minerals and rocks that contain this element and from soils and sediments formed by these rocks, but also from anthropogenic origin, with the use of pesticides, waste from mining and other industrial products

Table 3 Biometric measurements (mean values \pm SD, $n = 10$, range in parenthesis) and R , whole-fish mass to edible-tissue mass ratios

Species	Length, cm	Whole fish mass (g)	Edible mass (g)	R
<i>Micropogonias furnieri</i>	44 \pm 4 (39–52)	1005 \pm 322 (661–1542)	296 \pm 88 (166–437)	0.30 \pm 0.04
<i>Cynoscion leiarchus</i>	26 \pm 1 (25–28)	200 \pm 27 (156–240)	81 \pm 14 (55–99)	0.41 \pm 0.03
<i>Centropomus undecimalis</i>	46 \pm 12 (35–66)	974 \pm 692 (353–2139)	408 \pm 281 (158 \pm 928)	0.43 \pm 0.02
<i>Sardinella brasiliensis</i>	18 \pm 1 (17–20)	85 \pm 21 (61–118)	36 \pm 9 (18–50)	0.43 \pm 0.06

[25]. The accumulation of As in fish essentially occurs by ingestion of particulate materials suspended in water, food intake and the ion exchange of dissolved ions through the lipophilic membrane [26]. As is present in fish both in its organic form (non-toxic) and inorganic form (toxic), but in general, the largest amount found is in the organic form (as arsenobetaine) which is not considered toxic to humans [4, 26]. Also As content depends on the species, size, considered organs and habitat.

While the CODEX and FSANZ legislations are based on the inorganic form of As, Brazilian law only specifies As limits, irrespective to the chemical species involved. Once only the total amount of As was determined in the Brazilian fish by INAA, it cannot be stated the risk associated to its consumption to the health of final consumers in the country. Further investigation on the inorganic As content and per capita fish consumption are required as well as the monitoring of its content according to capture site in order to draw a better panorama of the impact or As presence in fish to the Brazilian population.

Conclusions

In this study element mass fractions of As, Br, Cd, Co, Cs, Fe, Hg, K, Na, Pb, Rb, Se and Zn in *M. furnieri*, *Cynoscion leiarchus*, *Centropomus undecimalis* and *Sardinella brasiliensis*, some of the most consumed fish species in São Paulo city were determined. *Centropomus undecimalis* was the only species to present element mass fractions under the limits of national and international legislations for all elements, with the exception of As results that surpassed the Codex limits. Results for As for all the other species were above those permitted by the Brazilian legislation. Nevertheless, it cannot be affirmed that these species are toxic for humans and should be avoid as most of the As in fish is in the organic form arsenobetaine that is assumed to be of no toxicological concern. Further investigations on As species are necessary and sustainable monitoring of hot places in the productive chain are needed.

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