Environmental Science and Pollution Research
https://doi.org/10.1007/s11356-019-04258-3

RESEARCH ARTICLE

Arsenic, selenium, and metals in a commercial and vulnerable fish from southwestern Atlantic estuaries: distribution in water and tissues and public health risk assessment

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Received: 5 September 2018 / Accepted: 15 January 2019

Abstract

The anadromous catfish *Genidens barbus* is a vulnerable and economically important species from the Southwestern Atlantic Ocean. Concentrations of As, Co, Fe, Se, and Zn were determined in water and muscle, gill, and liver of catfish from two southwestern Atlantic estuaries (Brazil and Argentina) and health risk via fish consumption was evaluated. High spatial variability was observed in the metals, As, and Se distribution for both estuaries. Considering all tissues, element concentrations (mg/kg, wet weight) were As = 0.41–23.50, Co = 0.01–2.9, Fe = 2.08–773, Se = 0.15–10.7, and Zn = 3.97–2808). Most of the trace elements tended to be higher in Brazil than in Argentina, except for Co, Fe, Se, and Zn in liver and Fe and Co in muscle and gill, respectively. Arsenic accumulation order was muscle > liver ≥ gill. Only As (muscle) was above the maximum recommended by international guidelines at both estuaries. The target hazard quotient ranged from 0.10 to 1.58, suggesting that people may experience significant health risks through catfish consumption. Supposing that the inorganic/toxic As ranged between 1 and 20% of the total, the recommended maximum intakes per capita bases were 6.1–95 and 8.4–138 kg/year (wet weight) for Brazil and Argentina, respectively. Carcinogenic risk for As intake was within the acceptable range but close to the recommended limit ($> 10^{-4}$). These results highlights the importance of quantifying the As species in catfish muscle in order to generate more reliable risk estimates.

Keywords Arsenic · Estuary · Fish · Food composition · Neutron activation analysis · Pollution

Responsible editor: Philippe Garrigues

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Introduction

According to FAO (2018), the global fisheries and aquaculture production (“seafood”) in 2016 was 171 million tons, where the global per capita fish consumption reached 20.5 kg/year. An important and growing percentage of fish consumed in developed countries comes from imports from developing regions, owing to high demand and static or declining local fishery production. Nevertheless, several commercial fish species that inhabit polluted waters are exposed to a wide range of contaminants that may accumulate in tissues and reach toxic levels (Neff 1997; Kalia and Khambholja 2015; Avigliano et al. 2016b).

Arsenic (As) is one of the most worrying non-essential element in seafood because it is a hazardous substances (Chou and De Rosa 2003) and has carcinogenic properties (ATSDR 2007). In several cases, the concentration of As in marine organisms exceed the levels present in land production

Published online: 25 January 2019

food (Taylor et al. 2017). The US Food and Drug Administration (USFDA 1993) has indicated that seafood consumption represents ~90% of total human exposure to As. Arsenic found in the water of the South American region is mainly of natural origin, being one of the toxic elements of greatest concern for health in the area (Schenone et al. 2007, 2014; Rosso et al. 2013; Avigliano et al. 2015a). Particularly in south-western Atlantic estuaries, relatively high values of As have been reported in water and muscle of edible fish (Angeli et al. 2013; Avigliano et al. 2015a; Avigliano et al. 2016b; Gao et al. 2018). It has been indicated that the marine and estuarine catfish (family Ariidae) have a very high capacity to accumulate As in muscle (Angeli et al. 2013; Gao et al. 2018), where values higher than 40 mg/kg dry weight (dw) have been reported in species such as *Cathorops spixii* and *Genidens genidens* (Angeli et al. 2013).

On the other hand, high values of natural and anthropic essential element such as Co, Fe, Se, and Zn have been reported in surface water and fish muscle from South American water bodies (Avigliano and Schenone 2015; Avigliano et al. 2016b; da Rocha et al. 2017). Although these elements are essential, high intake rates could cause damage to health (FAO/WHO 1984; Goldhaber 2003; Mozaffarian 2009). For example, Se may directly influence myocardial function and response to injury (Mozaffarian 2009), while the high intake of Zn can bring gastrointestinal diseases (Goldhaber 2003). In this regard, it necessary to study the trace elements accumulation in fish species and estimate the potential risk for consumers, especially As due to its carcinogenic potential.

The anadromous catfish *Genidens barbus* was one of the most economically important species in estuaries from the southwestern Atlantic Ocean (Reis 1986; Tavares and Luque 2004; Velasco et al. 2007; MINAGRO 2018). The catfish has been included in the Red List of endangered species in Brazil (MMA 2014; Di Dario et al. 2015) and was classified as vulnerable in Argentina (Baigún et al. 2012). Then, its marketing and fishing have been prohibited since 2015 in Brazilian fishing areas (MMA 2014; Di Dario et al. 2015), due to a constant and marked decrease in catches caused by poor management policies and over-exploitation. Despite its vulnerable condition, the species is still captured in Argentina, where there is little data on the state of its populations. However, the resource recovery and the efficiency of fisheries management do not just depend on control of catch rates. At this point, it is important to evaluate if the habitat of *G. barbus* is compromised in terms of pollution and integrate that information with future management and conservation strategies. On the other hand, considering a potential pollution scenario, it is necessary to evaluate if the different populations are suitable for human consumption. Moreover, the determination of trace elements in tissues that are not consumed directly (liver and gill) is important for the fishmeal industry and to know the capacity to accumulate pollutants of this vulnerable species. This information is useful for public health in Argentina (where fishing is allowed) and for Brazil, in case the fishery recovers in the future.

The present study aims to analyze the presence and distribution of total As, Se, and metals (Co, Fe, and Zn) in water and different organs (muscle, gill, and liver) of catfish *G. barbus*, in two commercially important catch areas, and to assess the human health risk associated with muscle consumption.

Materials and methods

Sample collection

Water and adult catfish were caught in the Paranaguá Estuarine Complex (PEC) and Río de la Plata Estuary (RPE) (Fig. 1) in November 2016. PEC belongs to the Mountain subtropical rainforest ecoregion and the water surface temperature range from 18 to 30 °C (Lana et al. 2001), while RPE pertains to the template Paraná flooded savanna and the water temperature varies from 8 to 24 °C (Guerrero et al. 1997).

Because the catfish makes annual migrations between freshwater and saltwater environments (Avigliano et al. 2017), the concentrations of trace elements in tissues is the result of exposure to these different environments. Then, three water samples were collected representing the internal, middle, and external areas of each estuary (Fig. 1) to represent the distribution of As, Se, and metals along the salt gradient by which the catfish migrates annually (Avigliano et al. 2017). For each sampling point, a water sample was collected manually at 0.5-m depth with 0.5 L polyethylene-terephthalate bottles and transported to the laboratory at 4 °C. The salinity was measured at the sampling sites using a probe Horiba U-52.

The catfish were caught in the transition between the internal and middle areas from RPE (Paraná Guazú River) and PEC (Pontal do Sul) (Fig. 1). Catfish were caught using gillnets, hooks, and longlines; killed by percussive stunning (Van De Vis et al. 2003), and transported on ice to the laboratory. Fish were selected for analysis considering commercial consumption sizes (total length range 390–670 mm). Descriptive statistics of the individuals used is shown in Table 1.

Sample preparation and element quantification

Water

Water samples were filtered under vacuum using cellulose acetate filters (0.45 μm) and acidified to 0.2% (*v*/*v*) (pH < 2) with nitric acid (Merck Pro-Analysis) (APHA 2012). Concentration of As, Se, and metals was analyzed in triplicate by inductively coupled plasma mass spectrometry (ICP-MS)

Fig. 1 Sampling sites of water and fish (*Genidens barbus*) collected from Paranaguá Estuarine Complex (PEC) and Río de la Plata Estuary (RPE). Red points show the water sampling site (estuary areas: 1 = internal; 2 = middle; 3 = external), while red arrows indicate fish catch areas

using an Agilent 7500 (Agilent, Waldbronn, Germany) equipped with a Micro Mist nebulizer (Glass Expansion) and a quartz spray chamber.

Fish

Lapilli otoliths were removed in order to estimate the fish age. The left otolith of each pair was embedded in epoxy resin and sectioned transversely through the core to a thickness of 700 μm using a Buehler Isomet low-speed saw (Hong Kong, China). The number of rings or years (Reis 1986) in the otolith sections were counted with the piece immersed in ultrapure water using a stereomicroscope (Leica EZ4-HD, Singapore).

Liver, gill, and muscle (below the dorsal fin) of each specimen were dissected with a decontaminated ceramic knife. All laboratory tools were decontaminated using 10% HNO_3 *v*/*v* (Merck KGaA, Garmstadt, Germany) and rinsed two times with Milli-Q water (18.2 MΩ, Millipore, São Paulo, Brazil) between each dissection. The tissues were weighed and freeze-dried (Rificor L-A-B3, Buenos Aires, Argentina) for 24 h. Muscle and gill freeze-dried samples were ground with the assistance of liquid nitrogen by using the automatic cryogenic mill (Spex CertiPrep Inc., New Jersey, USA), while liver was ground in a mortar.

Arsenic, Co, Fe, Se, and Zn concentration in tissues was estimated by neutron activation analysis (NAA) according to the protocol detailed by Avigliano et al. (2016b). Each freeze-dried tissue (~ 300 mg) was pelletized and irradiated separately (Marrero et al. 2007). The irradiations were undertaken at the RA-3 reactor (thermal flux 3.10^{13} cm^{-2}/s; nominal power: 8 Mw) for 5 h at a predominantly thermal position. After the end of irradiation, two measurements (7 and 30 days decay) were made using GeHP detectors (Canberra, Meriden, USA) with 30% efficiency and 1.8 keV resolution for the 1332.5 keV^{60} Co peak.

The certified reference materials DORM-4 (fish protein certified reference material for trace elements, Ontario,

Table 1 Descriptive statistics (mean ± standard deviation and range) of individuals from each sampling site. *N* = sample size

	N	Total length (cm)		Total weight (g)		Age (year)	
Brazil	11	501 ± 104	(37.5–67.0)	2435 ± 1351	(890–3640)	8.3 ± 1.8	(6–13)
Argentina	12	568 ± 55	(49.0–62.0)	2004 ± 775	(1115–4250)	9.3 ± 2.0	(7–11)

Canada) was irradiated together with the samples for quantification. The concentration of elements was calculated by using a software developed at the laboratory and expressed in milligrams per kilogram wet weight (ww).

Quality assurance and quality control

The certified reference materials NIST1640a (trace element in freshwater, National Institute of Standards and Technology, USA) and SLEW-3 (trace element in estuarine water, National Research Council, Canada) were analyzed to support quality assurance and quality control (QA/QC) of the measurements in water. Analysis of these reference materials showed acceptable accuracy, with recovery from 99 to 109% (Table 2). The detection limits (LOD) based on three times the standard deviation of the blank signal were 0.01 for As and Se, 0.1 for Co, 0.03 for Fe, and 1.9 for Zn μg/L. Estimates of precision determined by the relative standard deviation percentage (RSD%) of triplicate determinations were lower than 2%.

The NAA laboratory is accredited under ISO/IEC 17025: 2005 by the Argentine Accreditation Agency (OAA) since 2001 (Resnizky et al. 2006) and it is inter-calibrate with the ones located in other countries (Munita et al. 2001). MR-CCHEN-003 standard reference material (trace elements in mussel muscle, Chilean Nuclear Energy Commission, Santiago de Chile, Chile) was analyzed to support the QA/QC of As, Se, and metals measurements in tissues. Analysis of MR-CCHEN-003 showed good agreement with a value obtained from 99 to 109% (Table 2).

The LOD (expressed in mg/kg, ww) calculated as three times the square root of the background level for the measured gamma peak (Knoll 2010) were 0.07 for As, 0.008 for Co, 1.9 for Fe, 0.10 for Se, and 1.25 for Zn. RSD of four replicates for tissue samples were lower than 4%.

Health risk from consuming fish

In order to estimate the non-carcinogenic and carcinogenic health risk via fish consumption, target hazard quotient (THQ) (Tao et al. 2012; USEPA 2015) was estimated.

The toxic effects of As are produced mostly by inorganic forms such as As (III) and As (V), however, fish mainly contains arsenobetaine, an organic non-toxic form of As (Kalia and Khambholja 2015; Gao et al. 2018). It has been found that the inorganic/organic As ratio ranged usually between 1 and 20%, except in some fish species, in which toxic As represented up to 30% (Lawrence et al. 1986; Gao et al. 2018). In this sense, a conservative approach was performed to estimate the non-carcinogenic and carcinogenic health risk through the catfish consumption, supposing that the normal amount of inorganic As ranged between 1 and 20% of the total (total As was not used). A similar approach has been performed by Kalantzi et al. (2015), who have used an inorganic/organic As ratio taken from literature. Moreover, the average consumption per capita of fish was considered (without discriminating species).

Estimates were based on Eq. 1, performed for each sampling sites separately:

$$THQ = \frac{Ef \times Fir \times Ed \times C}{Rfd \times Wab \times AT} \times 10^{-3} \quad (1)$$

where, *Ef* is exposure frequency (12 and 24 days/year for Argentina and Brazil, respectively) and *Fir* is the food ingestion rate (400 g/person/day). The average consumption per capita is of 4.8 and 9.6 for Argentina (12 days/year × 400 g/person/day) and Brazil (24 days/year × 400 g/person/day), respectively (FAO 2016); *Ed* is the exposure duration (70 years) (USEPA 1991); *C* is elemental concentration in fish muscle (mg/kg, ww). For As, 1 and 20% of the total As concentration in muscle was used; *Wab* is the average adult body weight (65 kg for an adult)

Table 2 Quality control results (mg/kg) obtained in the analysis of standard reference materials (SRM)

Element	SRM	Certified value	Experimental value	Relative values (%)
Water				
As	NIST1640a	8.0 ± 0.1	8.6 ± 0.1	108
	SLEW-3	1.36 ± 0.09	1.35 ± 0.09	99
Co	NIST1640a	20.2 ± 0.2	20.9 ± 0.5	107
Fe	NIST1640a	36.8 ± 1.8	43.0 ± 1.5	117
Se	NIST1640a	20.2 ± 0.2	20.7 ± 0.6	104
Zn	NIST1640a	52.2 ± 0.3	59.9 ± 0.4	109
Muscle				
As	MR-CCHEN-003	13.7 ± 1.8	13.5 ± 0.53	99
Co	MR-CCHEN-003	0.829 ± 0.077	0.83 ± 0.07	100
Fe	MR-CCHEN-003	585 ± 58	631 ± 27	108
Se	MR-CCHEN-003	4.42 ± 0.45	4.47 ± 0.35	101
Zn	MR-CCHEN-003	119.6 ± 9.5	119.7 ± 2.9	100

(Del Pino et al. 2005); *AT* is the average exposure time for non-carcinogens (365 day/year, 70 years); *Rfd* is the oral reference dose (mg/kg/day). *Rfd* were 0.0003 for inorganic As, 0.06 for Co, 0.7 for Fe, 0.005 for Se, and 0.3 for Zn (USEPA 2015).

THQ values higher than 1 mean that the level of exposure is greater than the reference dose; a daily exposure at this level could cause some health risks (Yi et al. 2011; Tao et al. 2012). Furthermore, in order to estimate a recommended limit weight for consumption of catfish, THQ has been matched to 1, using previously detailed parameters.

The carcinogenic risk (CR) for As was obtained by using the cancer slope factor (CSF = 1.5 mg/kg/day) (USEPA 2010):

$$CR = \frac{Ef \times Fir \times Ed \times [As] \times CSF}{Wab \times AT} \times 10^{-3} \quad (2)$$

Carcinogenic risk higher than 10^{-6} (chance of developing cancer throughout life are 1 in > 1,000,000) are considered to be negligible, range from 10^{-4} to 10^{-6} are typically considered acceptable, and values lower than 10^{-4} are considered unacceptable (USEPA 2010).

Statistical analysis

Element concentration in tissue did not fit the normal distribution or homogeneity of variance (Shapiro–Wilk, $p < 0.05$; Levene, $p < 0.05$) even after transformation $\log(x + 1)$. To ensure that differences in total length, total weight, and age fish did not confound patterns in elemental composition, the effect of these biological parameters on elemental concentrations were examined using Spearman correlation and analysis of covariance (ANCOVA). Length, total weight, and age fish were treated as the covariates, and location as the main factor (an ANCOVA was performed for each trace element separately). ANCOVA is robust to violations of the assumption of homogeneity of variance (Olejnik and Algina 1984). No correlation or co-variation was found between biological parameters and element concentrations ($p > 0.05$).

Nonparametric statistics were used to compare trace element levels between sampling sites and tissues. Mann–Whitney *U* test was used to compare element concentrations between sampling sites for muscle, liver, and gill. Moreover, Friedman test was performed to assess differences between tissues for each sampling sites. The statistical analyses were performed by using the PAST 3 software.

Results and discussion

Elements in water

Salinity (PSU) was 0, 15, and 27, and 0, 0.5, and 10 for internal, middle, and external areas from PEC and RPE, respectively. Arsenic concentration in water ranged from 0.4 to 1.4 μg/L and 1.5 to 15.8 μg/L for PEC and RPE, respectively (Table 3). Arsenic is of natural origin in PEC and RPE basins (Schenone et al. 2007; Rosso et al. 2011a, 2011b, 2013; dos Anjos et al. 2012; Rodríguez Castro et al. 2017). Total As levels in water found in this study were comparable to those reported by other authors for the middle area of the RPE (~ 3.9 μg/L) (Avigliano et al. 2015a). On the other hand, higher values of As (up to ~ 90 μg/L) were recorded in the Samborombón Bay (Schenone et al. 2007; Rosso et al. 2013; Rodríguez Castro et al. 2017), located in the southeast of the RPE. dos Anjos et al. (2012) have reported As concentrations from 8.7 to 22.5 μg/L in the PEC, being As (III), As (V) (16–88%), and arsenate (27–59%) the most important species found. Nevertheless, dos Anjos et al. (2012) have shown that the As concentration and speciation has a strong seasonal variation, probably due to different biogeochemical and hydrological scenarios. As dissolved phase from PEC depends strongly upon the type and concentration of suspended material and pH (parameters with strong seasonal variation) (Prestes et al. 2006; dos Anjos et al. 2012), which could explain the relatively low levels found in this work.

High spatial variability was observed for Co, Fe, Se, and Zn in both PEC and RPE systems (Table 3). Concentration of Co ranged between < 0.1 and 0.5 μg/L, while Se ranged from 3.0 to 78.1 μg/L (Table 3). Water levels of Fe (42–795) and Zn (< 1.9–78.9) were higher in PEC than in RPE.

Table 3 Mean (±SD) concentrations of trace elements (μg/L) in water samples from Brazil (Paranaguá estuarine complex) and Argentina (Río de la Plata estuary)

	Brazil			Argentina		
	Internal	Middle	External	Internal	Middle	External
As	0.4 ± 0.01	1.0 ± 0.01	1.4 ± 0.00	1.5 ± 0.11	4.9 ± 0.10	15.8 ± 0.16
Co	0.20 ± 0.00	< 0.1	< 0.1	< 0.1	0.50 ± 0.01	< 0.1
Fe	795 ± 6.36	146 ± 2.34	419 ± 6.70	61.2 ± 0.37	163 ± 0.98	42.0 ± 0.42
Se	3.0 ± 0.18	78.1 ± 1.17	35.7 ± 0.25	3.4 ± 0.10	4.0 ± 0.22	36.5 ± 0.01
Zn	75.1 ± 1.13	31.6 ± 0.32	78.9 ± 0.32	4.4 ± 0.03	18.0 ± 0.11	< 1.9

According to previous works, the concentration of some trace elements in RPE is geographically variable (Villar et al. 1999a, 1999b; Camilión et al. 2003; Ronco et al. 2008). For example, Zn values in sediments between 35 and 703 mg/kg (dw) were reported, while Fe varied between 1.7 and 4.5 mg/kg (dw), depending on the sampling site in the estuary (Villar et al. 1999a, 1999b; Camilión et al. 2003; Ronco et al. 2008). Spatio-temporal variation of water flow and sediment discharge in PEC and RPE could explain the high variability in the concentrations of elements.

The bioavailability of trace elements in water is related to different factors such as pH, temperature, and salinity (Langston 1983; dos Anjos et al. 2012). For example, it is known that As is precipitated with Fe during mixing at the freshwater–seawater interface (Langston 1983), whereas low salinity seems to promote the Zn motility from sediment to water (Riba et al. 2003). Even the As speciation in fish tissues seems to be heavily influenced by salinity (Gao et al. 2018). In this sense, the bioavailability of the elements studied may vary along the salt gradients studied; however, it is necessary to carry out additional studies to understand that environmental factors have a direct influence on availability.

Elements in tissues

In terms of environmental pollution, the determination of trace elements in water and different tissues is necessary to know if there is a transfer of contaminants from environmental matrices to the organisms and which are the target tissues/organs (Monferrán et al. 2016). In relation to consumption, tissues such as muscle can be ingested directly, while other tissues can be used to produce fishmeal, used to feed other animals such as pig, poultry and fish (Monferrán et al. 2016).

Concentrations of trace elements in tissues are given in Table 4. Arsenic concentration (mg/kg, ww) in muscle, gill, and liver ranged between 6.28 and 16.54, 0.41 and 1.72, and 1.26 and 2.90 for RPE and 5.82 and 23.50, 0.83 and 7.33, and 1.01–4.30 for PEC, respectively. Cobalt (mg/kg, ww) in tissues ranged between 0.01 and 2.9, while Se varied from 0.15 to 10.7 mg/kg (ww). Iron (mg/kg, ww) in muscle, gill, and liver ranged from 2.99 to 8.20, 48.6 to 95.9, and 137 to 773 for RPE and 2.08 to 4.78, 68.0 to 192, and 67.9 to 348 for PEC, respectively. Zinc levels (mg/kg, ww) in muscle, gill, and liver ranged between 3.97 and 1736, 176 and 446, and 392 and 2808 for RPE and 4.14 and 45.1, 363 and 2186, and 141 and 483 for PEC, respectively.

The most concentrated elements in gill and liver were Zn, Fe, Se and As (Zn > Fe > Se > As > Co), while for muscle, Zn, Fe, and As were the highest (Zn > Fe > As > Se > Co for PEC and As > Zn > Fe > Se > Co for RPE). For water, the trends varied in relation to the estuarine areas. Particularly, the trend was Fe > Zn > Se > As > Co for the internal and external areas from PEC and internal and external areas from RPE. The sequences Fe > Se > Zn > As > Co and Fe > Se > As > Zn ~ Co were observed for the middle area from PEC and external area from RPE, respectively. However, like tissues, the elements with the highest concentration in water were Zn, Fe, Se, and As, showing some pattern for both matrices. The difference observed in the order of concentration between tissues and water could be due to different routes or mechanism of incorporation, which can vary between tissues and elements (Clearwater et al. 2002).

Table 4 Mean (±SD) concentrations of trace elements (mg/kg, wet weight) in organs of *Genidens barbus* collected from Brazil (Paranaguá estuarine complex) and Argentina (Río de la Plata estuary). Different letters indicate statistical significant different ($p < 0.05$) between sampling sites

	Brazil	Argentina
Muscle		
As	14.5 ± 6.01 [a]	10.46 ± 2.79 [a]
Co	0.01 ± 0.005 [a]	0.007 ± 0.002 [b]
Fe	3.87 ± 0.82 [a]	4.60 ± 2.03 [a]
Se	0.40 ± 0.13 [a]	0.26 ± 0.08 [b]
Zn	17.6 ± 13.7 [a]	7.60 ± 4.28 [b]
Gill		
As	2.71 ± 2.05 [a]	0.74 ± 0.40 [b]
Co	0.07 ± 0.03 [a]	0.11 ± 0.03 [b]
Fe	120 ± 30.6 [a]	75.3 ± 14.2 [b]
Se	4.29 ± 1.56 [a]	2.21 ± 0.87
Zn	737 ± 527	341 ± 79.8
Liver		
As	2.69 ± 1.31 [a]	1.73 ± 0.51 [a]
Co	0.08 ± 0.05 [a]	1.32 ± 0.72 [b]
Fe	181 ± 100 [a]	265 ± 177 [b]
Se	3.05 ± 1.31 [a]	5.58 ± 2.33 [b]
Zn	267 ± 117 [a]	1543 ± 682 [b]

Levels of Se and Zn in muscle were higher in PEC than in RPE ($167 < U < 173$, $0.01 < p < 0.03$), while no differences were observed for Fe and As ($112 < U < 160$, $0.08 < p < 0.35$). Moreover, Co in muscle was higher in RPE than in PEC ($U = 72$, $p = 0.0002$). Arsenic, Se, Fe, and Zn concentration in gill were higher in PEC than in RPE ($89 < U < 93$, $0.0003 < p < 0.0010$), while Co was higher in RPE ($U = 203$, $p = 0.002$). Levels of Co, Fe, Se, and Zn in liver were higher in RPE than in PEC ($45 < U < 61$, $0.0001 < p < 0.07$), while no differences were observed for As ($U = 34$, $p = 0.16$).

Catfish is a diadromous migrant may move between environments with different salinity regimes (Avigliano et al. 2015b, 2016a, 2017). Avigliano et al. (2017) have found several migratory patterns, including freshwater residence and three types of cyclical migration between freshwater, estuarine, and marine environments. Then, could the plasticity in the use of habitat explain the wide variability in the concentration of elements found here? In this sense, the concentration of metals, As, and Se between different organisms may also be associated with the differential use of the habitat (pelagic, bottom frequenter, and benthic fish), as well as the consumption of different prey (Bustamante et al. 2003; Taylor et al. 2017; Zhang et al. 2018). In several cases, bottom frequenter and benthic fish have higher concentrations of trace elements than pelagic fish (Bustamante et al. 2003; Taylor et al. 2017; Gao et al. 2018; Zhang et al. 2018). *G. barbus* is a bottom frequenter and feeds on fish and benthonic invertebrates such as molluscs (Gastropoda, Bivalvia, Ostracoda) and polychaetes (Mendoza-Carranza and Vieira 2008). Gao et al. (2018) have reported high total As concentration (12–238 mg/kg dw) in potential preys such as whelk and scallop caught in Brazilian estuaries, which could be related to the high levels of As found in *G. barbus* muscle.

Arsenic accumulation order was muscle > liver > gills for RPE and muscle > liver ≈ gills for PEC (Table 5). The Friedman test revealed statistically significant differences between the three tissues from RPE ($T > 100$, $p < 0.0001$). In PEC, As concentration was significantly higher in muscle than in liver and gill ($T = 73$, $p = 0.0001$). Cobalt, Fe, Se, and Zn accumulation order was liver > gills > muscle for RPE ($T >$ 100, $p < 0.0001$). In PEC, Se accumulation order was gill > liver > muscle ($T = 38$, $p < 0.0001$), while liver > gills > muscle was found for Zn ($T = 73$, $p < 0.0001$). The sequence liver ≈ gills > muscle was found for Fe ($T = 18$, $p = 0.0002$) and Co ($T = 24$, $p < 0.0001$).

Pattern of metals, As, and Se accumulation in different tissues vary among species and environments. It is known that muscle is not a target organ for the accumulation during acute exposure; however, this tissue is a good indicator of chronic exposures (Jovičić et al. 2015; Monferrán et al. 2016). When pollutants exceed all defense barriers, the body begins to accumulate pollutants in this tissue (Monferrán et al. 2016). On the other hand, the incorporation of trace elements in gill can be associated by the absorption of pollutions on the gill surface, but also by the element complexation with the mucous (Clearwater et al. 2002; Dural et al. 2006; Erdoğrul and Erbilir 2007). The relatively high accumulative ability of the liver is the result of the activity of metallothioneins (Ploetz et al. 2007; Messaoudi et al. 2009). Considering the high power of accumulation of the liver, several authors have recommended this organ as the good environmental indicator of exposure to pollutants (Messaoudi et al. 2009; Jarić et al. 2011).

Table 5 Results and parameters of Friedman test between muscle (M), liver (L), and gill (G) of *Genidens barbus* for each element

	Sequence	T	p value
Brazil			
As	M > L = G	73.00	< 0.0001
Co	L = G > M	24.00	< 0.0001
Fe	L = G > M	18.00	0.0002
Se	G > L > M	38.00	< 0.0001
Zn	G > L > M	73.00	< 0.0001
Argentina			
As	L > M > G	> 100	< 0.0001
Co	L > G > M	> 100	< 0.0001
Fe	L > G > M	> 100	< 0.0001
Se	L > G > M	> 100	< 0.0001
Zn	L > G > M	> 100	< 0.0001

The results obtained in the present study were compared with the literature (Table 6). In *G. barbus*, the As trend was similar (muscle > liver and gill) to that observed in other catfish species from Brazilian coast (Gao et al. 2018) (species not informed) and in fish from other continents such as *Silurus glanis* (Squadrone et al. 2013) and *Sparus aurata* (Kalantzi et al. 2015) (Table 6). Unlike *G. barbus*, in other migratory species from RPE such as *Lycengraulis grossidens* and *Odontesthes bonariensis* have been reported relatively high levels of As in liver, followed for gill or muscle (Avigliano et al. 2016b). These patterns of As accumulation have also been found in other European species such as *Dicentrarchus labrax* (Kalantzi et al. 2015) and *Sander lucioperca* (Subotić et al. 2013). In *S. lucioperca*, the concentrations of Co, Se, and Zn were higher in liver, followed by gill and muscle; however, Fe levels were higher in the gill (Subotić et al. 2013). Like *G. barbus* from RPE, in several anadromous species such as such as *Anguilla anguilla*, *Mugil cephalus*, and *L. grossidens* (Yilmaz 2009; Avigliano et al. 2016b) have been reported high levels of Zn in liver, followed by gill and muscle. Nevertheless, like *G. barbus* from PEC, higher levels of Zn were reported in gill than in liver of other species such as *Synodus* sp. (El-Moselhy et al. 2014).

In relation to other species (Table 6), the high levels of As, Fe, and Zn found in tissues suggest that *G. barbus* has a high bioaccumulation power. High As concentration has been found in catfish muscle (up to 23.5 mg/kg, ww), but for most fish species, the total As level is usually below 5 mg/kg (ww) (Qiu et al. 2011; Liu et al. 2012; Squadrone et al. 2013; Kalantzi et al. 2015; Avigliano et al. 2016b). However, the literature reports a few examples with As concentrations in fish muscle higher than 10 mg/kg (ww) (Lawrence et al. 1986; Neff 1997; Angeli et al. 2013; Gao et al. 2018). Gao et al. (2018) have reported As concentration from 42.5 to 238 mg/kg dw (~ 8.5–48 mg/kg, ww) in different species fish from Brazilian coast. Angeli et al. (2013) have informed maximum levels from 27 to 40 mg/kg dw (~ 5.4–8 mg/kg, ww) in other Ariidea species such as *C. spixii* and *G. genidens* collected in PEC. On the other hand, Lawrence et al. (1986) have informed As levels up to 13.2 mg/kg (ww) in fish (several fish families) from Canadian waters.

Table 6 Trace elements in tissues of fish from Argentina, Brazil, and other regions of the world

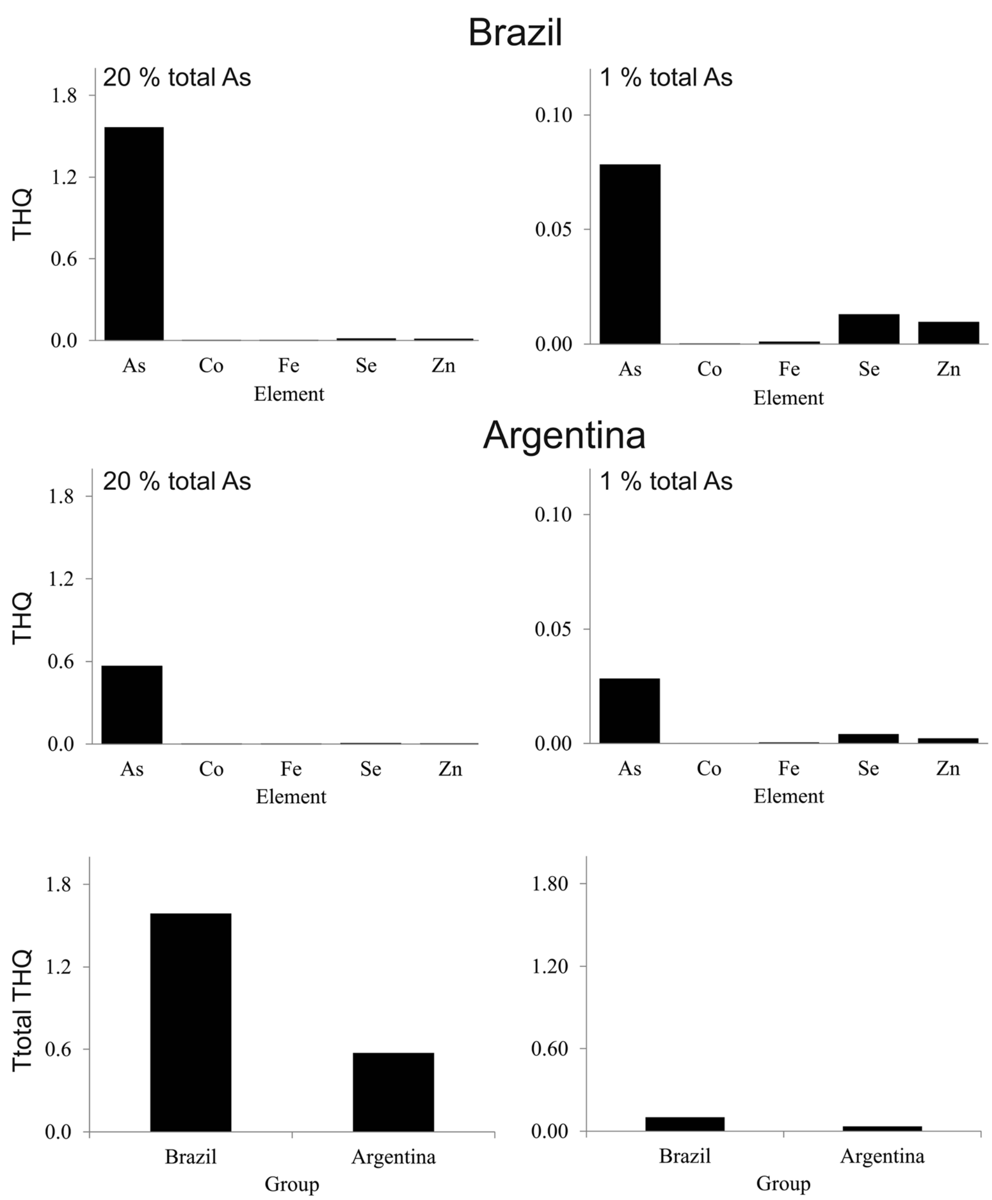
Specie	Site	Tissue	Unit (mg/kg)	As	Co	Fe	Se	Zn	Reference
Mugil liza	Plata River Estuary, Argentina	Muscle	ww	–	–	–	–	48.8	Marcovecchio (2004)
		Liver		–	–	–	–	52	
Micropogonias furnieri	Plata River Estuary, Argentina	Muscle	ww	–	–	–	–	20.5	Marcovecchio (2004)
		Liver		–	–	–	–	44.3	
Lycengraulis grossidens	Paraná River Delta, Argentina	Muscle	ww	0.9	0.01	5.2	–	6.8	Avigliano et al. (2016b)
		Liver		1.3	0.10	369.6	–	187.7	
		Gills		0.7	0.02	57.1	–	30.3	
Odontesthes bonariensis	Paraná River Delta, Argentina	Muscle	ww	0.1	0.01	2.2	–	5.8	Avigliano et al. (2016b)
		Liver		1.0	0.09	149.0	–	41.1	
Odontesthes bonariensis	Plata River Estuary, Argentina	Muscle	ww	0.03	0.21	7.53	0.55	12	Avigliano et al. (2015a)
Genidens genidens	Paranaguá Estuary, Brazil	Muscle	dw	2.2–5.4	–	–	–	20.7–86.9	Angeli et al. (2013)
Cathorops spixii	Paranaguá Estuary, Brazil	Muscle	dw	3.3–27.2	–	–	–	4.2–80.0	Angeli et al. (2013)
Catfish	North Sea and Açu Port, Brazil	Muscle	ww	8.9	–	–	–		Gao et al. (2018)
		Liver		2.5	–	–	–		
Anguila anguila	Mugla Lake, Turkey	Muscle	ww	–	–	–	–	106.7	Yilmaz (2009)
		Liver		–	–	–	–	199.3	
		Gills		–	–	–	–	147.8	
Caranx sp.	Red Sea, Egypt	Muscle	ww	–	–	7.12	–	2.88	El-Moselhy et al. (2014)
		Liver		–	–	71.9	–	27.3	
		Gills		–	–	46.0	–	15.1	
Ctenopharyngodon idellus	Huangtan River, China	Muscle		0.07	–	–	–	4.9	Liu et al. (2012)
		Liver		0.03	–	–	–	63	
		Gills		0.08	–	–	–	21	
Dicentrarchus labrax	Aegean Sea, Greece	Muscle	ww	1.06	0	5.49	0.15–0.2	6.3	Kalantzi et al. (2015)
		Liver		1.27	0.02	29.9	2.7–3.5	42.2	
		Gills		0.5	0.05	56.7	0.2–0.6	20.5	
Epinephelus sp.	Red Sea, Egypt	Muscle	ww	–	–	3.35	–	2.42	El-Moselhy et al. (2014)
		Liver		–	–	291	–	59.8	
		Gills		–	–	44.5	–	29	
Mugil cephalus	Mugla Lake, Turkey	Muscle	ww	–	–	–	–	98.6	Yilmaz (2009)
		Liver		–	–	–	–	402.6	
		Gills		–	–	–	–	176.9	
Oreochromis niloticus	Mugla Lake, Turkey	Muscle	ww	–	–	–	–	84.7	Yilmaz (2009)
		Liver		–	–	–	–	136.9	
		Gills		–	–	–	–	104.8	
Sander lucioperca	Danube River, Serbia	Muscle	dw	0.177	0.00017	17.9	0.001	15.1	Subotić et al. (2013)
		Liver		0.507	0.027	241	0.83	58.3	
		Gills		0.257	0.0057	73.0	0.58	40.1	
Sparus aurata	Aegean Sea, Greece	Muscle	ww	2.99	ND	2.77	0.16–0.23	4.9	Kalantzi et al. (2015)
		Liver		1.47	0.05	36.6	0.70–0.74	18.7	
		Gills		1.15	0.05	27.0	0.29–0.34	17.86	
Silurus glanis	Po River, Italy	Muscle	ww	0.06	–	–	–	–	Squadrone et al. (2013)
		Liver		0.01	–	–	–	–	

Table 6 (continued)

Specie	Site	Tissue	Unit (mg/kg)	As	Co	Fe	Se	Zn	Reference
		Gills		0.01	–	–	–	–	
Synodus sp.	Red Sea, Egypt	Muscle	ww	–	–	2.81	–	1.92	El-Moselhy et al. (2014)
		Liver		–	–	142.4	–	29.3	
		Gills		–	–	324.4	–	42.8	

The levels of Fe (all tissues), Co (all tissues), and Zn (muscle and gill) were similar to those reported for other eurialine species from RPE like *O. bonariensis* and *L. grossidens* (Avigliano et al. 2016b). However, Zn levels in liver of *G. barbus* were higher than those reported for other species from PEC and RPE such as *O. bonariensis*, *L. grossidens*, *C. spixii*, and *G. genidens* (Table 6). In relation to Se, the concentration found in the muscle, gill, and liver in this work

Fig. 2 Target hazard quotients (THQ) of each element and total THQ for two possible scenarios: 20% and 1% of the total As concentration



was higher than those recorded for *S. lucioperca*, *Sp. aurata*, and *D. labrax* (Subotić et al. 2013; Kalantzi et al. 2015).

Health risk from consuming fish

The levels of As in muscle were between 10 and 14 times higher than the recommended maximum levels established (1 mg/kg) by Argentine Food Code (AFC 2012), Brazilian National Health Surveillance Agency (ANVISA 2013), and European Commission (EFSA 2009). According to AFC (2012), ANVISA (1998) and FAO/World Health Organization (1984), the concentrations of Zn in muscle were below the recommended limits (50 mg/kg for FAO and ANVISA and 100 mg/kg for AFC). There is no recommended limit for Co, Fe, and Se (AFC 2012; ANVISA 2013).

Using the conservative THQ calculation approach (estimated as the worst scenario, 20% of the total As), the risk estimation was 1.58 for PEC and 0.57 for RPE (Fig. 2), suggesting that people would experience significant health risks from the intake of metals, As and Se through catfish consumption. The recommended maximum intakes per capita bases on this conservative approach (THQ = 1) were 6.1 and 8.4 kg/year (ww) for PEC and RPE, respectively.

When the 1% of the total As concentration was used, the risk estimated was 0.10 for PEC and 0.034 for RPE, indicating that people would not experience health risks (Fig. 2). In this case, the recommended maximum intakes were 95 and 138 kg/year (ww) for PEC and RPE, respectively.

Arsenic was the major risk contributor, accounting up to 98% of the total THQ. Long-term ingestion of inorganic As in humans could be associated with adverse health effects such as skin lesions (chronic arsenicism), developmental toxicity, cardiovascular diseases, neurotoxicity, and abnormal glucose metabolism (EFSA 2009).

Chances of developing cancer throughout life for 1 and 20% of the total As concentration were within the acceptable range, varying from 3.5×10^{-4} to 7.0×10^{-4} and 1.3×10^{-4} to 2.5×10^{-4} for PEC and RPE, respectively. Nevertheless, these values were close to the recommended limit (10^{-4}) indicating that the potential carcinogenic risk should not be ignored.

It is very important to remark that the main adverse effects are mainly attributed to inorganic As species, and that the dominating compound in fish muscle is arsenobetaine (non-toxic organic species) (Ciardullo et al. 2010; Özcan et al. 2016). Toxic inorganic arsenicals such as As (III) and As (V) were found in catfish muscle (species not informed) caught in the Brazilian coast, where these toxic compound represented only 1.6% of the total As (Gao et al. 2018). Then, if the toxic species in *G. barbus* represented a similar proportion, the risk index would be below 1. In this sense, our work highlights the importance of quantifying the As species in catfish muscle in order to generate more reliable risk estimates.

Moreover, it is important to clarify that in the study area are consumed not only catfish, but also others from freshwater, estuarine, and maritime shelf with an average consumption per capita of 4.8 and 9.6 for Argentina and Brazil, respectively (FAO 2016). It is possible that some of the others species fish have lower As concentration in muscle, which would further reduce the estimated risk.

Conclusion

This study fills a gap by providing data on total As, Se, and metal concentration and its compartments distribution in *G. barbus* from southwestern Atlantic estuaries. Highest concentrations of As were associated to muscle. In relation to the risk consumption, total As concentrations found in muscle were above the proposed limit values for human consumption. The conservative THQ calculation approach used suggests that people would experience significant health risks from the intake of metals, As and Se through catfish consumption (As was the most important contributor). Carcinogenic risk for As intake was within the acceptable range, nevertheless, these values were close to the recommended limit. Then, it is necessary to make As speciation analysis in order to calculate the probability of non-carcinogenic and carcinogenic risk with greater accuracy.

Acknowledgements The authors thank Rita Plá for her valuable assistance during the preparation of this manuscript. The also wish to acknowledge the anonymous reviewers for their constructive comments, which helped improve the manuscript.

Funding The authors thank CONICET, Universidad de Buenos Aires (UBACYT 20020150100052BA); ANPCyT (PICT 2015-1823); Comisión Nacional de Energía Atómica (CNEA); and CNPQ (141267/2015-1) for financial and logistic support.

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