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Toxic element determination in fish from Paraná River Delta (Argentina) by neutron activation analysis: Tissue distribution and accumulation and health risk assessment by direct consumption

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ABSTRACT

The concentrations of As, Co, Fe, Hg, and Zn were determined by INAA in muscle, gills, liver and scale of silversides (*Odontesthes bonariensis*) and sardine (*Lycengraulis grossidens*) from Paraná River Delta (Argentina) and the human health risk related to the consumption of muscle was evaluated. Detection limits were among 0.001 and 0.3 mg/kg, the RSD values were below 12% and certified reference material showing good accuracy. Considering all tissues and species, elements concentrations (mg/kg, ww) were: As: (0.35–1.30), Co (0.008–0.29), Fe (2.22–369.5), Hg (nd–1.11) and Zn (5.83–187.6). Most of the trace elements tended to be higher in *L. grossidens*, except for Co, Fe and Zn in gills and Hg in liver. Elements accumulation order for both species was Zn > Fe > As > Hg > Co in muscle and scale and Fe > Zn > As > Hg > Co for gills and liver. The highest concentrations of As and Co were found in liver, Hg in muscle and liver, Fe and Zn in liver and scale for sardine, and gills and liver for silversides. The levels of Hg in muscle were above the maximum recommended established by national or international guidelines. The THQ of each metal and the total THQ due to fish consumption were less than 1 for general population, suggesting that people would not experience significant health risks. However, for fishermen group, the total THQ was higher than 1, indicating the potential health risks of chronic exposure to contaminants.

1. Introduction

Commercial fish species that inhabit polluted water bodies worldwide are exposed to a wide range of contaminants that may accumulate in tissues and reach harmful levels (Al-Yousuf et al., 2000; Mol, 2011; Schenone et al., 2014). Trace elements found in the surface water of the South American region are of natural origin (e.g. As, V, Mo and U) and anthropic origin (e.g. Pb, Hg and Cr) (Avigliano et al., 2015; Rosso et al., 2013; Schenone et al., 2014, 2007). Nevertheless, heavy metal pollution in surface water bodies (e.g. lagoons, lakes and rivers) from this area may be mainly caused by increasing agricultural and industrial activities along with urban expansion (Avigliano et al., 2015). Particularly in the Paraná River Delta and Río de la Plata estuary (Fig. 1), relatively high values of toxic trace elements as As, Fe, Hg, Pb and Zn have been reported in water and muscle of edible fish (Avigliano et al., 2015; Marcovecchio, 2004; Marcovecchio and Moreno, 1993). In this context, it becomes necessary to assess the heavy metal and metalloid contents in commercial fish species and the resulting potential effects for consumers.

The silverside (*Odontesthes bonariensis*) and the sardine (*Lycengraulis grossidens*) (Fig. 2) are species euryhaline of Argentina, Uruguay, Brazil and Chile (Avigliano and Volpedo, 2013a; Dyer, 2006). In addition, the silverside was introduced in Europe and Asia. Fishing and commercial use of silverside and sardine makes them economically important species (Minagro, 2016). They are mostly caught in the Paraná River Delta and Río de la Plata estuary. The silverside particularly represents the second most important fishery resource for Argentina and Uruguay. A large proportion of the production is marketed for locally consumption and exported to Europe, Asia, and the United States of America (Minagro, 2016).

Nowadays, an increasing number of consumers, politicians and managers require information on contaminants in biota to evaluate the health and well-being of organisms and consumers

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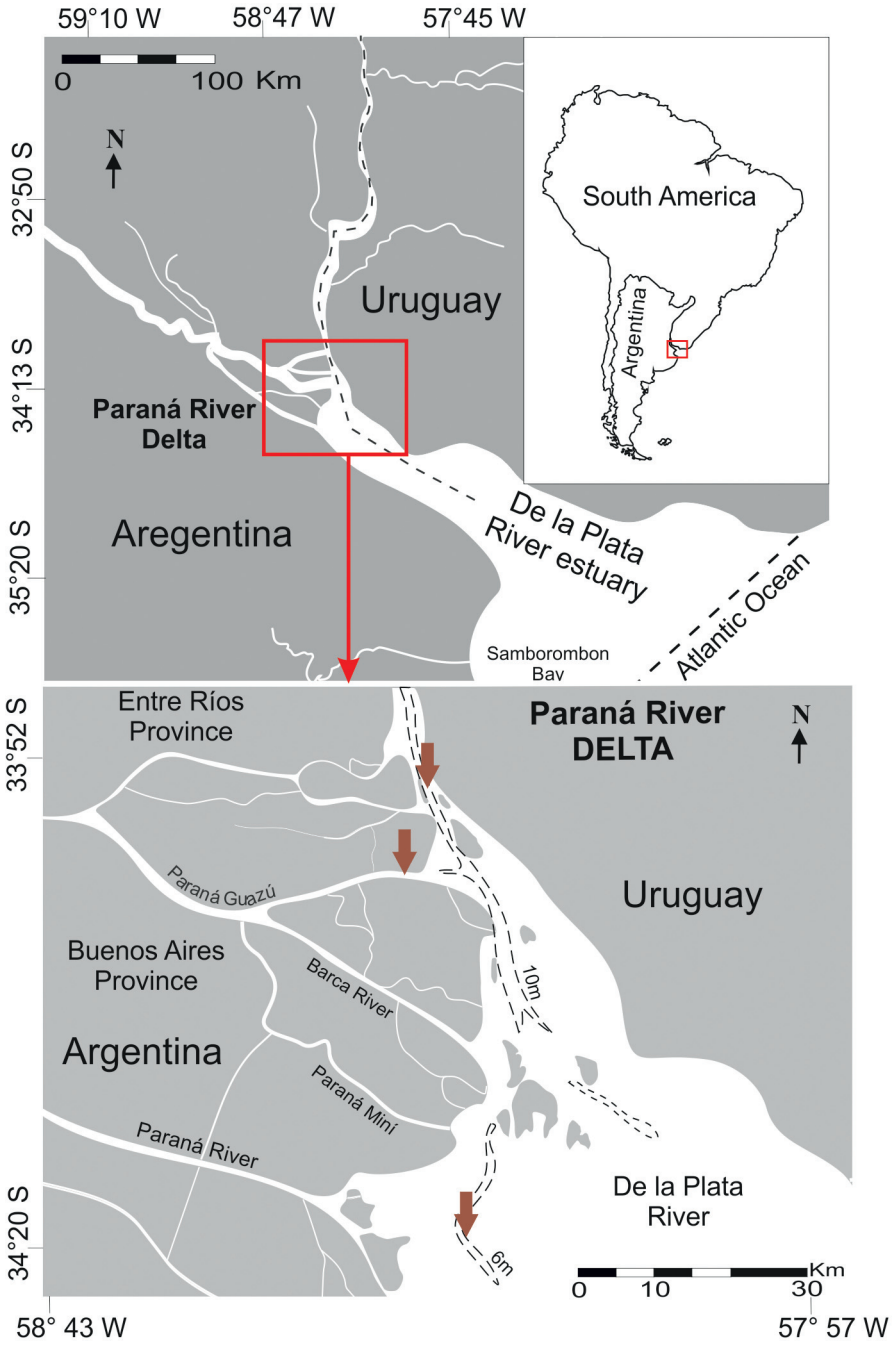

Fig. 1. Sampling sites in the Paraná River Delta, Plata Basin, South America.

(Burger et al., 2007). Many of research works focus on the accumulation of different elements within the muscle tissue, which is the main edible part of fish (Avigliano et al., 2015; Leung et al., 2014). Besides, the analysis of toxic elements in different fish tissues is important, considering that these tissues can be used to produce fish meal, used to feed other animals (pigs, poultry, etc.), including their use in aquaculture (Monferrán et al., 2016a). The presence of metal-binding proteins in some fish tissues, such as metallothioneins in liver, can lead to higher metal accumulation in liver than in muscle (Uysal et al., 2009). Tissue distribution pattern depends on both the trace elements involved and the animal species. Therefore, the analysis of this problem deserves particular attention (Monferrán et al., 2016a).

Among main analytical techniques used for the measurement of toxic or trace elements in fish tissue are inductively coupled plasma-optical emission (ICP-OES) (Habte et al., 2015; Uysal et al., 2008; Velusamy et al., 2014), and mass spectrometry (ICP-MS) (Avigliano et al., 2015; Schenone et al., 2014), atomic absorption spectroscopy (AAS) (Baharom and Ishak, 2015; Uysal et al., 2009), and more recently, instrumental neutron activation analysis (INAA) (Busamongkol et al., 2014; Heidarieh et al., 2013; Mohamed et al., 2016; Moon et al., 2015; Pantelica et al., 2012; Patra et al., 2014). Even though the INAA shows relative complexity, its sensitivity is comparable to ICP-MS and needs a minimum sample preparation since digestions are not needed. This point significantly reduces the time of sample pretreatment and cross contamination (Greenberg et al., 2011). In addition, INAA has greatly advanced in recent years lowering costs and it is becoming more readily available for studies of contaminants in different environmental matrices. The absence of the need to use analytical

Fig. 2. Silverside *Odontesthes bonariensis* (a) and sardine *Lycengraulis grossidens* (b) collected in Paraná River Delta (UNESCO Biosphere Reserve, BRDelta, Buenos Aires province, Argentina). Scale bar = 2.5 cm.

blanks is still an advantage of the technique (IAEA, 2001). Based on the above considerations, the objectives of the present study were: 1, to determine the content of trace elements (As, Co, Fe, Hg and Zn) in tissues (muscle, gills, liver and scale) of silversides (*O. bonariensis*) and sardine (*L. grossidens*) from Paraná River Delta (Argentina) and, 2, to analyze the human health risk related to the consumption of muscle for general population and fishermen.

This work identifies fish species of risk to human health in the region of study and contributes to food security and management practices.

2. Materials and methods

2.1. Study area

The Paraná River Delta (PRD) with an area of 14,000 km^2 is one of the largest deltas of South America (Fig. 1). It is a freshwater wetland that shows high environmental heterogeneity and biological diversity (Kandus and Adamoli, 1993) and is located in the Lower Plate Basin, Argentina and Uruguay. The southeast region that borders the Río de la Plata estuary is part of the UNESCO Biosphere Reserve (BRDelta) since 2000 (with a total area of 1000 km^2) (Fig. 1). The principal human activities in the BRDelta for survival and commercial purposes are the willow forest exploitation and fisheries.

2.2. Samples collection and preparation

Samples were collected according to the current regulations filling with standards and guidelines required by the Fisheries Provincial Direction of the Ministry of Agriculture. In this sense, the required permits of scientific fishing and transit guides that enable the capture and transport of specimens were processed. Adult fish were collected overnight by using a 3-layer 3 × 3 cm mesh net of 10 m length during November 2014. Once the nets were recovered, fish were killed by percussive stunning (Van De Vis et al., 2003) and transported on ice (in individual Ziploc® bags) to the laboratory. Fish were randomly selected for analysis considering commercial consumption sizes (total length range: 220–270 mm, N = 7 for *L. grossidens*; 250–300 mm, N = 7 for *O. bonariensis*). The axial muscle below the pectoral fin (±6 g) of each specimen was dissected with a decontaminated ceramic knife. Furthermore, scales, liver and gills were extracted through the same procedure. All laboratory tools were soaked in 10 % HNO_3 v/v (Merck KGaA, Garmstadt, Germany) for 48 h, rinsed five times with distilled water and then five times with ultrapure Milli-Q water (18.2 MΩ, Millipore, São Paulo, Brazil) (Türkmen and Ciminli, 2007). After dissection, the tissues were weighed by using an electronic balance (±0.001 g) (Sartorius AG ED2242, Göttingen, Germany) and freeze.

Once in the instrumental neutron activation analysis (INAA) laboratory, samples were stored in a freezer at about −30 °C. Gills, scale, liver and muscle samples have been freeze-dried by means of a Ricifor L-A-B3 (Buenos Aires, Argentina) freeze-dried machine, for 24 h. Liver was ground in a mortar. Gills, scale and muscle freeze-dried samples were ground with the assistance of liquid nitrogen by using the automatic Spex CertiPrep cryogenic mill (Spex CertiPrep Inc., New Jersey, USA), with one grinding cycle of about 1 min per gill samples (rate 15cps, 1 min of pre-cooling); one 30 s cycle per scale samples (rate 15 cps, 1 min of pre-cooling) and one cycle of about 2 min per muscle samples (rate 15 cps, 1 min of pre-cooling). Ground samples were freeze-dried again, for 24 h.

2.3. Determination of element concentrations by instrumental neutron activation analysis

Instrumental neutron activation analysis (INAA) was used for the determination of As, Co, Fe, Hg, and Zn concentrations. Neutron activation analysis (INAA) is a selective, very sensitive, and accurate technique for multi-elemental determination in a wide variety of matrices, independently of the chemical state of the elements (Marrero et al., 2007). According to Eckhoff et al. (1968), in the INAA, a small sample of the material to be analyzed is exposed to a thermal neutron flux from a reactor. Some of the stable nuclei can absorb a neutron by means of neutron capture reactions, better known as neutron/gamma reaction (n/γ). Many of these nuclei are radioactive and they are disintegrated with subsequent emission of a photon. Different γ rays are characteristic of each particular disintegration. Therefore, analyzing the γ rays emitted by the "activated" sample, it is possible to determine the present elements (through energy) and quantity (trough the intensity of the γ-rays). In this regard, the analysis method of neutron activation uses these characteristic decays of gamma rays to identify and quantify elements. For quantification and quality control, reference materials are irradiated together and measured all in the same detector with identical measurement geometry. By comparing the samples peak areas with the peak areas corresponding to the reference materials, the sample concentrations are calculated by using the following general equation of activation (Eckhoff et al., 1968):

$$A = \sigma \Phi N_T (1 - e^{-\gamma t}) e^{-\gamma t} \quad (1)$$

Where, A is activity in number of decays per unit time; Φ is the neutron flux, cm^{-2}/s; σ is the reaction probability, cm^2,N_T is the number of nuclei radiated (T stands for Target); γ is the decay constant (number of decays per unit time); t is the time of irradiation lasts.

This work is innovative in the combination of certified reference materials employed in order to perform the determinations. The certified reference materials NIST 1633b (coal fly ash) (Gaithersburg, Maryland, USA), IAEA-436 (trace elements and methylmercury in tuna fish fresh homogenate) (Vienna, Austria), DORM-2 (dogfish muscle certified reference material for trace metals) (Ontario, Canada) and Perkin Elmer Pure Plus N9300253 (Waltham, USA) standard solution were irradiated for quantification.

The determinations were performed in the Department of Nuclear Chemistry of Nuclear Chemistry and Health Sciences Management of the Ezeiza Atomic Centre (Argentine National Atomic Energy Commission) according to the protocol developed by Conti et al. (2016). This laboratory is accredited under ISO/IEC 17025: 2005, before the Argentine Accreditation Agency (OAA) since 2001 (Resnizky et al., 2006).

Each freeze-dried tissue sample was divided into four parts (300 mg each), wrapped in aluminium, pelletized and irradiated separately (Marrero et al., 2007). The irradiations were undertaken at the RA-3 reactor (thermal flux 3.1013 cm^2/s, 8 MW) for 5 h at a predominantly thermal position. The RA-3 research reactor with an 8 MW nominal power is a pool type reactor, moderated and cooled by light water, with graphite as reflector. The reactor operates in continuous cycles of 120 h/week using fuel of low enrichment uranium (Jasan et al., 2014).

Two measurements, with 7 and 30 days decay after the end of irradiation, were done using GeHP detectors (CANBERRA Industries Inc., Meriden, USA) (30% efficiency, 1.8 keV resolution for the 1332.5 keV^{60} Co peak).

For gamma spectra acquisition, Gamma Vision software was employed and elemental concentrations were calculated by using software developed at the INAA Laboratory (Marrero et al., 2007). This program automates the use of the equation of activation (Eq. (1)).

Fish muscle contents were measured for dry tissue. However, in order to compare these values with the recommended and suggested guidelines, they were corrected to wet weight (ww).

2.3.1. Quality assurance and quality control

Our laboratory inter calibrate the equipment used with the ones located in other countries (Munita et al., 2001) to ensure the quality of the measurements.

The MR-CCHEN-003 standard reference material (trace elements in mussel muscle) (Chilean Nuclear Energy Commission, Santiago de Chile, Chile) was analyzed to support the quality control of As, Co, Fe and Zn measurements. Additionally, DORM-2 standard reference material (dogfish muscle) was analyzed to support the quality control of Hg measurements. Both reference materials showed good accuracy (Table 1).

The detection limits (LOD) were calculated as three times the square root of the background level for the measured gamma peak (Eq. (2)) (Knoll, 2010; Marrero et al., 2007).

$$LOD = 3\sqrt{C_b} \tag{2}$$

Where C_b is the average number of counts from the background level for the measured gamma peak.

Detection limits for tissue samples (in mg/kg) were 0.01 for As, 0.001 for Co, 0.3 for Fe, 0.05 for Hg and 0.27 for Zn.

Estimates of precision were determined by the relative standard deviation percentage (RSD%) of quadruplicate for tissue samples. RSD values below 15% were accepted, with the data indicating good precision (Currie, 1999).

3. Health risk from consuming fish

In order to assess the non-carcinogenic health risk by consuming fish by local people, target hazard quotients (THQ) (Tao et al., 2012; USEPA, 2015) for *L. grossidens* and *O. bonariensis* were calculated. Calculations were based on the Eq. (3), performed for Eq. (2) subpopulation groups: general population and fishermen (as especially sensitive group), separately:

$$\mathrm{THQ} = \frac{\mathrm{EfEdFirC}}{\mathbf{RfdWabTa}} \times 10^{-3} \tag{3}$$

Where, *Ef* is exposure frequency. For general population, an exposure frequency of 3 days/year, while for fishermen, it was 20 days/year (FAO, 1997); *Ed* is the exposure duration (70 years) (USEPA, 1991); *Fir* is the food ingestion rate (200 g/person/day) (Monferrán et al., 2016a); *C* is the element concentration in muscle fish (mg/Kg, wet weight); *Wab* is the average adult body weight (65 kg for an adult in Argentina (Del Pino et al., 2005); *Ta* is the average exposure time for non-carcinogens (365 day/year, 70 years); *Rfd* is the oral reference dose (mg/Kg/day). The *Rfds* used were: 0.0003, 0.0003, 0.7, 0.0001, and 0.3 for As, Co, Fe, Hg and Zn, respectively (USEPA, 2015).

For the purposes of this paper, in accordance with the EPA guidelines, it was assumed that cooking has no effect on the toxicity of elements in muscle fish (USEPA, 1989). Then, the ingested dose is equal to the absorbed contaminant dose. In this study, the total THQ is treated as the arithmetic sum of the individual metal THQ values (Eq. (4)), derived by the method of Yi et al. (2011).

$$\text{Total THQ} = \sum_i THQ_i \tag{4}$$

Where, *i* represents the THQ for each element.

THQ values less than 1 means that the level of exposure is smaller than the reference dose; a daily exposure at this level is believed to be unlikely to cause any health risks (Tao et al., 2012; Yi et al., 2011). Therefore, in order to calculate the recommended limit weight for consumption of these species (or exposure frequency × food ingestion rate), we match the equation Total THQ (Eq. (4)) to 1, using previously detailed parameters and the concentrations of As, Co, Fe, Hg and Zn in muscle obtained in this work.

3.1. Statistical analysis

The trace element concentration did not fit the normal distribution and homogeneity of variance (Shapiro–Wilk, $p < 0.05$; Levene, $p < 0.05$) even after transformation log(x). Therefore, nonparametric statistics were used to compare trace element levels between species and tissues (Sokal and Rohlf, 2012). Post hocinter-group comparisons of element levels (between pairs of species) were performed by the non-parametric Mann–Whitney *U* test for two independent samples. We applied the non-parametric Kruskal–Wallis test for k independent samples to test the differences between the levels of eighteen elements (As, Co, Fe, Hg and Zn) between four different tissues (liver, muscle, scale and gills) of two fish species (*L. grossidens* and *O. bonariensis*).

Differences were considered to be statistically significant at $p < 0.05$. The statistical analyses were performed by using the InfoStat® software. All values were expressed as mean ± standard deviation (N = 7).

4. Results and discussion

4.1. Element concentrations in fish and distribution in different compartments

Concentrations of trace elements in muscles, liver, gills and scale of fish are given in Table 2. Trace elements concentrations (in mg/kg, ww) were: As (nd–1.30), Co (0.00846–0.209), Fe (2.22–369), Hg (nd–1.11) and Zn (5.83–187).

Most of the trace elements tended to be higher in *L. grossidens*, except for Co, Fe and Zn in gills and Hg in liver (Table 2). The Mann-Whitney *U* test revealed significant differences between fish

Table 1
Quality control results (mg/kg) obtained in the analysis of standard reference materials; MR-CCHEN-003 (trace elements in mussel muscle) was used for As, Co, Fe and Zn and DORM-2 (trace elements in dogfish muscle) for Hg.

Element	Certified value	Experimental value	Recovery values
As	13.7 ± 1.8	13.3 ± 0.64	97.08
Co	0.829 ± 0.077	0.73 ± 0.09	88.05
Fe	585 ± 58	613 ± 64	104.78
Hg	4.64 ±0.26	5.00 ±1.00	107.75
Zn	119 ± 9.5	126 ± 5.19	105.88

Table 2
Mean (±SD) concentrations of trace elements (mg/kg wet weight) in some organs of fish species collected from Paraná River Delta and parameters of Mann–Whitney *U* tests (N = 7).

	Element	*Lycengraulis grossidens-sardine*	*Odontesthes bonariensis-silverside*	*Z*	*P*
Muscle	As	0.859 ± 0.488	0.0922 ± 0.0120	63	0.001*
	Co	0.0112 ± 0.00843	0.00846 ± 0.00336	48	0.540
	Fe	5.22 ± 1.71	2.22 ± 0.650	62	0.002*
	Hg	0.597 ± 0.172	0.510 ± 0.0561	50	0.280
	Zn	6.85 ± 1.94	5.827 ± 1.41	45	0.710
Gills	As	0.676 ± 0.390	0.525 ± 0.266	18	0.030*
	Co	0.0190 ± 0.00231	0.209 ± 0.0743	21	0.001*
	Fe	57.1 ± 10.8	166 ± 27.2	23	0.004*
	Hg	0.323 ± 0.0589	ND		
	Zn	30.3 ± 5.13	120 ± 12.0	21	0.001*
Liver	As	1.30 ± 0.607	0.986 ± 0.683	17	0.352
	Co	0.103 ± 0.0836	0.0867 ± 0.0234	32	0.745
	Fe	370 ± 76.5	149 ± 94.8	16	0.018*
	Hg	0.717 ± 0.282	1.11 ± 0.289	39	0.118
	Zn	188 ± 97.4	41.1 ± 10.1	15	0.004*
Scale	As	0.346 ± 0.221	ND		
	Co	0.0260 ± 0.00854	0.0290 ± 0.01	40	0.873
	Fe	29.8 ± 13.1	18.7 ± 9.05	54	0.101
	Hg	ND	ND		
	Zn	61.9 ± 10.4	40.3 ± 7.80	61	0.004*

* Asterisks indicates statistical significant different ($p < 0.05$); Z: Mann–Whitney *U* test statistic; P: p-value; ND: not detected.

species with regard to the same elements ($p < 0.05$). Highest Asand Fe concentrations in muscle were found in *L. grossidens*. In gills, Co, Fe and Zn concentrations were found to be higher in *O. bonariensis*, while As showed a high concentration in *L. grossidens.* In liver, Fe and Zn concentrations were higher in *L. grossidens*, while Zn showed a high concentration in *L. grossidens* scale. There are no previous comparisons as to the concentration of trace elements in tissues between both species. Literature is scarce in relation to the concentration of trace elements in *L. grossidens* tissues. Eysink (1990) has reported a concentration of 0.26 mg/kg of Hg in muscle of specimens caught in Sao Paulo, Brazil. As in our results, this value is higher in *L. grossidens* in relation to that found in *O. bonariensis* captured in San Roque Lake (Argentina). Even so, the Hg value obtained by Eysink (1990) is similar or lower than those reported by other authors for *O. bonariensis* captured in some lagoons in Argentina (Avigliano et al., 2015).

These differences could be related to different physiological factors and/or ecological (habitat use, eating habits, etc.). Both species are migratory, however, *O. bonariensis* makes seasonal migrations between the Paraná Delta and the Río de la Plata estuary (Avigliano and Volpedo, 2013b), while there are two populations of *L. grossidens* (Mai et al., 2014). One of them is resident and the other, anadromous, making annual reproductive migrations to the sea (Mai et al., 2014). In relation to food, both species are filter feeders and feed on molluscs, crustaceans and small fish. However, there is evidence that the resident population of *L. grossidens* is essentially ichthyophagous (Bortoluzzi et al., 2006; Escalante and Grosman, 2001).

The concentration of As, Co, Fe, Hg, and Zn reported for muscle, gills, liver and scale of different species, including those studied in this work is summarized in Table 3. The levels of As, Fe and Zn in muscle of *O. bonariensis* were generally lower than those reported by other authors for the same species, with the exception of San Roque Reservoir (Córdoba, Argentina) where high values of As were reported (Monferrán et al., 2016a,b). On the other hand, Co and Hg levels were similar to those reported for other sites in the Plata basin (Avigliano et al., 2015; Rosso et al., 2013). In relation to Hg, the concentration found in the muscle in this work was higher than that recorded by Monferrán et al. (2016a,b). The concentration of Hg in muscle in *L. grossidens* was higher than the reported for the city of Sao Paulo (Brazil) (Eysink, 1990). Trace elements accumulation order for both species was Zn> Fe> As> Hg> Co in muscle and scale and Fe> Zn> As> Hg> Co for gills and liver. The sequence Fe> Zn> As> Hg> Co was also observed in muscle, liver and gills of catfish (*Silurus glanis*) and pikeperch (*Sander lucioperca*) (Subotić et al., 2013). While the sequence Zn> Fe> As> Hg> Co was previously reported for gills and liver of carp (*Cyprinus carpio*) (Subotić et al., 2013). Furthermore, the sequence Zn > As> Hg was also observed in other species as *Mylopharyngodon piceus, Erythroculter ilishaeformis, Coreius guichenoti, Rhinogobio cylindricus* despite having different habits (Yi et al., 2011). *M. piceus* and *R. cylindricus* are benthic species while *E. ilishaeformis* and *C.guichenoti* swim at different depths of the water column (Yi et al., 2011).

With the exception of Hg, the order of concentration of the different elements in water, in the Río de la Plata estuary is similar to that found in gills and liver (Fe> Zn> As> Co> Hg) in this work (Avigliano et al., 2015). In the upper basin of the Paraná river, levels of Zn between 14.4-42.0 μg/L and higher concentrations of Fe (up to 476 μg/L) have been reported, both elements from natural origin (Avigliano and Schenone, 2015). However, the levels of these elements increase down the river, between the delta and the Río de la Plata estuary (Zn = 81 and Fe = 681 μg/L) (Avigliano and Schenone, 2015), probably as a consequence of the large cities located by the river (e.g. Buenos Aires, La Plata and Rosario in Argentina and Montevideo in Uruguay). The As is of natural origin in the study area and particularly high values are recorded in the Samborombón Bay (up to 106 μg/L) (Rosso et al., 2011), located in the southeast of the Río de la Plata estuary.

High concentration of Hg (1.9–6.8 mg/kg) was found in sediments from different tributaries to Río de la Plata estuary (Ronco et al., 2008), while in the water values they are less than 0.071 μg/L (Avigliano et al., 2015). Mercury is especially concerning because its inorganic form is biologically transformed in aquatic environments into methylmercury (MeHg), a lipophilic organic compound that bioaccumulates and biomagnifies as it moves up the aquatic food chain (Carrasco et al., 2011; Olmedo et al., 2013). As a result, human populations with an elevated dietary intake have the highest potential exposure to MeHg and are at an increased risk for developing neurotoxic effects.

If we analyse the order of decreasing concentration between tissues, variations between species and trace elements are observed. For As, the order of concentration was liver > muscle >

Table 3
Trace elements in tissues of fish from the Plata Basin and other regions.

Specie	Site	Tissue	Unit (mg/kg)	As	Co	Fe	Hg	Zn	Reference
Lycengraulis grossidens	Paraná River Delta, Argentina	Muscle	ww	0.9	0.0	5.2	0.6	6.8	This paper
		Liver		1.3	0.1	369.6	0.7	187.7	
		Gills		0.7	0.0	57.1	0.3	30.3	
		Scale		0.3	0.0	29.8	–	62.0	
Odontesthes bonariensis	Paraná River Delta, Argentina	Muscle	ww	0.1	0.0	2.2	0.5	5.8	This paper
		Liver		1.0	0.1	149.0	1.1	41.1	
		Gills		0.5	0.2	166.3	–	120.3	
		Scale		–	0.0	18.7	–	40.3	
Lycengraulis grossidens	Iguape, Sao Pablo, Brazil	Muscle	ww		–	–	0.26	–	(Eysink, 1990)
Odontesthes bonariensis	Río de la Plata estuary, Argentina	Muscle	ww	0.03	0.01	7.53	0.3	12	(Avigliano et al., 2015)
Odontesthes bonariensis	Chasicó Lake, Argentina	Muscle	ww	0.76	0.01	4.56	0.42	18.4	(Avigliano et al., 2015)
Odontesthes bonariensis	Quequén Salado River, Argentina	Muscle	dw	1.23	–	–	–		(Rosso et al., 2013)
Odontesthes bonariensis	Chascomús lagoon, Argentina	Muscle	dw	–	–	–	–	8.12–88.4	(Vazquez et al., 2015)
		Liver		–	–	–	–	62–641	
		Gills		–	–	–	–	16.2–228	
		Scale		–	–	–	–	38.7–307	
Odontesthes bonariensis	San Roque Lake, Argentina	Muscle	dw	2.6–3.9	–	10–29	0.04–0.09	52–62	(Monferrán et al., 2016a, 2016b)
		Liver		17.1–17.5	–	166–619	0.013	94–98	
		Gills		9.9–17.3	–	141–358	0.029	113–133	
Other species									
Anguila anguila	Mugla Lake, Turkey	Muscle	ww	–	–	–	–	106.71	(Yilmaz, 2009)
		Liver		–	–	–	–	199.32	
		Gills		–	–	–	–	147.84	
Caranx sp.	Red Sea, Egypt	Muscle	ww	–	–	7.12	–	2.88	(El-Moselhy et al., 2014)
		Liver		–	–	71.9	–	27.3	
		Gills		–	–	46.05	–	15.1	
Ctenopharyngodon idellus	Huangtan River, China	Muscle		0.07	–	–	0.005	4.9	(Liu et al., 2012)
		Liver		0.03	–	–	0.01	63	
		Gills		0.08	–	–	0.02	21	
		Scale		0.02	–	–	0.003	25	
Cyphocharax voga	Chascomús lagoon, Argentina	Muscle	dw	0.27	0.058	52.1	–	20.8	(Schenone et al., 2014)
		Scale		0.34	0.22	131	–	57.2	
Dicentrarchus labrax	Aegean Sea, Greece	Muscle	ww	1.06	0	5.49	0.07	6.38	(Kalantzi et al., 2015)
		Liver		1.27	0.02	29.96	0.02	42.26	
		Gills		0.5	0.05	56.7	0.01	20.52	
Epinephelus sp.	Red Sea, Egypt	Muscle	ww	–	–	3.35	–	2.42	(El-Moselhy et al., 2014)
		Liver		–	–	291.7	–	59.8	
		Gills		–	–	44.5	–	29	
Lutjanus malabaricus	Hailing Bay, China	Muscle	ww	0.14	–	–	0.29	16	
Micropogonias furnieri	De la Plara estuary, Argentina	Muscle	ww	–	–	–	0.11	20.5	(Marcovecchio, 2004)
		Liver		–	–	–	0.13	44.3	
Mugil cephalus	Mugla Lake, Turkey	Muscle	ww	–	–	–	–	98.6	(Yilmaz, 2009)
		Liver		–	–	–	–	402.61	
		Gills		–	–	–	–	176.93	
Mugil liza	De la Plara estuary, Argentina	Muscle	ww	–	–	–	0.4	48.8	(Marcovecchio, 2004)
		Liver		–	–	–	0.53	52	
Oreochromis niloticus	Mugla Lake, Turkey	Muscle	ww	–	–	–	–	84.76	(Yilmaz, 2009)
		Liver		–	–	–	–	136.95	
		Gills		–	–	–	–	104.82	
Sander lucioperca	Danube River, Serbia	Muscle	dw	0.177	0.00017	17.9	1.327	15.14	(Subotić et al., 2013)
		Liver		0.507	0.027	241.0	1.667	58.37	
		Gills		0.257	0.0057	73.0	1.527	40.11	
Sparus aurata	Aegean Sea, Greece	Muscle	ww	2.99	ND	2.77	0.1	4.99	(Kalantzi et al., 2015)
		Liver		1.47	0.05	36.6	0.02	18.77	
		Gills		1.15	0.05	27.0	0.01	17.86	
Silurus glanis	Po River, Italy	Muscle	ww	0.06	–		0.34	–	(Squadrone et al., 2013)
		Liver		0.01	–	–	0.25	–	
		Gills		0.01	–	–	0.08	–	
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	
Trachinotus blochii	Hailing Bay, China	Muscle	ww	0.22	–	–	0.22	23.5	(Qiu et al., 2011)

dw: Dry weight; ww: Wet weight.

gills > scale in *L. grossidens* and liver > gills > muscle in *O. bonariensis*. For Co, the order was liver> gills> scale> muscle in both species. For Hg, muscle > liver > gills and liver > muscle in *L. grossidens* and *O. bonariensis,* respectively. Finally, for Fe and Zn, the trends were liver> scale> gills> muscle and gills > liver > scale > muscle in *L. grossidens* and *O. bonariensis*, respectively. The Kruskal–Wallis test revealed statistically significant differences for several trace elements among tissues (Table 4). Both species showed the highest concentrations of As, Zn and Fe in the liver ($p < 0.004$). For Co, the highest concentrations fluctuated between the liver in *L. grossidens* ($p < 0.003$) and the gills in *O. bonariensis,* while for Hg, the highest concentrations fluctuated between the liver and the muscle in *L. grossidens* ($p < 0.005$) and the liver and the gills in *O. bonariensis* ($p < 0.0003$) (Table 4). Comparing with other works, patterns of accumulation of As in different tissues vary among species and environments (Table 3). In *S. lucioperca* the trend was similar to that observed in *O. bonariensis* (liver> gills> muscle). In the species *S. aurata* and *Silurus glanis* higher values of As in the muscle have been reported in relation to the gills and liver (Kalantzi et al., 2015; Squadrone et al., 2013).

In the pikeperch (*Sander lucioperca*), the levels of Co, Hg and Zn were higher in liver, followed by gills and muscle. However, in the pikeperch, Fe levels were higher in the gills and not in the liver (Subotić et al., 2013). In other river species as *Silurus glanis,* Hg concentration was higher in the muscle, followed by the liver and the gills (Squadrone et al., 2013). As in *L. grossidens* in several anadromous species have been reported high levels of Zn in liver, followed by gills and muscle, such as eel (*Anguilla anguilla),* mullet (*Mugil cephalus*), and even freshwater species such as Nile tilapia (*Oreochromis niloticus*) (Yilmaz, 2009), *Sander lucioperca* (Subotić et al., 2013) and those marine as *Dicentrarchus labrax, Sparus aurata* (Kalantzi et al., 2015), *Epinephelus* sp. (El-Moselhy et al., 2014). However, in other species as *Synodus* sp. higher levels of Zn were reported in gills in relation to the liver (El-Moselhy et al., 2014), as observed in this work for *O. bonariensis*. In relation to Fe, other species such as *S. lucioperca*, *D. labrax, S. aurata, Epinephelus sp., Caranx sp*. (El-Moselhy et al., 2014; Kalantzi et al., 2015; Subotić et al., 2013) showed the same pattern of accumulation observed for *L. grossidens* while in *Synodus sp*. (El-Moselhy et al., 2014) was observed the same trend as in *O. bonariensis.*

The concentration of Co, Fe and Zn was higher in the scales in relation to muscle in both species. This trend has been previously reported in the small shad (*Cyphocharax voga*) caught in lagoons associated to the Plata basin (Schenone et al., 2014), in species of other continents as *Tilapia nilotica* from Egypt (Rashed, 2001). Some authors suggest that it may act as a detoxification pathway accumulating toxic elements in scales (Rashed, 2001; Schenone et al., 2014). However, the concentration of As and Hg was low in the scales in relation to the rest of tissues as previously observed by other authors in the grass carp (*Ctenopharyngodon idellus*) (Liu et al., 2012).

Table 4
Results and parameters of Kruskal–Wallis tests between four different tissues for each trace element and fish species. a, b and c: Different letters indicate statistical significant differences among tissues ($p < 0.05$).

	Lycengraulis grossidens-sardine					
Element	Muscle	Gills	Liver	Scale	H	P
As	b	b	b	a	13.5	0.003
Co	a	a	b	a	13.8	0.003
Fe	a	bc	c	ab	20.4	0.000
Hg	b	a	b	ND	11	0.004
Zn	a	ab	c	b	18.2	0.000
	Odontesthes bonariensis-silverside					
As	ab	a	b	ND	6.0	0.035
Co	a	a	a	a	0.0	0.100
Fe	a	bc	b	ab	21.5	0.000
Hg	a	ND	a	ND	0.01	0.501
Zn	a	b	b	a	5.8	0.000

a, b, c: Different letters indicate statistical significant different between tissues ($p < 0.05$); H: Kruskal–Wallis test statistic; P: p-value; ND: not detected.

5. Health risk from consuming fish

The levels of Hg in muscle were above the recommended maximum levels established by the Argentine Food Code and the European Commission (Table 5). The concentrations of As and Zn were below the recommended limits (there is no recommended limit for Co and Fe).

For the general population, the THQ of each metal (0.04 for As, 0.00088 for Co, 0.00014 for Fe, 0.14 for Hg and 0.00055 for Zn) and total THQ (0.18) due to fish consumption were less than 1 (Fig. 3), suggesting that people would not experience significant health risks from the intake of individual and all metals through fish consumption. For the fishermen group, the THQ of each metal were less than 1 (0.26 for As, 0.005 for Co, 0.00089 for Fe, 0.93 for Hg and 0.0035 for Zn), while the total THQ was 1.21, indicating potential health risks (Fig. 3).

For both groups, THQ values of Hg and As were higher than the comparable values for Co, Fe and Zn. The potential health risk of Fe was the lowest, which may be attributed to its higher oral reference dose. The estimated THQ for individual metal decreased in the following sequence: Hg > As > Co > Zn > Fe. In relation to the total THQ, the Hg was the major risk contributor, accounted for 76.8% of the total THQ. The following highest risk contributor element was As, representing about 22.3% to the total THQ. The risk contributions of Co, Fe and Zn were relatively low at about 0.46%, 0.07% and 0.29%, respectively.

In short, only the group of fishermen is associated with a non-carcinogenic health risk for direct consumption of contaminated food with the values reported here. The risk would mainly be associated to contamination by Hg and As that represents the 99.1% of total THQ. In this respect, the frequent consumption of these fish could cause damage to health or impair the quality of life. All the same, the specific health effects of the observed levels of Hg and As in this work are not easy to determine because these elements may have additive effects (Hallenbeck, 1993). For that matter, it is difficult to determine the dose-response relationship. For information purposes, we can comment that non-carcinogenic effects associated with the ingestion of mercury-contaminated fish are ataxia, loss of peripheral vision, “pins and needles” feelings, usually in hands, feet, and around the mouth, lack of coordination of movements, impairment of speech and hearing, and walking muscle weakness dysarthria (USEPA, 2009). Relatively high concentrations are associated with impaired hearing, cerebral palsy and severe developmental retardationin prenatally exposed children as well as sensory disturbance as a symptom of fatal methylmercury poisoning in exposed laboratory workers (Avigliano et al., 2015; EFSA, 2012). The main adverse non-

Table 5
Permissible limits for fish consumption according to organisms different (mg/kg wet weight).

	As	Co	Fe	Hg	Zn	Pb[a]
Argentinean Food Codex (AFC, 2012)	1	–	–	0.5–1	100	0.3
European Commission (EFSA, 2012, 2010, 2009)	1	–	–	0.5–1	–	0.3
FAO/WHO (FAO/WHO, 1989, 1984)	–	–	–	–	50	0.5

[a] Lead was not determined in this work. Guideline values are reported for comparative purposes.

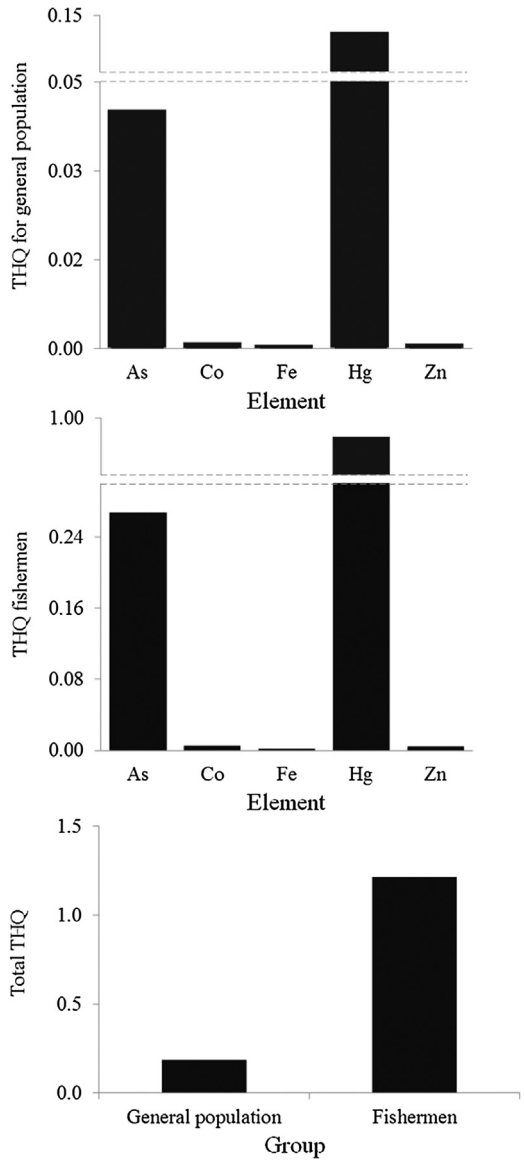

Fig. 3. Target hazard quotients of each element and total THQ for general population and fishermen groups.

carcinogenic effects reported to be associated with long term ingestion of inorganic arsenic in humans are skin lesions (e.g. chronic arsenicism), developmental toxicity, neurotoxicity, cardiovascular diseases, abnormal glucose metabolism and diabetes (EFSA, 2009). As early as the beginning of the century, physicians noted an increased incidence of clinical skin alteration and high risk of lung and kidney cancers in patients from Argentina (e.g. Córdoba province). The high arsenic content of drinking water from wells of natural origin in this region was found to be the cause (Aballay et al., 2012; Bundschuh et al., 2012; Pou et al., 2011; Steinmaus et al., 2010).

It is important to clarify that the adverse effects of As in humans is attributed to inorganic arsenic species and it is known that the dominating As compound present in fish is arsenobetaine (considered to be harmless) (Ciardullo et al., 2010; Özcan et al., 2016). However, toxic inorganic arsenicals, including arsenous acid (AsIII) and arsenic acid (AsV), were also found in muscle fish (Ciardullo et al., 2010; Özcan et al., 2016). Organic arsenic species such as monomethylarsonous acid and dimethylarsinic acid were also found in fish and they are classified as cancer promoters (Özcan et al., 2016). Given this, it is possible that the risk in relation to As may be slightly overestimated considering that we perform the calculation with the total As concentration, with no discrimination of the most toxic species.

In this work, some potentially toxic elements such as Pb were not determined. However, if we take into account the Pb values reported for muscle of *O. bonariensis* collected at the Río de la Plata estuary, 90 km south from the Paraná Delta (0.19 mg/kg) (Avigliano et al., 2015), the total THQ would have an increase of only 0.2% in relation to the total THQ calculated in this work for both groups. Consequently, Pb would not contribute significantly to the risk index.

The maximum limit of consumption per capita calculated by matching the equation of total THQ to 1 was of 3.30 kg/year. Considering that in the area are consumed not only the species studied here, but also others from the Plata Basin and maritime platform with an average consumption per capita of up to 12.5 kg for general population (FAO, 1997), it is possible that part of the population is ingesting more than 3.30 kg/year of fish. This is particularly worrying considering coastal or fishing populations, where the total consumption could double the average rate for the area. In these cases, there would be a real risk for people considering only the two species studied here. On the other hand, considering that these species are exported to different countries such as Netherlands, Antilles, Bolivia, Cyprus, Spain, Greece, Italy, Israel, Russia, USA, Moldova and Ukraine (Minagro, 2016), it should be necessary to promote the study of fish stocks of the species to ensure that commercial specimens come from populations that are not a risk to human consumption.In relation to the above arguments, we suggest to extend such studies on the rest of species of economic importance to the basin and to evaluate exposure to contaminants through direct intake.

6. Conclusion

This study fills a gap by providing information on trace elements concentrations and compartments distribution in two fish from Paraná River Delta. Most of the trace elements tended to be higher in *L. grossidens* (except for Co, Fe and Zn in gills and Hg in liver).In general, higher concentrations of the studied elements are associated to tissues such as liver and gills. In relation to the risk consumption, trace element concentrations found in edible muscles of *O. bonariensis* and *L. grossidens* are below the proposed limit values of toxic compounds for human consumption: such as As, Co, Fe and Zn. However, the levels of Hg in muscle were above the recommended maximum levels. The total THQ was higher than 1 only for fishermen population, indicating potential human health risks, being Hg and As the more contributive elements to calculate the risk (99.1%).

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