Journal of Marine Systems 181 (2018) 53–62

Contents lists available at ScienceDirect

Journal of Marine Systems

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

Metals in coastal zones impacted with urban and industrial wastes: Insights on the metal accumulation pattern in fish species

Noelia S. La Colla[a,*], Sandra E. Botté[a,b], Jorge E. Marcovecchio[a,c,d]

[a] Instituto Argentino de Oceanografía (IADO – CONICET/UNS), Camino La Carrindanga km 7.5, 8000 Bahía Blanca, Argentina
[b] Departamento de Biología, Bioquímica y Farmacia, Universidad Nacional del Sur, San Juan 670, 8000 Bahía Blanca, Argentina
[c] Universidad de la Fraternidad de Agrupaciones Santo Tomás de Aquino, Gascón 3145, 7600 Mar del Plata, Argentina
[d] Universidad Tecnológica Nacional – FRBB, 11 de Abril 445, 8000 Bahía Blanca, Argentina

ARTICLE INFO

Keywords:
Estuaries
Pollution
Health and safety
Aquatic environment

ABSTRACT

The pollution of aquatic environments is a worldwide problem of difficult solution since these areas are used for the disposal and dilution of anthropogenic wastes. This study evaluated the concentrations of Cd, Cu, Ni and Zn in the gills, liver and muscle tissues of six economically important fish species from the Bahía Blanca estuary in Argentina, a coastal environment that is under anthropogenic pressure.

Metal contents in 147 fish samples were determined by digestion and a subsequent analysis with an ICP OES. The concentrations (μg/g, wet weight) of each metal in the fish tissues ranged from below the limit of detection for the four metals to 5.2 in the case of Cd, 340 for Cu, 20 for Ni, and 101 for Zn. The results suggested that metal burden in fishes varied with the species and metal elements, with Cd, Cu and Zn mean maximum accumulation towards the liver tissue. Ni showed a high number of samples with concentrations below the limit of detection.

Among species, *Cynoscion guatucupa* was found to have the highest concentrations of Cu and Zn in the liver tissues, whereas the gills and liver tissues of *Mustelus schmitti* showed the lowest levels of Ni and Zn. As regards the human health risks, two samples of muscle tissue belonging to *C. guatucupa* reached to Cd levels that exceeded the permissible levels for human consumption. Moreover, the estimated daily intakes calculated suggest that people would not experience significant health risks from the intake of individual metals through fish consumption.

1. Introduction

Metal accumulation in coastal systems is a worldwide problem of difficult solution since these environments are commonly used for disposal and dilution of terrestrial wastes (Spencer et al., 2006), contributing to the continuous deterioration of the environment. A great range of metals can reach the coastal waters through river discharges, urban, agricultural and industrial wastewaters (Azimi et al., 2005; Waeles et al., 2007), underground water, atmospheric deposition, between others (Bai et al., 2015; Duarte and Caçador, 2012; Fu et al., 2013; Pérez-López et al., 2011; Ye et al., 2012; Zhao et al., 2012). As mixing in coastal zones is not always complete, the formation of hot spots is often usual and found close to the anthropogenic discharges (Malhadas, 2008; Viegas et al., 2009).

Global population growth is also of environmental concern since this expansion leads to increases in the number of industries, constructions, factories and the land uses for agriculture and cattle, between others. Moreover, the rapid growth without a proper planning brings about problems in the disposal of the increase garbage and waste generated. In countries with coastal areas, around 80% of the people live within 100 km of the coastline (Martínez et al., 2007; McGranahan et al., 2006). In Argentina, the country where the studies were carried out, 21 million people live near to coastal zones, representing 52.2% of the total population (INDEC, 2010).

Pollution of aquatic environments by metals is considered a major threat to organisms inhibiting those areas, including fish species. Previous studies (*e.g.* Atchison et al., 1987; Wood, 2011) on the possible consequences of metal exposure to fish in aquatic environments have suggested that fish appear to undergo inhibitory effects and/or behavioral changes, shifts in the appearance of the gills and a variety of other effects, such as necrosis of the kidneys and fatty metamorphosis of the liver (*e.g.* Bryan, 1971). Estuaries are known to offer physiologically suitable physicochemical conditions, abundant prey resources and low predation risk (Sardiña and Lopez Cazorla, 2005). Moreover, estuarine ecosystems are essential to the renewal of fisheries resources, as they serve not only as nursery grounds for fish species but also as adequate

---

* Corresponding author.
E-mail addresses: nlacolla@iado-conicet.gob.ar (N.S. La Colla), sbotte@iado-conicet.gob.ar (S.E. Botté), jorgemar@iado-conicet.gob.ar (J.E. Marcovecchio).

https://doi.org/10.1016/j.jmarsys.2018.01.012
Received 14 September 2017; Received in revised form 11 January 2018; Accepted 22 January 2018

habitats for adults during the spawning period (Lopez Cazorla, 2000). Thus, the protection of these essential fish habitats represents a crucial issue for ecosystem management and conservation (Beck et al., 2001).

Metal accumulation in fish organs has been focused, in general, on liver and gill tissues (Jaric et al., 2011). Active metabolic paths within these tissues concentrate higher amounts of metals than those of others, such as muscle tissues (Dural et al., 2007). The liver is the major site of accumulation, biotransformation and/or excretion of contaminants in fish (Triebskorn et al., 1997). The gills are the first organ exposed to resuspended sediment particles and the main route of metal uptake from water (Qadir and Malik, 2011). Nevertheless, metal content in the dorsal muscle is usually analyzed due to its importance for human consumption (Marcovecchio et al., 1991). As fishes are a major part of the human diet, pollutants that are bioaccumulated by aquatic inhabitants are subsequently transferred to humans through the food chain (*e.g.* Jaric et al., 2011).

This study was performed in the Bahía Blanca estuary (BBE) in Argentina, a coastal environment that is under anthropogenic pressure (Botté et al., 2007). Metal studies in fishes from the BBE have scarce previous published works, and are related mostly to the period 1985–1986 (Marcovecchio et al., 1988a, 1988b, 1991), even though several other metal studies had been conducted in sediments, water, and particulate matter (*e.g.* Botté et al., 2007, 2010; Fernández Severini et al., 2009; La Colla et al., 2015).

This coastal environment is inhabit by many economically important fish species (Colautti et al., 2010; Jaureguizar et al., 2006; Lopez Cazorla, 2005; Lopez Cazorla et al., 2014) that are both locally consumed and involved in international trades, mainly with Spain and African countries. Thus, as the health risk evaluation of the ecosystem exposed to environmental stress is of vital importance, the current study focuses on report the concentrations of Cd, Cu, Ni and Zn in the gills, liver and muscle tissues belonging to the fish species *Brevoortia aurea*, *Odontesthes argentinensis*, *Micropogonias furnieri*, *Cynoscion guatucupa*, *Mustelus schmitti* and *Paralichthys orbignyanus*. Altogether, it is expected that the information reported here will be useful for long term of the Bahía Blanca estuarine fish species.

Moreover, among the six fish species under analysis, *O. argentinensis* and *P. orbignyanus* are commonly captured all along the year and thought to be permanent inhabitants of the BBE waters (Lopez Cazorla, 2004, 2005; Valiñas et al., 2012). On the other hand, the juveniles of *B. aurea*, *M. furnieri*, *C. guatucupa* and *M. schmitti* are the ones who inhabit the BBE, whereas the adults live in the near-coastal zones and enter the estuary during the spawning period (Lopez Cazorla, 1985, 1987, 1996, 2004). Thus, it is hypothesized that the metal concentrations could vary according to the fish species and their migratory behavior.

This article is part of a series of studies dealing with the effects of urban and industrial impact on the accumulation pattern of metals on biotic and abiotic substrates (*i.e.* La Colla et al., 2015, 2017).

2. Materials and methods

2.1. Study area

The second largest estuary of Argentina (South America) is the Bahía Blanca estuary (BBE) (Fig. 1), which is located on the southeast coast of the country. It is a mesotidal system formed by a series of NW-SE tidal channels, separated by flats and islands (Perillo and Piccolo, 1991), and with two important cities located on its northern margins, Bahía Blanca (350,000 inhabitants) and Punta Alta (60,000 inhabitants). Both cities have mean discharges of 75,000 m^3/day that flows into the estuary (CTE, 2003), with an incomplete pre-treatment.

The BBE is a coastal system regularly exposed to metals, mainly as a consequence of agricultural activities along with urban expansion and anthropogenic waste discharges from the surrounding areas. Pollution of this marine environment has progressively increased over the years due to the economic and demographic development. Industries from a petrochemical center are located in the harbor area (Limbozzi and Leitào, 2008), probably generating large amounts of wastewater. One of the most important deep-water port systems of Argentina is located also on the northern coast of the BBE, contributing with the mobilization of thousands of tons of sediment from deepening and maintenance activities on the navigation channels.

Previous research on the ichthyofauna of this coastal environment of great economical as well as biological value identified ~30 fish species (period 1979–1983) (Lopez Cazorla, 2004). The BBE is essential to fish biology since several fish species inhabit its coasts during either one or more stages of their life cycle. In line with this, extensive salt marshes cover the intertidal zones of the estuary benefiting the development of an adequate habitat for the growth of fish (Valiñas et al., 2012).

2.2. Cleaning procedures

All material used during dissection and in laboratory analyses was cleaned according to internationally recommended protocols (APHA-AWWA-WPCF, 1998). The cleaning procedure involved washing the material with non-ionic detergent, rinsing it three times with tap water and afterwards another three times with deionized water. The material was then soaked for 24 h in a diluted acid nitric solution (5% HNO_3) and finally rinsed three times with deionized water.

2.3. Sample collection and preparation

A total of 147 individuals belonging to the species *B. aurea* (n: 26), *O. argentinensis* (n: 37), *M. furnieri* (n: 36), *C. guatucupa* (n: 17), *M. schmitti* (n: 20) and *P. orbignyanus* (n: 11) were caught with nets by local fishermen, from the middle-inner zone of the BBE (Fig. 1). After the individuals were captured, fish samples were transported with ice to the laboratory. For each individual were recorded body weight, in kg, and body length, measured to the nearest cm. Dissection was then performed in order to obtain tissue sub-samples from the gills, liver and dorsal muscle. After that, samples were homogenized, put in polyethylene bags and cooled at < 20 °C. The common and scientific names, weight and length ranges of the sampled fish individuals are listed in Table 1 for a better comprehension of the data analyzed.

Samples were collected consecutively in the years 2011, 2012 and 2013, during the spring season. The election of this season for sample collection is based on previous data from the BBE regarding catches per unit of effort. The spring season has the highest performance of catches per unit of effort for specimens of *M. schmitti*, *M. furnieri*, and a good performance in the case of *P. orbignyanus* and *O. argentinensis* (Lopez Cazorla, 2004).

2.4. Analytical procedure

A determination procedure was applied for metal analyses, based on Canli and Atli (2003) and with further modifications (La Colla et al., 2017). Muscle sub-sample portions of 0.6 ± 0.01 g (wet weight) and, liver and gills sub-sample portions of 0.4 ± 0.01 g (wet weight) were weighted. These tissue sub-samples were subjected to an acid pre-digestion with 5 ml of HNO_3 (65%) for at least 3 h. Then, 1 ml of $HClO_4$ was added and the samples were put in a glycerin bath at 110 ± 10 °C for 72 h or until the volume was reduced to < 1 ml. The acidic extracts were transferred to centrifuge tubes and 0.7% HNO_3 was added up to 10 ml of final dissolution. Metals were analyzed by means of a Perkin-Elmer DV 1200 inductively coupled plasma-optical emission spectrometry (ICP OES). The following wavelength lines were used for the ICP OES analyses: Cd 228.802 nm, Cu 327.393 nm, Ni 231.604 nm and Zn 206.200 nm.

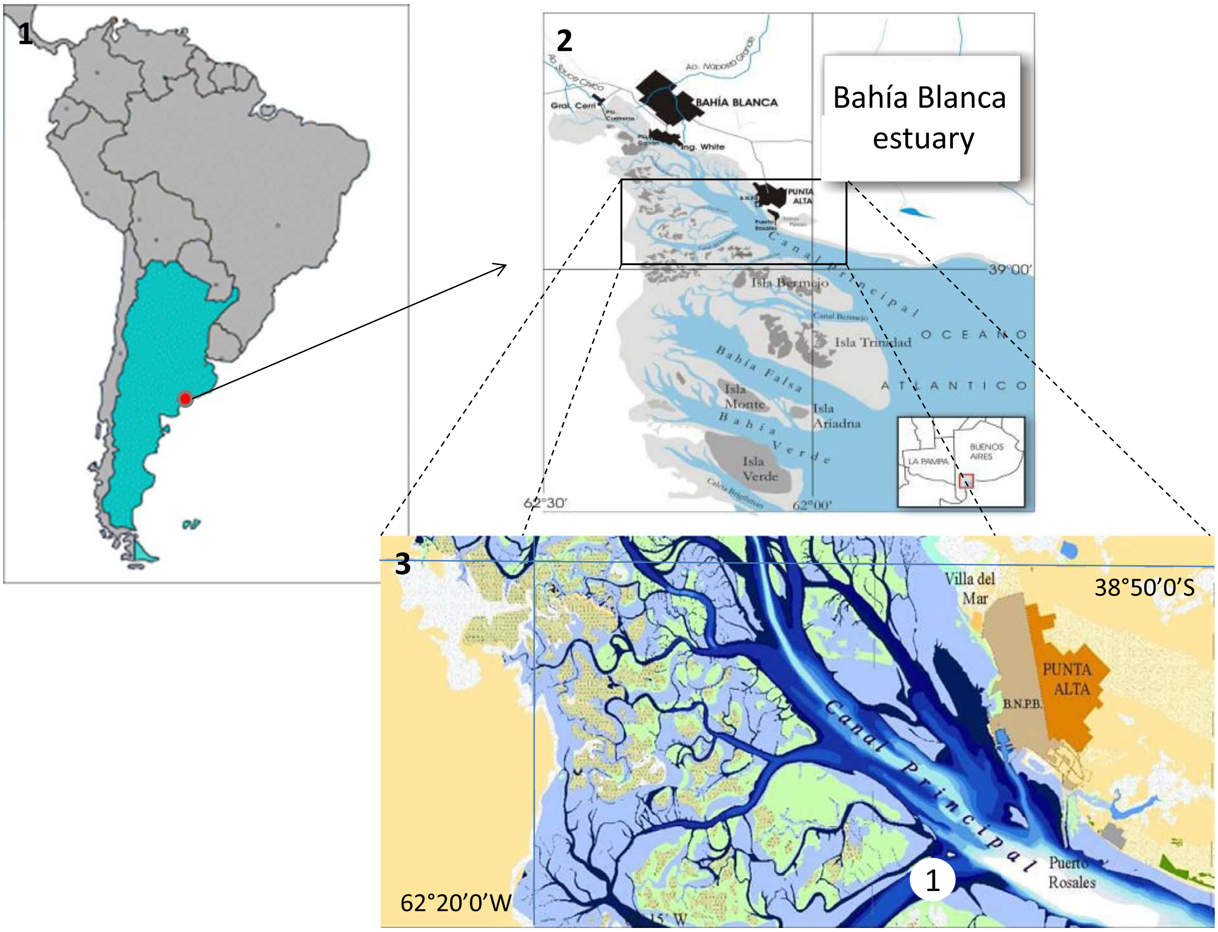

Fig. 1. Location map of sampling site in the Bahía Blanca estuary, Argentina. 1: Map of South America; 2: Map of the Bahía Blanca estuary; 3: Specific sampling site within the estuary, indicated with the number 1.

2.5. Health risk assessment

In order to assess health risks by consuming edible fishes, metal values achieved in muscle tissues, using wet weight, were compared with both national and international guidelines that establish metal maximum allowable concentrations in fish muscles. The maximum concentrations allowed by the Argentinean legislation, according to the CAA (Resolutions 116/2012 and 356/2012, 2012) and SENASA (Resolutions 4238/68, 2014), are (in μg/g): 1 for Cd, 10 for Cu, 150 for Ni and 100 for Zn. The maximum values set by the international guidelines, according to FAO/WHO (1983, 1989), are (in μg/g): 0.5 for Cd, 30 for Cu and 30 for Zn. The European Commission (EC, 2006) has maximum limits set only for Cd of 0.05 μg/g. No guidelines are established for Ni accumulation in fish muscle.

The relevance of these data was also evaluated in terms of the potential human health risks, comparing the metal concentrations found with the estimated daily intake (EDI). The EDI for metals was determined by the following equation (Li et al., 2015; Yi et al., 2017):

$$\mathrm{EDI} = \frac{(\mathrm{C} \times \mathrm{I})}{\mathrm{B}} \tag{1}$$

where C is the metal concentration in fish tissues obtained on bases of wet weight (mg/kg wet weight), I is the average daily consumption of fish in the local area (0.013 kg/day; FAO, 2016) and B represents the average body weight (70 kg).

Table 1
Characteristics of fish species obtained in the Bahía Blanca estuary. SD: standard deviation.

Common name	Scientific name	Mean body weight (kg) ± SD	Mean body length (cm) ± SD
Brazilian menhaden	*Brevoortia aurea*	0.34 ± 0.18	30 ± 4.8
Silverside	*Odontesthes argentinensis*	0.18 ± 0.096	28 ± 4.6
White-mouth croaker	*Micropogonias furnieri*	0.30 ± 0.24	27 ± 9.1
Stripped weakfish	*Cynoscion guatucupa*	0.50 ± 0.36	34 ± 10
Narrownose smooth-hound	*Mustelus schmitti*	0.38 ± 0.16	47 ± 6.6
Flounder	*Paralichthys orbignyanus*	0.22 ± 0.087	27 ± 3.5

2.6. Quality assurance and quality control

The potential presence of metals in chemicals used for digestion was determined, thus blanks were used simultaneously in each batch of analysis to authenticate the analytical quality. All analyses were done in duplicate, and the uncertainty based on one relative standard deviation of replicates was < 15%. The analytical method detection limit (MDL) for each metal (μg/g) was: 0.11 for Cd, 1.4 for Cu, 0.04 for Ni and 0.28 for Zn. The analytical quality was tested against reference materials (mussel tissue flour R.M. Nº6) provided by the National Institute for Environmental Studies (NIES), from Tsukuba (Japan) as well as from the United Nations Environment Programme (UNEP). The concentrations found were within 90–115% of the certified values for the four measured elements.

2.7. Statistical analyses

All statistical analyses were carried out using STATISTICA 7.0 (StatSoft, Inc.), following Zar (1996). The non parametric test Kruskal-Wallis ANOVA was used throughout the results section as the data analyzed did not meet the assumptions of the parametric statistics and there were no possible transformations. The non parametric tests were performed to assess differences in metal concentrations between tissues, between fish species and between adults and juveniles of the same fish species. Based on the results of these analyses, multiple comparisons with the Kolmogorov-Smirnov test were then performed. The accumulation behavior of metals in the gills, liver and muscle tissues according to their fish length were examined in terms of the correlation coefficient (r) with the Spearman correlation tests.

The acceptable level of statistical significance used in the study was $p < 0.05$. Metal concentrations reported as below analytical MDL were substituted by one half the MDL for statistical analyses (Jones and Clarke, 2005) and no analyses were performed when 40% or more of the concentrations of the metal evaluated were below the MDL (Federal Register, 1984). Error values represent standard deviation. Graphics were performed using software R in version 3.2.0 from the R-project (Wickham, 2009).

3. Results and discussion

The concentrations of Cd, Cu, Ni and Zn were critically examined in the different organs of the evaluated fish species. Average metal levels, according to the metal, fish species, organ and period of sampling, are shown in Fig. 2. Maximum and minimum values found for each metal in the different tissues and for all the fish species are also displayed in Table 2.

3.1. Cadmium

Cd is a non-essential element for organisms, except for its discovered biological role in marine diatoms (Lane and Morel, 2000), and has been demonstrated to be highly toxic to both wildlife and humans. It is a deleterious contaminant in seafood and can be highly accumulated by marine organisms (Pan and Wang, 2012).

The liver tissues were highlighted as those with the highest mean Cd concentrations for all the species under evaluation (Fig. 2) and with the maximum total values (Table 2). Concentration ranges were between < 0.11 μg/g and maximums (all in wet weight) of: 1.9 μg/g for *B. aurea*, 0.84 μg/g for *O. argentinensis*, 5.2 μg/g for *M. furnieri*, 2.6 μg/g for *C. guatucupa*, 3.5 μg/g for *M. schmitti* and 0.27 μg/g for *P. orbignyanus*. With regards to Cd concentrations in the gills and muscle tissues of the six fish species under analyses, values found were contrastingly lower than in the liver tissues, achieving concentrations below the MDL in > 40% of the samples.

Length was significantly correlated with Cd values in the liver tissues (Fig. 3), even though the correlations showed some differences between fish species and dates of sampling. Throughout the sampling date 2013, the only period that analyzed both juveniles and adults of *M. furnieri* and *M. schmitti*, length was significantly correlated with Cd values in the liver tissues of both fish species ($r = 0.72$ and $r = 0.69$, respectively). The same sampling date also showed higher Cd concentrations in the gill tissues of juveniles of *M. schmitti* compared to adults ($p < 0.05$). In the case of *B. aurea*, length was significantly related to Cd values in the liver tissues during the sampling date 2013 ($r = 0.87$). As for *O. argentinensis*, in 2011, the year with the widest range of size classes analyzed, length was positively correlated with Cd values in the liver tissues ($r = 0.70$). On the contrary, neither *C. guatucupa* nor *P. orbignyanus* showed correlations between Cd values and length.

3.2. Copper

Copper is an essential element required for different enzymes of living organisms but can be toxic at high concentrations. It is a common component in anti-biofouling paints which are applied on the surfaces of ships and in offshore engineering (Pan and Wang, 2012), thus Cu is usually monitored in aquatic environments.

The liver tissues exhibited the highest mean contents of Cu and the maximum values (Fig. 2 and Table 2). Concentration ranges varied between < 1.4 μg/g and maximums for each species: 7.4 μg/g for *B. aurea*, 31 μg/g for *O. argentinensis*, 15 μg/g for *M. furnieri*, 340 μg/g for *C. guatucupa*, 5.0 μg/g for *M. schmitti* and 18 μg/g for *P. orbignyanus*. Cu concentrations in the gills and muscle tissues of each of the species evaluated (with the exception of *P. orbignyanus*) were below the MDL in > 40% of the samples. Differences were found within size classes of many fish species under evaluation. In the case of *M. furnieri*, maximum concentrations of Cu were achieved in the liver tissues of juveniles from the sampling date 2013, in comparison to values found for adults ($p < 0.05$). This aforementioned sampling date, as previously stated, was the only one that included the use of tissues from both juveniles and adults. On the contrary, Cu values found in the liver tissues of adults of *C. guatucupa* from the sampling period 2011 showed higher contents than those registered in juveniles samples ($p < 0.05$), analyzing both juveniles and adults with size classes ranging between 15 and 40 cm.

Also, for *M. schmitti* and *P. orbignyanus*, positive correlations between metals were achieved. The correlations were achieved between Cu and Zn in the liver tissues ($r = 0.68$) of *M. schmitti* and between Cu and Ni ($r = 0.94$) in the gill tissues of *P. orbignyanus*.

Cu concentrations in fish tissues evaluated in the present study are in concordance with the same metal values found in the dissolved and particulate seawater fractions in the BBE and during the same sampling period (La Colla et al., 2015). Cu dissolved concentrations were above the permissible levels and particulate concentrations remained higher than previous values found in the BBE many times. Thus, it is not unusual to find that Cu has the highest second concentrations below Zn, and specifically in liver tissues, having the liver an important role in contaminant storage (Evans et al., 1993).

3.3. Nickel

Nickel is an essential element at low concentrations for many organisms but is toxic at higher concentrations (Authman et al., 2015). It is present in soil, water, air, and in the biosphere. It is emitted into the environment from both natural and man-made sources. Ni is released during nickel mining and by industries and also released by oil-burning power plants, coal-burning power plants and trash incinerators, between others (Al-Attar, 2007). Once released to the environment, Ni forms complexes with many ligands, making it more mobile than most metals.

Ni distribution among fish species was less pronounced compared to the previous metals (Fig. 2). For instance, *O. argentinensis*, *C. guatucupa*

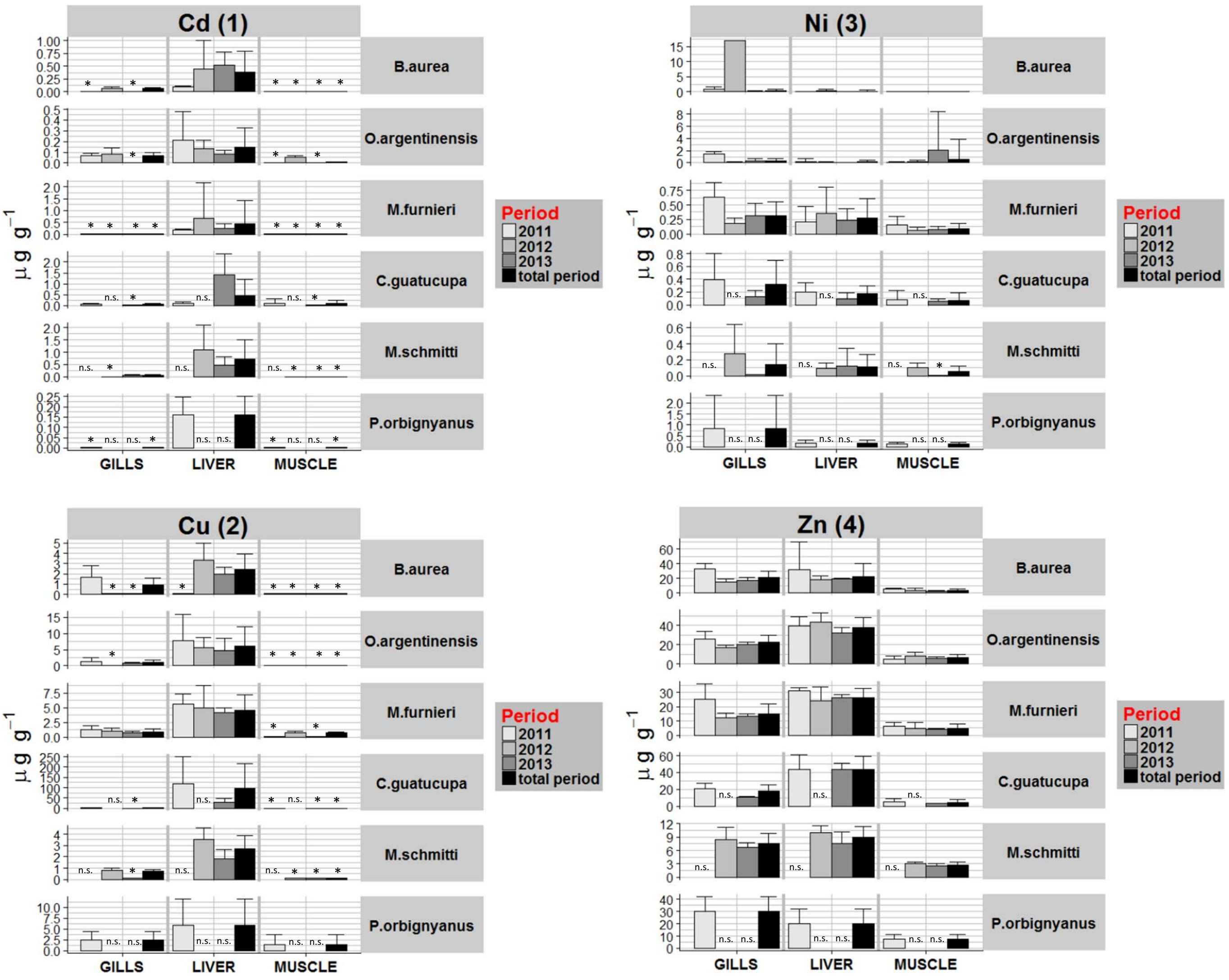

Fig. 2. Mean concentration and standard deviation of metals (expressed in μg/g) in the gills, liver and muscle tissues of the six fish species. The period under analysis for each mean value is taken into account, and the mean value of the entire period of analysis is highlighted in black bars. Panel 1 display Cd values, panel 2 Cu values, panel 3 Ni values and panel 4 Zn values. n.s.: no sample; *: metal concentration below the method detection limit (< MDL).

Table 2
Maximum and minimum metal concentrations, corresponding to all sampling data and fish species. Data is grouped together according to the tissue of analysis.

Metal element	Gill tissues		Liver tissues		Muscle tissues	
	Min. (μg/g)	Max. (μg/g)	Min. (μg/g)	Max. (μg/g)	Min. (μg/g)	Max. (μg/g)
Cd	< 0.11	0.25	< 0.11	5.2	< 0.11	0.71
Cu	< 1.4	5.7	< 1.4	340	< 1.4	8.6
Ni	< 0.04	3.8	< 0.04	1.6	< 0.04	20
Zn	5.2	49	4.5	101	< 0.28	18

and *M. schmitti* showed no significant Ni variations between gills and liver ($p > 0.05$) and concentrations in the muscle tissues were not compared statistically due to the high number of values below the MDL (over 40%). Maximum concentrations found were 20 μg/g in the muscle tissues of *O. argentinensis*, and 1.6 and 1.2 μg/g in the gill tissues of *C. guatucupa* and *M. schmitti*, respectively. For the entire period under analyses, positive correlations were found between Ni and Zn in the liver tissues of *M. schmitti* ($r = 0.81$).

In the case of *B. aurea*, the highest contents of Ni were found in the gill tissues ($p < 0.05$), with concentrations ranging between < MDL and 1.8 μg/g. Also, a positive correlation was found between Ni and Zn ($r = 0.68$) in the liver tissues ($p < 0.01$). Throughout the sampling date 2013, length was negatively correlated with Ni values in the gill tissues ($r = -0.86$) (Fig. 3b).

For *M. furnieri*, Ni values were highest in the liver tissues ($p < 0.0001$) with values ranging from < MDL to 1.5 μg/g. Positive correlations were also found between Ni and Zn in the gill tissues ($r = 0.66$).

In the case of *P. orbignyanus*, the present study revealed similar levels in the liver, gills and muscle tissues ($p > 0.05$), with maximum values registered in gills (3.8 μg/g).

Ni concentrations in fish tissues evaluated in the present study are in concordance with the same metal values found in the dissolved and particulate seawater fractions in the BBE and during the same sampling period (La Colla, 2016). Ni concentrations in both seawater fractions were below the limits of detection in > 90% of the samples agreeing with the low concentration found in fish tissues.

3.4. Zinc

Zn is the second most abundant trace element after Fe and is

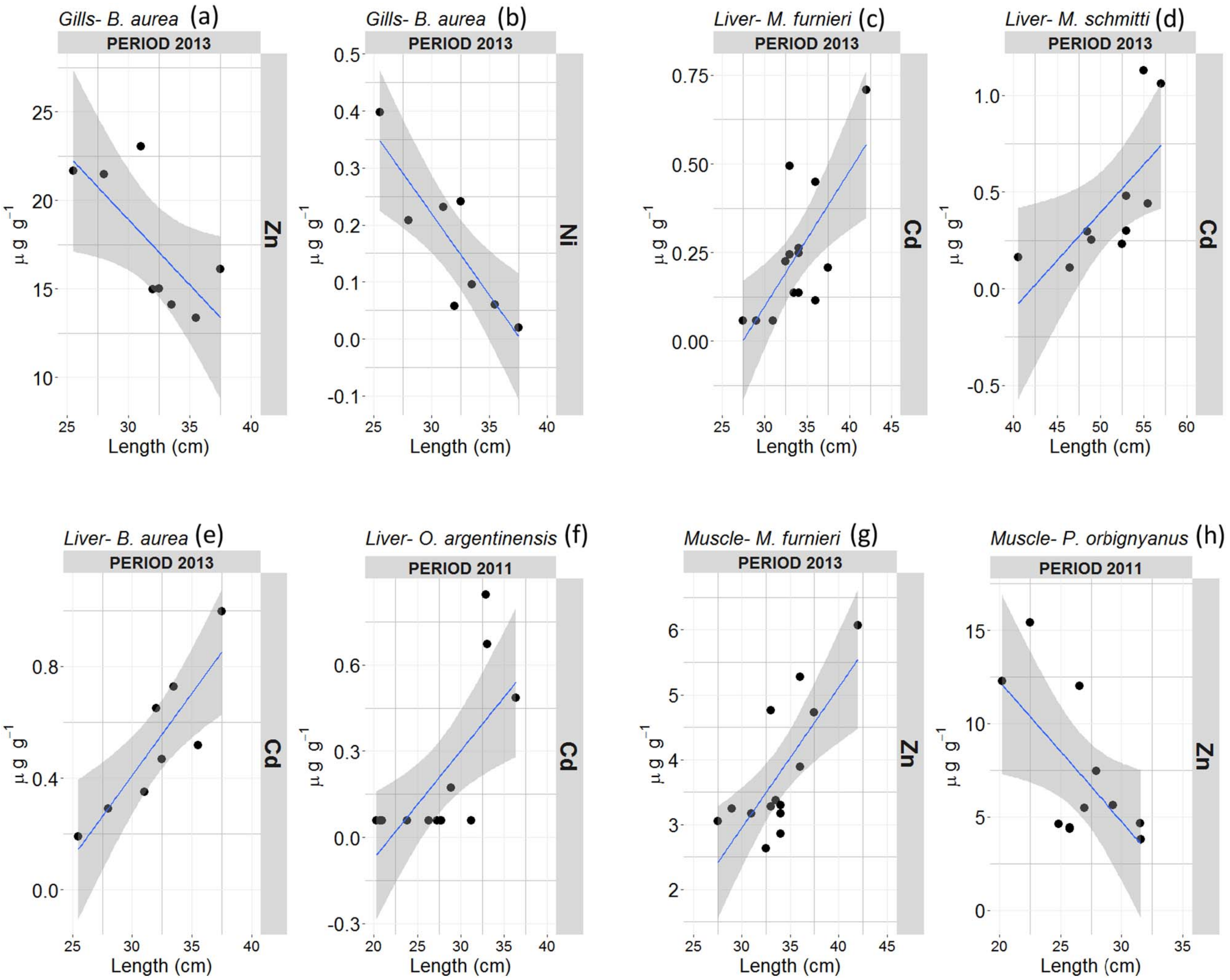

Fig. 3. Correlations between fish length and metal concentrations in gills, liver and muscle tissues, according to the period of analysis and the fish species. Metal concentrations are expressed in µg/g. Panels (a) and (b) establish correlations between gill tissues and fish length; Panel (c), (d), (e) and (f) establish correlations between liver tissues and fish length; Panels (g) and (h) establish correlations between muscle tissues and fish length.

essential for metabolic processes in living organisms (Pan and Wang, 2012). It has a tendency to accumulate in the fatty tissues of aquatic organisms, including fish, and is known to affect their reproductive physiology (Rahman et al., 2012).

For *B. aurea*, *M. schmitti* and *P. orbignyanus*, the present study revealed similar mean Zn levels in the liver and gill tissues, and both higher than those from the muscle tissues ($p < 0.001$, $p < 0.001$ and $p < 0.05$, respectively) (Fig. 2). Concentrations showed maximum values of 100 and 40 µg/g for the liver and gill tissues of *B. aurea*, of 13 µg/g in the liver tissues of *M. schmitti* and a highest concentration of 49 µg/g in the gills of *P. orbignyanus*. Maximum values for the overall Zn concentrations are displayed in Table 2.

For the species *O. argentinensis*, *M. furnieri* and *C. guatucupa*, the highest mean Zn levels were found in liver tissues ($p < 0.001$, $p < 0.0001$ and $p < 0.01$, respectively) (Fig. 2), with values ranging from < 0.28 to 65 µg/g, 48 µg/g and 78 µg/g respectively.

The species also achieved differences between size classes. *M. furnieri* registered, in 2011, maximum concentrations of Zn in the liver and muscle tissues of juveniles when compared to adults ($p < 0.01$). Also, in *M. furnieri* metal correlations were found between Ni and Zn in the gill tissues ($r = 0.66$), and length was positively correlated with Zn values in the muscle tissues ($r = 0.75$) (Fig. 3g).

On the contrary, maximum mean values of Zn in the liver tissues of adults of *C. guatucupa* were achieved when compared to juveniles ($p < 0.05$). Muscle samples of *C. guatucupa* also registered higher Zn values in tissues of juveniles in comparison with data registered from adults ($p < 0.05$).

Length was negatively correlated with Zn values (Fig. 3), even though the correlations showed some differences between species and dates of sampling. Throughout the sampling date 2013, decreases in Zn values in the gill tissues with increases in the length were found in *B. aurea* ($r = -0.86$) (Fig. 3a). For *P. orbignyanus*, length was negatively correlated with Zn values in the muscle tissues ($r = -0.65$) (Fig. 3h).

3.5. The role of fish tissues in metal distribution

This study showed that the highest mean concentrations of metals were recorded in the gills and liver tissues ($p < 0.05$), whereas the lowest values were found in the muscle tissues. Such pattern had already been observed in a number of other studies, covering a wide spectrum of fish species (*e.g.* Dural et al., 2007; Karadede et al., 2004; Yilmaz et al., 2010).

The liver is often considered to be a good monitor of water metal pollution since it is the organ in which the main metabolic activities are developed, such as storage, redistribution, detoxification and/or transformation. Meanwhile, the gills are the uptake site of dissolved ions where metal concentrations increase, especially at the beginning of exposure, before the metal enters into other parts of the organism (Dural et al., 2007). For these reasons, the liver and gill tissues of fish are normally recommended as good indicators of anthropogenic impacts on the marine ecosystems.

Cd, Cu and Zn mean distribution towards the liver tissues could be linked to the role that the hepatic tissue performs in the metabolism of metals. The liver is important for being the organ in which the main metabolic activities are developed (Evans et al., 1993). Metals are transported from other tissues into the hepatic one for the subsequent storage and/or elimination by the induction of metallothioneins, proteins involved in the binding of metals, or through the attachment on insoluble fractions (Klavercamp et al., 1984). Its synthesis is induced by the presence of high concentrations of metals such as Cd or Cu, being these proteins more selective for Cu in comparison to Cd or Zn (Salem et al., 2014). Also, these proteins act as metal deposits, by satisfying when needed different enzymatic and metabolic processes (Amiard et al., 2006).

The accumulation of metals in the liver could be based on the greater tendency of the elements to react with the oxygen carboxylate, amino group, nitrogen and/or sulphur of the mercapto group in the metallothionein proteins with their highest concentration in the liver (Al-yousuf et al., 2000). Moreover, the high concentration of non-essential metals such as Cd in the liver tissues might be due to the ability of Cd to displace the natural association of the metallothioneins to essential metals (Amiard et al., 2006), especially when the concentration of these types of metals is increased. Most of the fish species analyzed, except for *C. guatucupa* and *P. orbignyanus*, showed the ability to bioaccumulate Cd in liver tissues, as it is shown in other publications (*e.g.* Amiard et al., 2006). It is possible then to correlate Cd levels with the age of fishes (Eisler, 2010).

Ni levels showed no accumulation pattern towards any tissue, mostly due to the high number of samples with concentrations below the MDL. As for the detectable values found, the gills exhibited as the main site for the accumulation of this element.

3.6. Influence of fish species and their migratory behavior on tissue accumulation

Mean concentrations of both essential and non-essential metals in the gills, liver and muscle tissues of fish species showed great variations. Statistical comparisons revealed that metal levels were significantly different in each tissue and between different fish species. Also, according to their migratory behavior, a distinction is needed between samples belonging to fish species that are permanent inhabitants of the BBE and those species that inhabit both estuarine areas and the open sea.

In the sampling date 2013 as well as in the complete sampling period, the liver tissues of *C. guatucupa* achieved higher mean concentrations of Cu and Zn, compared to the values obtained in all the other fish species under analysis ($p < 0.01$ for all comparisons). As regards metal bioaccumulation, adults of *C. guatucupa* can be highlighted as good indicators of Cu and Zn levels in the liver tissues.

Due to the observed migration of juveniles of *C. guatucupa* out of the estuary (Lopez Cazorla, 1987, 2000), and taking into account the range of fish sizes analyzed during the study period, metal concentrations registered in tissues of *C. guatucupa* could implicate processes of metal accumulation from both the BBE and the coastal region nearby.

Possible differences in the ability of fish species such as *C. guatucupa* to bioaccumulate might arise as a consequence of studying juveniles and/or adults from the specific species. Metal concentrations in living organisms are related to their feeding habits (Al-yousuf et al., 2000). Also, the ratio area/volume and their growth are within the common factors responsible, at least in part, for the differences in the bioaccumulation processes (Bobori and Economidis, 1996).

Metal bioaccumulation in tissues is an outcome of the complex interaction of all the above-mentioned parameters. Metal accumulation is also sex-specific and can be correlated with weight and age, even though these relationships are not always straight (Has-Schön et al., 2015). The metal concentration-size correlations depend on several factors, such as (i) the specific metabolism of the metal in the fish and the tissue type considered; (ii) the competition between the opposing effects of ageing and tissue growth and (iii) the availability of the metal in the environment (Evans et al., 1993). Some studies have suggested that adult fishes might have better mechanisms for metal bioregulation, and juveniles might have higher metabolic rates, thus promoting higher metal accumulation rates in juveniles compare to adults (Canli and Atli, 2003; Cossa et al., 1992; De Wet et al., 1994). Nevertheless, other published literature stated that the excretion rate of Zn, Cu and Cd could be very slow with an accumulation rate greater than the rate of tissue growth during much of the lifetime (Al-yousuf et al., 2000).

In *C. guatucupa*, a detailed analysis of changes in the diet during the ontogeny of the species has been already described (Lopez Cazorla, 1996, 2005). They feed on crustaceans on its early stages, while the diet shifts to pelagic fishes in adulthood. These changes in diet might influence metal accumulation in fish tissues. Moreover, previous data from the BBE detected biomagnification processes for elements such as Cd and Cu, with the transference of these metals from particulate material towards mesozooplankton (Fernández Severini et al., 2009).

As for *P. orbignyanus*, this species registered the average maximum levels of Cu in gill tissues when compared to the rest of the species analyzed during the sampling period ($p < 0.001$), even though the values themselves were rather low. Average values of Ni and Zn in the gill tissues of *P. orbignyanus* from the sampling period (exclusively 2011) also exhibited maximum mean concentrations in comparison with the other fish species, but no statistical differences were achieved.

The size classes of *P. orbignyanus* analyzed during the sampling period belong to individuals of one to two years old and with maximum lengths of 30 cm. In the Bahía Blanca estuary, this species reaches almost seven years old with lengths of approximately 80 cm (Lopez Cazorla, 2005). Thus, the small range and quantity of samples analyzed probably influenced the ability of select *P. orbignyanus* as a bioindicator of metal levels in the BBE.

For *P. orbignyanus*, the negative bioaccumulation pattern found between Zn values in the muscle tissues and the length could be a consequence of the observed changes in the diet according to changes with age (Lopez Cazorla, 2005; Lopez Cazorla and Forte, 2005). Also, metal bioaccumulation is dependent on the series of parameters discussed in the above paragraph for *C. guatucupa* (*e.g.* feeding habits, growth). It is important to highlight that *P. orbignyanus* inhabits permanently the BBE (Lopez Cazorla, 2004, 2005) and consequently metal concentrations registered in its tissues reflect more accurately metal concentration in the studied estuarine environment.

M. schmitti was the fish species that registered the minimum mean concentrations of Ni and Zn in the gills and liver tissues when compared to the rest of the fish species analyzed during the study period. The majority of the samples comprised juvenile individuals, with size classes that give no certainty whether the individuals had already migrated out of the estuary and returned or still are exclusive inhabitants of the estuarine area. According to Lopez Cazorla (1987), *M. schmitti* remains inside the BBE until a total length of 50 cm and lengths found in this study ranged from 31 to 57 cm.

Many studies had suggested that fishes with a benthonic feeding behavior, due to the current contact with sediments and, more specifically, resuspended sediments, should be more often exposed to metals existing in the aquatic environment (*e.g.* Velusamy et al., 2014). Nevertheless, in this study as well as in other researches (*i.e.* El-Moselhy et al., 2014), non-significant differences were found between pelagic and benthonic species with regards to metal accumulation. One possible explanation for the lack of differences could be the fact that the BBE is very turbid and shallow estuary (mean depth 10 m), with variations in the water levels during the tidal cycle and with semidiurnal tidal waves. Thus, exposition to sediments could be not so different. Nevertheless, maximum mean metal levels in the gill tissues of *P. orbignyanus* were found, as well as correlations between the gills and length, being those indications that further information and studies are necessary.

Table 3
Estimated daily intake for individual metals from fish consumption. EDI: estimated daily intake; RfD: oral reference dose. All the units of concentrations are based on the wet weight.

Metal	Cd	Cu	Ni	Zn
RfD (mg/kg/day)	0.0010	0.040	0.040	0.30
Mean metal value (mg/kg)	0.064	0.82	0.17	4.9
EDI (mg/kg/day)	0.000012	0.00015	0.000032	0.00091

Precisely, the gills act as a good bioindicator of metal concentrations from both metals from the water column as well as from resuspended sediments.

M. furnieri reached the highest mean levels of some metals in comparison to *M. schmitti*, achieving higher Ni concentration in the gills from the sampling date 2013 ($p < 0.05$) and maximum Zn levels in the liver tissues from the sampling dates 2012 and 2013 ($p < 0.05$). Both *M. furnieri and M. schmitti* showed over the sampling period a majority of juvenile samples.

From the results it gives the impression that Zn levels in tissues of *M. furnieri* showed inconsistent results, demonstrating a bioaccumulation pattern while showing higher concentrations in the muscle tissues of juveniles compared to those of adults. These results could be explained by the scarce number of adults analyzed during the study period and so, the bioaccumulation pattern observed could be only a result of the increases in the size of individuals within the juvenile classes.

As for *B. aurea*, this species registered the average maximum levels of Zn in the gills and liver tissues from the sampling date 2012 ($p < 0.05$) when compared to *M. schmitti*. On account of the migratory behavior of the species (Lopez Cazorla, 1985), and since most of the samples analyzed were adults, the results achieved might implicate processes of metal accumulation from both the BBE as well as from the coastal region nearby.

O. argentinensis showed the highest mean Zn concentrations in the liver tissues during the study period compared to the rest of the metal elements in its tissues ($p < 0.05$). Exclusively in the sampling dates 2012 and 2013, mean Zn levels in the three tissues under analyses showed higher values than those from *M. furnieri* and *M. schmitti* ($p < 0.001$). Similar to *P. orbignyanus*, *O. argentinensis* inhabits permanently the BBE (Valiñas et al., 2012), thus metal concentrations registered in its tissues reflect more accurately metal concentrations from this estuarine environment.

3.7. Human health risk assessment

Contrasted to liver and gills metal concentrations, values found in the muscle tissues were the lowest. The muscle is not an active tissue for metal transformation and/or accumulation (Uysal et al., 2008). Nevertheless, the importance of evaluating metal concentrations in fish muscle from impacted aquatic environments relies on possible threats to public health due to its consumption (Marcovecchio et al., 1991).

Although Cu, Ni and Zn are essential elements and thus necessary for human health, exposure to high levels might result in adverse effects. For instance, high doses of Cu could result in liver and kidney damage, anemia, immunotoxicity and developmental toxicity, between others (ATSDR, 2004). Ni has been linked with immunotoxicity and hepatotoxicity (Squadrone et al., 2016), whereas chronic high Zn intake might result in severe neurological diseases, attributable also to copper deficiency (Hedera et al., 2009). Cd is a non-essential element and has been associated with nephrotoxicity, osteoporosis, neurotoxicity, carcinogenicity and genotoxicity, teratogenicity, and adverse effects on the endocrine and reproductive systems (EFSA, 2009).

In order to assess health risks by consuming edible fishes, metal values in muscle tissues, were compared with both national and international guidelines (Materials and method section). The Argentinean food legislation (CAA and SENASA) and international guidelines (FAO/WHO, EC), establishes the maximum content of some metals in fish muscle tissues above which, human consumption is not allowed. As regards these guidelines, Cd, Cu and Zn concentrations in the muscle tissues were in almost all cases considerably lower than the maximum levels established. Only an 11% of muscle tissues samples from *C. guatucupa* reached to Cd levels above the established upper limits (0.11 and 0.71 μg Cd/g).

Comparing metal concentrations found in muscle tissues in this study with existing data from previous surveys by Marcovecchio et al. (1988a, 1988b, 1991) (Zn: 17 ± 5.6 μg/g for *Mustelus schmitti*, 13 ± 4.7 μg/g for *Brevoortia aurea*, 24 ± 1.7 μg/g for *Cynoscion striatus*, 27 ± 4.8 μg/g for *Paralichthys brasiliensis*, 34 ± 6.4 μg/g for *Micropogonias furnieri*), showed that values from this previous study achieved higher Zn concentrations. As regards Cd values, all mean data from this study was lower than those previously recorded: Cd: 0.14 ± 0.50 μg/g for *Mustelus schmitti* (Marcovecchio et al., 1991), 0.030 ± 0.01 μg/g for *Brevoortia aurea*, 0.090 ± 0.06 μg/g for *Paralichthys brasiliensis*, 0.34 ± 0.25 μg/g for *Micropogonias furnieri* (Marcovecchio et al., 1988a). The exception was achieved for Cd in *C. guatucupa*, with higher in the present study (Cd: 0.060 ± 0.04 μg/g for *Cynoscion striatus* (Marcovecchio et al., 1988a)).

The dose of a metal that is obtained by fish consumption depends not only on the concentration of the specific metal in fish, but also on the quantity of the fish intake. Thus, the EDI of fish was calculated according to the Eq. (1) and showed that the EDIs for all the four metals were lower than the oral reference dose (RfD) for each metal (Table 3). Considering normal consumption habits, these results suggest that people would not experience significant health risks from the intake of individual metals through fish consumption. Although EDIs were not high, special care should be taken for some people consuming larger quantities of fish.

4. Conclusion

This study provides updated information on Cd, Cu, Ni and Zn concentrations in tissues of six fish species from the Bahía Blanca estuary, an Argentinian coastal environment that is under anthropogenic pressure. Metal concentrations in the different fish tissues and species, and their bioaccumulation rates showed great variations. The highest concentrations of metals were recorded in the gills and liver, opposite to the lowest values found in the muscle tissues. Cd, Cu and Zn maximum distribution towards the liver tissues could be linked to the role that the hepatic tissue has in their metabolism, as the liver is the organ in which the main metabolic activities are developed.

Because Zn is an essential metal element and fishes are known to have a high threshold level for Zn, is not unusual to find it to be the most abundant metal in the fish samples of the present study. Positive correlations were also found between the liver tissues of the majority of the fish species and the Cd concentrations.

As regards the species under analysis, *C. guatucupa* stood up as a good accumulator of Cu and Zn concentrations in its liver tissues and also reached to Cd levels in the muscle tissues that exceeded the permissible levels for human consumption. As hypothesized, the use of the resident species *O. argentinensis* and *P. orbignyanus* could be an advantage when analyzing the data obtained. Both positive and negative correlations were found between fish tissues and metal concentrations, and also there were differences achieved in metal values between juveniles and adults of the same fish species. Thus, the use of fish species with the entire life cycle within the estuarine area should reassure that these results are an outcome of the complex interaction of the biological parameters and not the result of the influences from the coastal environment close to the Bahia Blanca estuary.

The concentration of the metals in the muscle tissues of the studied species were considerably lower, in most cases, than the maximum levels set by the laws and also showed adequate EDIs values as regards human health risks. Consequently, muscle fish tissues were fit for human consumption in this region as well as in the countries involved in the international trades. Nevertheless, regular monitoring of metal concentrations still should be conducted in the future, as potential danger might appear, depending on the domestic wastewaters and agricultural/industrial activities taking place in an aquatic environment that is in continuous development.

Acknowledgements

Special thanks to Lic. Garcia for his help in sample analyses, and to the staff of the IADO IV research vessel for logistics and cooperation on board. Authors wish to thank Mr. Flores and Lic. Labudía for their collaboration in sample dissection and are greatly indebted with Dr. Lopez Cazorla for her constructive comments during the Ph.D. thesis. This research was part of the Ph.D. thesis of Noelia La Colla. This work was supported by the National Council of Scientific and Technological Research (CONICET-Argentina) (Grant No. PIP D-738, 2011) and the Universidad Nacional del Sur (Grant No. PGI 24/ZB59, 2013).

Conflict of interest

There are no conflicts of interest.

References

Al-Attar, A.M., 2007. The influences of nickel exposure on selected physiological parameters and gill structure in the teleost fish, *Oreochromis niloticus*. J. Biol. Sci. 7 (1), 77–85.

Al-yousuf, M.H., El-Shahawi, M.S., Al-Ghais, S.M., 2000. Trace metals in liver, skin and muscle of *Lethrinus lentjan* fish species in relation to body length and sex. Sci. Total Environ. 256 (2), 87–94.

Amiard, J.C., Amiard-Triquet, C., Barka, S., Pellerin, J., Rainbow, P.S., 2006. Metallothioneins in aquatic invertebrates: their role in metal detoxification and their use as biomarkers. Aquat. Toxicol. 76, 160–202.

APHA-AWWA-WPCF, 1998. In: Clesceri, L.S., Greenberg, A.E., Eaton, A.D. (Eds.), Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association, Washington.

Atchison, G.J., Henry, M.G., Sandheinrich, M.B., 1987. Effects of metals on fish behavior: a review. Environ. Biol. Fish 18 (1), 11–25.

ATSDR (Agency for Toxic Substances and Disease Registry), 2004. Toxicological Profile for Copper. U.S. Public Health Service. Agency for Toxic Substances and Disease Registry, Atlanta, GA.

Authman, M.M., Zaki, M.S., Khallaf, E.A., Abbas, H.H., 2015. Use of fish as bio-indicator of the effects of heavy metals pollution. J. Aquac. Res. Dev. 6 (4), 1–13.

Azimi, S., Rocher, V., Muller, M., Moilleron, R., Thevenot, D.R., 2005. Sources, distribution and variability of hydrocarbons and metals in atmospheric deposition in an urban area (Paris, France). Sci. Total Environ. 337 (1), 223–239.

Bai, J., Zhao, Q., Lu, Q., Wang, J., Reddy, R., 2015. Effects of freshwater input on trace element pollution in saltmarsh soils of a typical coastal estuary. J. Hydrol. 520, 186–192.

Beck, M.W., Heck Jr., K.L., Able, K.W., Childers, D.L., Eggleston, D.B., Gillanders, B.M., Weinstein, M.P., 2001. The identification, conservation, and management of estuarine and marine nurseries for fish and invertebrates: a better understanding of the habitats that serve as nurseries for marine species and the factors that create site-specific variability in nursery quality will improve conservation and management of these areas. Bioscience 51 (8), 633–641.

Bobori, D.C., Economidis, P.S., 1996. The effect of size, sex and season on the accumulation of heavy metals in perch (*Perca fluviatilis* L., Pisces: Cyprinidae) in Lake Koronia (Macedonia, Greece). Toxicol. Environ. Chem. 57 (1–4), 103–121.

Botté, S.E., Freije, R.H., Marcovecchio, J.E., 2007. Dissolved heavy metal (Cd, Pb, Cr, Ni) concentrations in surface water and porewater from Bahía Blanca estuary tidal flats. Bull. Environ. Contam. Toxicol. 79, 415–421.

Botté, S.E., Freije, R.H., Marcovecchio, J.E., 2010. Distribution of several heavy metals in tidal flats sediments within Bahía Blanca Estuary (Argentina). Water Air Soil Pollut. 210 (1–4), 371–388.

Bryan, G.W., 1971. The effects of heavy metals (other than mercury) on marine and estuarine organisms. Proc. R. Soc. Lond. B Biol. Sci. 177 (1048), 389–410.

Canli, M., Atli, G., 2003. The relationships between heavy metal (Cd, Cr, cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species. Environ. Pollut. 121 (1), 129–136.

Código alimentario argentino (CAA), 2012. http://www.anmat.gov.ar/alimentos/normativas_alimentos_caa.asp.

Colautti, D., Baigun, C., Lopez Cazorla, A., Llompart, F., Molina, J.M., Suquele, P., Calvo, S., 2010. Population biology and fishery characteristics of the smooth-hound *Mustelus schmitti* in Anegada Bay, Argentina. Fish. Res. 106 (3), 351–357.

Cossa, D., Auger, D., Averty, B., Lucon, M., Masselin, P., Noel, J., 1992. Flounder (*Plattichthys flesus*) muscle as an indicator of metal and organochlorine contamination of French Atlantic Coastal waters. Ambio 21, 176–182.

CTE (Comite Tecnico Ejecutivo), 2003. Programa integral de monitoreo Bahía Blanca. http://www.bahiablanca.gov.ar/areas-de-gobierno/medioambiente/comite-tecnico-ejecutivo/.

De Wet, L.M., Schoonbee, H.J., De Wet, L.P.D., Wild, A.J.B., 1994. Bioaccumulation of metals by southern mouthbrooder, *Pseudocrenilabrus philander* (Weber, 1897) from a minepolluted impoundment. Water SA 20, 119–126.

Duarte, B., Caçador, I., 2012. Particulate metal distribution in Tagus estuary (Portugal) during a flood episode. Mar. Pollut. Bull. 64, 2109–2116.

Dural, M., Göksu, M.Z.L., Özak, A.A., 2007. Investigation of heavy metal levels in economically important fish species captured from the Tuzla lagoon. Food Chem. 102 (1), 415–421.

EFSA, 2009. Cadmium in food. Scientific opinion of the panel on contaminants in the food chain. EFSA J. 980, 1–139. Available online. www.efsa.europa.eu.

Eisler, R., 2010. Compendium of Trace Metals and Marine Biota 2. Vertebrates, Elsevier, Amsterdam (602 pp.).

El-Moselhy, K.M., Othman, A.I., El-Azem, H.A., El-Metwally, M.E.A., 2014. Bioaccumulation of heavy metals in some tissues of fish in the Red Sea, Egypt. Egypt. J. Basic Appl. Sci. 1 (2), 97–105.

European Commission, 2006. Commission Regulation (EC) No 1881/2006 of 19 December 2006 Setting Maximum Levels for Certain Contaminants in Foodstuff. (2006R1881-EN-01.09. 2014-014.001-1).

Evans, D.W., Dodoo, D.K., Hanson, P.J., 1993. Trace element concentrations in fish livers: implications of variations with fish size in pollution monitoring. Mar. Pollut. Bull. 26 (6), 329–334.

FAO, 2016. El estado mundial de la pesca y la acuicultura 2016. In: Contribución a la seguridad alimentaria y la nutrición para todos. Rome, pp. 224.

FAO/WHO, 1983. Compilation of legal limits for hazardous substances in fish and fishery products. FAO Fish. Circ. 464.

FAO/WHO, 1989. National Research Council Recommended Dietary Allowances, 10th ed. National Academy Press, Washington, DC, USA.

Federal Register, 1984. Definition and procedure for determination of the method detection limit. EPA 40, 198–199 CFR Part 136, Appendix B, Revision 1.11.

Fernández Severini, M.D., Botté, S.E., Hoffmeyer, M.S., JMarcovecchio, J.E., 2009. Spatial and temporal distribution of cadmium and copper in water and zooplankton in the Bahía Blanca estuary, Argentina. Estuar. Coast. Shelf Sci. 85, 57–66.

Fu, J., Tang, X.L., Zhang, P., Balzer, W., 2013. Estuarine modification of dissolved and particulate trace metals in major rivers of East-Hainan, China. Cont. Shelf Res. 57, 59–72.

Has-Schön, E., Bogut, I., Vukovi, R., Galovi, D., Bogut, A., Horvati, J., 2015. Distribution and age-related bioaccumulation of lead (Pb), mercury (Hg), cadmium (Cd), and arsenic (As) in tissues of common carp (*Cyprinus carpio*) and European catfish (*Sylurus glanis*) from the Buško Blato reservoir (Bosnia and Herzegovina). Chemosphere 135, 289–296.

Hedera, P., Peltier, A., Fink, J.K., Wilcock, S., London, Z., Brewer, G.J., 2009. Myelopolyneuropathy and pancytopenia due to copper deficiency and high zinc levels of unknown origin II. The denture cream is a primary source of excessive zinc. Neurotoxicology 30, 996–999.

INDEC (Instituto Nacional de Estadística y Censos - Argentina), 2010. Http://www.indec.gob.ar.

Jaric, I., Višnjic-Jeftic, Z., Cvijanovic, G., Gacic, Z., Jovanovic, L., Skoric, S., Lenhardt, M., 2011. Determination of differential heavy metal and trace element accumulation in liver, gills, intestine and muscle of sterlet (*Acipenser ruthenus*) from the Danube River in Serbia by ICP-OES. Microchem. J. 98 (1), 77–81.

Jaureguizar, A.J., Ruarte, C., Guerrero, R.A., 2006. Distribution of age-classes of striped weakfish (*Cynoscion guatucupa*) along an estuarine–marine gradient: correlations with the environmental parameters. Estuar. Coast. Shelf Sci. 67 (1), 82–92.

Jones, R.P., Clarke, J.U., 2005. Analytical Chemistry Detection Limits and the Evaluation of Dredged Sediment. ERDC/TN EEDP-04-36. U.S. Army Engineer Research and Development Center, Vicksburg, MS.

Karadede, H., Oymak, S.A., Ünlü, E., 2004. Heavy metals in mullet, *Liza abu*, and cat-fish, *Silurus triostegus*, from the Atatürk Dam Lake (Euphrates), Turkey. Environ. Int. 30, 183–188.

Klavercamp, J.E., Mc Donald, W.A., Duncan, D.A., Wagenann, R., 1984. Metallothionein and acclimation to heavy metals in fish, a review. In: Cairns, V.W., Hodson, P.V., Nriagu, J.O. (Eds.), Contaminant Effects on Fisheries. Wiley, New York, pp. 99–113.

La Colla, N.S., 2016. Bioacumulación de metales en peces marinos y su distribución en columna de agua, bajo diferentes gradientes en el estuario de Bahía Blanca. PhD Thesis. Universidad Nacional del Sur, Argentina (240 pp.).

La Colla, N.S., Negrin, V.L., Marcovecchio, J.E., Botté, S.E., 2015. Dissolved and particulate metals dynamics in a human impacted estuary from the SW Atlantic. Estuar. Coast. Shelf Sci. 166, 45–55.

La Colla, N.S., Botté, S.E., Oliva, A.L., Marcovecchio, J.E., 2017. Tracing Cr, Pb, Fe and Mn occurrence in the Bahía Blanca estuary through commercial fish species. Chemosphere 175, 286–293.

Lane, T.W., Morel, M.M., 2000. A biological function for cadmium in marine diatoms. Proc. Natl. Acad. Sci. 97, 4627–4631.

Li, P., Zhang, J., Xie, H., Liu, C., Liang, S., Ren, Y., Wang, W., 2015. Heavy metal bioaccumulation and health hazard assessment for three fish species from Nansi Lake, China. Bull. Environ. Contam. Toxicol. 94 (4), 431–436.

Limbozzi, F., Leitào, T.E., Neves, R., 2008. Characterization of Bahía Blanca main existing pressures and their effects on the state indicators for surface and groundwater quality. In: Baretta, J., Mateus, M. (Eds.), Perspectives on integrated coastal zone management in South America, Lisboa, pp. 315–331.

Lopez Cazorla, A., 1985. Edad, crecimiento y comportamiento migratorio de *Brevoortia aurea* (Agassiz, 1829) (Osteichthyes, Clupeidae) de Bahía Blanca (Argentina).

Investig. Pesq. 49, 297–313.

Lopez Cazorla, A., 1987. Contribución al conocimiento de la ictiofauna marina del área de Bahía Blanca. PhD Thesis. Universidad Nacional de La Plata, Argentina (247 pp.).

Lopez Cazorla, A., 1996. The food of *Cynoscion striatus* (Cuvier) (Pisces: Sciaenidae) in the Bahía Blanca area, Argentina. Fish. Res. 28, 371–379.

Lopez Cazorla, A., 2000. Age structure of the population of weakfish *Cynoscion guatucupa* (Cuvier) in the Bahía Blanca waters, Argentina. Fish. Res. 46 (1–3), 279–286.

Lopez Cazorla, A., 2004. Peces. In: Piccolo, C.M., Hoffmeyer, M.S. (Eds.), Ecosistema del estuario de Bahía Blanca, Bahía Blanca, Argentina, pp. 191–201.

Lopez Cazorla, A., 2005. On the age and growth of flounder *Paralichthys orbignyanus* (Jenyns, 1842) in Bahía Blanca Estuary, Argentina. Hydrobiologia 537 (1–3), 81–87.

Lopez Cazorla, A., Forte, S., 2005. Food and feeding habits of flounder *Paralichthys orbignyanus* (Jenyns, 1842) in Bahia Blanca Estuary, Argentina. Hydrobiologia 549 (1), 251–257.

Lopez Cazorla, A., Molina, J.M., Ruarte, C., 2014. The artisanal fishery of *Cynoscion guatucupa* in Argentina: exploring the possible causes of the collapse in Bahía Blanca estuary. J. Sea Res. 88, 29–35.

Malhadas, S.M., 2008. Modelacao do impacte de emisarios submarinos em zonas costeiras-caso da Foz do Arelho. Msc. Thesis. IST, Universidad Técnica de Lisboa, Lisboa (95 pp.).

Marcovecchio, J.E., Moreno, V.J., Perez, A., 1988a. Determination of heavy metal concentrations in biota of Bahía Blanca, Argentina. Sci. Total Environ. 75 (2), 181–190.

Marcovecchio, J.E., Moreno, V.J., Perez, A., 1988b. The sole, *Paralichthys* sp., as an indicator species for heavy metal pollution in the Bahía Blanca estuary, Argentina. Sci. Total Environ. 75 (2), 191–199.

Marcovecchio, J.E., Moreno, V.J., Perez, A., 1991. Metal accumulation in tissues of sharks from the Bahía Blanca estuary, Argentina. Mar. Environ. Res. 31 (4), 263–274.

Martínez, M.L., Intralawan, A., Vazquez, G., Perez-Maqueo, O., Sutton, P., Landgrave, R., 2007. The coasts of our world: ecological, economic and social importance. Ecol. Econ. 63, 254–272.

McGranahan, G., Balk, D., Anderson, B., 2006. The rising tide: assessing the risks of climate change and human settlements in low elevation coastal zones. Environ. Urban. 12, 17–38.

Pan, K., Wang, W.X., 2012. Trace metal contamination in estuarine and coastal environments in China. Sci. Total Environ. 421, 3–16.

Pérez-López, R., JNieto, J.M., López-Cascajosa, M.J., Díaz-Blanco, M.J., Sarmiento, A.M., Oliveira, V., Sánchez-Rodas, D., 2011. Evaluation of heavy metals and arsenic speciation discharged by the industrial activity on the Tinto-Odiel estuary, SW Spain. Mar. Pollut. Bull. 62, 405–411.

Perillo, G.M.E., Piccolo, M.C., 1991. Tidal response in the Bahía Blanca Estuary, Argentina. J. Coast. Res. 7, 437–449.

Qadir, A., Malik, R.N., 2011. Heavy metals in eight edible fish species from two polluted tributaries (Aik and Palkhu) of the River Chenab, Pakistan. Biol. Trace Elem. Res. 143 (1524), 1540.

Rahman, M.S., Molla, A.H., Saha, N., Rahman, A., 2012. Study on heavy metals levels and its risk assessment in some edible fishes from Bangshi River, Savar, Dhaka, Bangladesh. Food Chem. 134 (4), 1847–1854.

Salem, Z.B., Laffray, X., Ashoour, A., Ayadi, H., Aleya, L., 2014. Metal accumulation and distribution in the organs of Reeds and Cattails in a constructed treatment wetland (Etueffont, France). Ecol. Eng. 64, 1–17.

Sardiña, P., Lopez Cazorla, A., 2005. Feeding habits of the juvenile striped weakfish, *Cynoscion guatucupa* Cuvier 1830, in Bahía Blanca estuary (Argentina): seasonal and ontogenetic changes. Hydrobiologia 532, 23–38.

SENASA (Servicio Nacional de Sanidad y Calidad Agroalimentaria), 2014. http://www.senasa.gov.ar/.

Spencer, K.L., MacLeod, C.L., Tuckett, A., Johnson, S.M., 2006. Source and distribution of tracemetals in the Medway and Swale estuaries, Kent. Mar. Pollut. Bull. 52, 226–231.

Squadrone, S., Burioli, E., Monaco, G., Koya, M.K., Prearo, M., Gennero, S., Abete, M.C., 2016. Human exposure to metals due to consumption of fish from an artificial lake basin close to an active mining area in Katanga (DR Congo). Sci. Total Environ. 568, 679–684.

Triebskorn, R., Köhler, H.R., Honnen, W., Schramm, M., Adams, S.M., Müller, E.F., 1997. Induction of heat shock proteins, changes in liver ultrastructure, and alterations of fish behavior: are these biomarkers related and are they useful to reflect the state of pollution in the field? J. Aquat. Ecosyst. Stress. Recover. 6 (1), 57–73.

Uysal, K., Emre, Y., Kose, E., 2008. The determination of heavy metal accumulation ratios in muscle, skin and gills of some migratory fish species by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) in Beymelek Lagoon (Antalya/Turkey). Microchem. J. 90, 67–70.

Valiñas, M.S., Molina, L.M., Addino, M., Montemayor, D.I., Acha, E.M., Iribarne, O.O., 2012. Biotic and environmental factors affect Southwest Atlantic saltmarsh use by juvenile fishes. J. Sea Res. 68, 49–56.

Velusamy, A., Kumar, P.S., Ram, A., Chinnadurai, S., 2014. Bioaccumulation of heavy metals in commercially important marine fishes from Mumbai Harbor, India. Mar. Pollut. Bull. 81 (1), 218–224.

Viegas, C.N., Nunes, S., Fernández, R., Neves, R., 2009. Streams contribution on bathing water quality after rainfall events in Costa do Estoril- a tool to implement an alert system for bathing water. J. Coast. Res. 56, 1691–1695.

Waeles, M., Riso, R.D., Le Corre, P., 2007. Distribution and seasonal changes of lead in an estuarine system affected by agricultural practices: the Penze estuary, NW France. Estuar. Coast. Shelf Sci. 74, 570–578.

Wickham, H., 2009. ggplot2: Elegant Graphics for Data Analysis. Springer Science & Business Media.

Wood, C.M., 2011. An introduction to metals in fish physiology and toxicology. In: Homeostasis and Toxicology of Essential Metals. 31A.

Ye, F., Huang, X., Zhang, D., Tian, L., Zeng, Y., 2012. Distribution of heavy metals in sediments of the Pearl River Estuary, Southern China: implications for sources and historical changes. J. Environ. Sci. 24 (4), 579–588.

Yi, Y., Tang, C., Yi, T., Yang, Z., Zhang, S., 2017. Health risk assessment of heavy metals in fish and accumulation patterns in food web in the upper Yangtze River, China. Ecotoxicol. Environ. Saf. 145, 295–302.

Yilmaz, A.B., Sangun, M.K., Yaghoglu, D., Turan, C., 2010. Metals (major, essential to non-essential) composition of the different tissues of three demersal fish species from İskenderun Bay, Turkey. Food Chem. 123, 410–415.

Zar, J.H., 1996. Biostatistical Analysis, third ed. Prentice Hall, New Jersey, USA.

Zhao, S., Feng, C., Quan, W., Chen, X., Niu, J., Shen, Z., 2012. Role of living environments in the accumulation characteristics of heavy metals in fishes and crabs in the Yangtze River Estuary, China. Mar. Pollut. Bull. 64, 1163–1171.