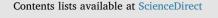
ELSEVIER



Marine Pollution Bulletin

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

# Presence of trace elements in the silverside Odontesthes argentinensis

## Gustavo A. Thompson\*, Alejandra V. Volpedo

CONICET, Universidad de Buenos Aires, Instituto de Investigaciones en Producción Animal (INPA), Buenos Aires, Argentina

## ARTICLE INFO

Keywords: Odontesthes Marine silverside Pollution Coastal environment South America

## ABSTRACT

The silverside *Odontesthes argentinensis* is an economically significant resource for commercial fisheries in South America. We evaluated the presence of trace elements in the stomach content and fish tissues (muscle and otoliths) of *O. argentinensis*. In addition, we assessed the presence of trace elements in its prey (zooplankton) and in seawater in a coastal temperate area. The most abundant trace elements found in the water, zooplankton, stomach content, and fish tissues (muscle and otoliths) constituted of Ba, Mn, Sr and Zn, while Cd, Cu and Pb were observed in lower concentrations. We concluded that *O. argentinensis* specimens captured from the environment, within the length range analyzed for muscle samples (total length: < 21 cm), are deemed fit for human consumption because the concentrations of trace elements mostly meet the standards established in the Argentine Food Code. The information obtained in this study is vital for *O. argentinensis* farming in closed systems.

## 1. Introduction

The marine silverside Odontesthes argentinensis (Valenciennes, 1835) is a large species considered having a geographically wide distribution along the Southwestern Atlantic Ocean coast, between Rio de Janeiro, Brazil (22°S) and Rawson, Argentina (43°S) (Dyer 2000; Di Dario et al. 2014). This species, an economically significant resource for local fishermen in southern South America (De Buen 1953; Chão et al. 1985; Sampaio 2006), is captured by artisanal fishermen during the cold months, and by recreational coastal fishermen during the warm months. Due to the development of significant efforts for the farming of O. argentinensis in captivity, knowledge on the transference of trace elements from their natural environment and the accumulation of these elements in O. argentinensis specimens, is of interest to human health and to prospective farming using closed systems (Sampaio 2006; Rodrigues et al. 2009). In Japan, there are several farms and intensive farming systems of silverside (Velasco et al. 2008). Tavares et al. (2014) indicated that the production techniques of silverside farming are gradually improving, and that the farming cycle can be completed in closed systems. However, there is a lack of consensus on the relative importance of the dietary intake of trace elements in fish (Ni et al. 2000). Fish can incorporate trace elements, either from consumed food through the intestines or through the gills from the water they inhabit (Campana 1999). Laboratory studies suggested a substantial contribution to the total uptake of some trace elements by food but, due to methodological shortcomings, the environmental relevance of these results has been questioned (Reinfelder et al. 1998).

The most studied environmental trace elements are Cd, Cu, Pb, Mn and Zn, because they may present an environmental hazard (Reinfelder et al. 1998). In addition, Cd, Cu, and Pb could have an important an-thropogenic source.

CrossMark

The successive accumulation and increase in concentration of a compound from prey to predator and with higher trophic levels, is known as biomagnification. This cumulative tendency, is of particular concern in ecological and human risk assessments (Newman 2015). In particular, the biomagnification of trace elements occurs when their concentrations in the tissues of an organism exceed those in its food or in an adjacent trophic level (Reinfelder et al. 1998). Connell (1989) proposed to restrict the term biomagnification solely referring to concentration increases that result from food intake alone.

The aim of this study was to analyze the relationship between the concentration of trace elements in the stomach content, muscle and otoliths of *Odontesthes argentinensis* and that in its environment (seawater and plankton), in order to infer plausible routes of transfer from the environment to the fish.

## 2. Materials and methods

Water samples, plankton and specimens of *O. argentinensis* were collected from January–February of 2013 and 2014 in the Partido de la Costa, Buenos Aires Province, Argentina (36°39'S–56°40'W) and processed, through the use of inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin Elmer Optima 2000 DV optical emission spectrometer), to determine the concentrations of Ba, Cd, Cu, Mn, Pb, Sr

E-mail address: gustavo@ege.fcen.uba.ar (G.A. Thompson).

http://dx.doi.org/10.1016/j.marpolbul.2017.09.011

0025-326X/  $\odot$  2017 Elsevier Ltd. All rights reserved.

<sup>\*</sup> Corresponding author.

Received 7 July 2017; Received in revised form 5 September 2017; Accepted 6 September 2017 Available online 12 October 2017

#### Table 1

|    | Muscle            |                   |              | Seawater         |                 |              |  |  |
|----|-------------------|-------------------|--------------|------------------|-----------------|--------------|--|--|
|    | Certified values  | Measured values   | Recovery (%) | Certified values | Measured values | Recovery (%) |  |  |
| Ва | ND                |                   |              | 99.4             | $101.2 \pm 0.7$ | 102          |  |  |
| Cd | $0.043 \pm 0.008$ | $0.046 \pm 0.011$ | 109          | 99.1             | $97.8 \pm 1.2$  | 99           |  |  |
| Cu | $2.34 \pm 0.16$   | $2.32 \pm 0.20$   | 99           | 102              | $103.9 \pm 2.9$ | 102          |  |  |
| Mn | $3.66 \pm 0.34$   | $3.46 \pm 0.45$   | 95           | 100              | $101 \pm 0.2$   | 101          |  |  |
| Pb | $0.065 \pm 0.007$ | $0.067 \pm 0.009$ | 103          | 99.7             | $88.9 \pm 0.9$  | 89           |  |  |
| Sr | ND                |                   |              | 100              | $113.7 \pm 2.6$ | 114          |  |  |
| Zn | $25.6 \pm 2.3$    | $23.9 \pm 1.84$   | 93           | 99.2             | $98.1 \pm 0.5$  | 99           |  |  |

Concentration of trace elements (mean  $\pm$  SE, in mg kg<sup>-1</sup> dry weight, n = 3) found in certified reference material DORM-2 (dogfish muscle, NRC, Canada) and (mean in mg L<sup>-1</sup>, n = 3) found in working standard prepared by diluting Perkin Elmer<sup>®</sup> Pure Plus standard reference material in artificial seawater. ND. No data available.

and Zn. The ICP-AES method was used both in its radial and axial viewing modes (Table 1). Total length (LT) in mm and total weight (WT) in g of collected specimens of O. argentinensis were measured. Water samples were collected, preserved, prepared, and analyzed according to standardized methods (APHA 1995). Water samples were preserved by addition of 2 mL of nitric acid (1% V/V) per liter of sample and filtered through a nylon meshed filter of 0.45 µm of pore to ensure the absence of suspended solids, that would interfere with the determination of metals. This procedure overestimated the dissolved Mn available to be taken by fish. Plankton samples were collected by using a 30 cm diameter net with a mesh size of  $60 \,\mu\text{m}$ . The resultant concentrates were stored until they were vacuum-filtered through acidwashed pre-weighed filter papers and dried in a desiccator until constant weight (Ho et al. 2007). Filters with plankton were heated in nitric acid (50% V/V) and then placed in a muffle at 450 °C for 24 h (modified from Medeiros et al. 2012). Samples were then cooled, filtered and brought to a final volume with nitric acid (10% V/V). Results were corrected based on control blanks. All laboratory tools used to process O. argentinensis specimens were soaked in 10% nitric acid for 48 h, rinsed five times with distilled water, and then an additional five times with ultra pure Milli-Q water. Between 2013 and 2014, 123 specimens (LT: 5.5-33.0 cm) were selected. Each specimen had its muscle (approximately 1 g), full stomach and both otoliths removed. Muscle and stomach content were further dried in an oven at 80 °C for 96 h, weighed and muffled at 450 °C for 24 h (modified from Medeiros et al. 2012). Acid digestion was performed with nitric acid (50% V/V) followed by heating, and the resulting samples were taken to a final volume with nitric acid (10% V/V). Otoliths were placed in nitric acid (10% V/V) until dissolution and filtered in order to remove suspended solids and determine trace elements. Pro-analysis reagents were used throughout the study. The accuracy of the analytical method was validated using certified reference standards of trace elements in water and muscle (Table 1). The experimental values obtained for the concentration of trace elements were in concordance (95% confidence level) with the concentrations of certified materials (Table 1). A blank was used for calibration of all measurements. The detection limits of ICP-AES in  $\mu$ g L<sup>-1</sup> based on three times the standard deviation of the blank signal were 8 (Ba), 4 (Cd), 5 (Cu), 5 (Mn), 12 (Pb), 10 (Sr) and 6 (Zn). Seawater samples were diluted ten times (2013 samples) and five times (2014 samples), therefore detection limits of ICP-AES increased ten and five times, respectively.

Spearman's correlation was used in measurement of the strength of the associations between trace elements in each tissue type and year. For the purpose of statistical analysis, left-censored values (below the detection limit of ICP-AES) were replaced with one-half their respective detection limits (Antweiler and Taylor 2008). To determine the significance of the differences on the concentrations of each trace element from the different years sampled, one-way analysis of covariance (ANCOVA) was performed on log- or rank-transformed trace element concentrations in muscle, stomach content and otoliths. LT was the covariate. Significant differences between concentrations were determined a posteriori through multiple contrasts using the Tukey HSD test for unequal samples. The bioaccumulation factor (BAF) was determined as the ratio of the concentration of each trace element in the organism (muscle, stomach content or otoliths) to the concentration of each trace element in water (BAF =  $C_B / C_W$ ). The biomagnification factor (BMF) is the ratio of the chemical concentration in the organism to the concentration at a lower trophic level (organism's diet or prey):  $BMF = C_B / C_D$ . The chemical concentration was expressed in units of mass of chemical per kg of organism (C<sub>B</sub>), mass of chemical per L of seawater (C<sub>w</sub>) and mass of chemical per kg of prey (C<sub>D</sub>), respectively. The weight of the organism and the weight of the food were expressed on a wet weight or dry weight basis. Most frequently, the weight of the organism is expressed on a wet weight basis (Gobas and Morrison 2000). It would be more accurate to use Connell's definition of biomagnification and the estimation factor defined as Food Biomagnification factor (BMF<sub>food</sub>), due to O. argentinensis' nature of being selective about its food source, rather than consuming what is available in its environment.  $\ensuremath{\mathsf{BMF}_{\mathsf{food}}}$  is estimated as the ratio of the chemical concentration in the organism (muscle) to the concentration in the organism's stomach content (BMF  $_{\rm food}$  =  $C_{\rm B}$  /  $C_{SC}$ ). BAF for Mn was not estimated, due to the overestimation of Mn concentration in seawater.

### 3. Results and discussion

The most abundant trace elements determined in water, zooplankton and stomach content samples were Ba, Mn, Sr and Zn, while those found in lower concentrations were Cu, Pb, Cd (Table 2).

The concentrations of all trace elements, except that of Zn in stomach contents, were significantly higher from specimens collected in 2014 (stomach content composed mainly of megalopa larvae; unpublished results) than found in specimens collected in 2013 (ANCOVA, Table 2). The proportions and concentrations of trace elements recorded in stomach contents differed from the values determined in plankton samples (Table 2). This difference would correspond to an existence of food selectivity in *O. argentinensis* throughout its development. A significant and positive correlation (P < 0.05) was found between the concentrations of Mn, Sr and Zn as ascertained in the food content in both years, and likewise between the concentrations of Cu and Pb (r: 0.68, P < 0.001) analyzed in the stomach content in 2013.

The concentrations of Cd, Cu and Mn in the otoliths were found to be under the detection limits of ICP-AES. The concentrations in otoliths and muscle were dissimilar between both years analyzed (Table 3).

In analyzing the presence of different elements in each tissue type, we detected that the concentrations of Ba, Mn, Sr and Zn in muscle was correlated to each other from 2013 and 2014 samples (r > 0.37, P < 0.009). The concentration of Ba and Sr in the otoliths was positively correlated during both years (r > 0.54, P < 0.009), while that of Pb and Zn was only positively correlated in 2013 (r: 0.71, P < 0.001).

A correlation was also observed between food and muscle for Cu in 2013 (r: 0.82, P < 0.001) and for Ba and Zn in 2014 (r > 0.66,

#### Table 2

Concentration of trace elements: median and range values in the stomach content of *Odontesthes argentinensis* specimens captured during 2013 and 2014. Medians with different capital letters on the same line show a statistically significant difference (P < 0.05). Additionally, records of trace metals for zooplankton and seawater are displayed. LT: total length range recorded in cm. DW: dry weight. A: axial viewing mode. R: attenuated radial view mode. (\*): estimated from left-censored data (half of the lower detection limit). (\*): overestimated concentration due to the preparation method.

|     |                          |       | 2013                                  |      |                                | 2014                                     |                               |                         |  |
|-----|--------------------------|-------|---------------------------------------|------|--------------------------------|--|-------------------------------|-------------------------|--|
|     | Torch Wavelength<br>(nm) |       | · · · · · · · · · · · · · · · · · · · |      | Seawater<br>μg L <sup>-1</sup> | Stomach content<br>μg g <sup>-1</sup> DW | Zooplankton $\mu g g^{-1} DW$ | Seawater $\mu g L^{-1}$ |  |
| LT  |                          |       | 10.6 (7.2–21)                         |      |                                | 6.5 (5.5–33)                             |                               |                         |  |
| (n) |                          |       | 52                                    |      |                                | 31                                       |                               |                         |  |
| Ba  | Α                        | 233.5 | 11 <sup>A</sup> (0.2–102)             | 18   | 70                             | 68 <sup>B</sup> (9.8–497)                | 31                            | 20*                     |  |
| Cd  | Α                        | 228.8 | 0.11 <sup>A</sup> (0-22.4)            | 0.10 | 20*                            | $2.8^{\text{B}}$ (0–38)                  | 0.03*                         | 10*                     |  |
| Cu  | Α                        | 324.7 | 2.8 <sup>A</sup> (0–70)               | 4.3  | 25*                            | 23.7 <sup>B</sup> (0–255)                | 6                             | 12.5*                   |  |
| Mn  | Α                        | 257.6 | $11^{A}$ (1.7–130)                    | 55   | 11–41°                         | 148 <sup>B</sup> (5.8–1757)              | 160                           | 26°                     |  |
| Pb  | А                        | 220.3 | $2.3^{A}(0-101)$                      | 4.5  | 118                            | 49 <sup>B</sup> (9.8–795)                | 0.09*                         | 30*                     |  |
| Sr  | R                        | 407.7 | 62 <sup>A</sup> (31–193)              | 109  | 5840-6234                      | $1560^{B}$ (12–17,568)                   | 141                           | 4429                    |  |
| Zn  | Α                        | 213.8 | 219 <sup>A</sup> (39–3690)            | 12   | 128-650                        | 303 <sup>A</sup> (46–1687)               | 58                            | 118                     |  |

#### Table 3

Concentration of trace elements: median and range in muscle and otoliths of *O. argentinensis* captured during 2013 and 2014. LT: total length range recorded in cm. DW: dry weight. Medians with different capital letters on the same line show a statistically significant difference (P < 0.05). (\*) estimated from left-censored data (half of the lower detection limit).

|     | Otoliths ( $\mu g g^{-1} I$ | OW)                             | Muscle ( $\mu g g^{-1}$ DW) |                           |  |  |
|-----|-----------------------------|---------------------------------|-----------------------------|---------------------------|--|--|
|     | 2013                        | 2014                            | 2013                        | 2014                      |  |  |
| LT  | 10.6 (7.2–21)               | 7.5 (5.2–9.8)                   | 10.6 (7.2–21)               | 7.5 (5.2–9.8)             |  |  |
| (n) | 52                          | 50                              | 52                          | 50                        |  |  |
| Ba  | 11 <sup>A</sup> (0–26)      | 497 <sup>B</sup> (0–4544)       | 22 <sup>C</sup> (1–881)     | $6.4^{\rm D}(2-20)$       |  |  |
| Cd  | 9*                          | 12*                             | 0.17(0.02-0.34)             | 0.3*                      |  |  |
| Cu  | 11*                         | 15*                             | 6.5 <sup>A</sup> (3–16)     | 4.24 <sup>B</sup>         |  |  |
|     |                             |                                 |                             | (0 - 11)                  |  |  |
| Mn  | 11*                         | 15*                             | 4.1 <sup>A</sup> (1.7–7.3)  | $2.5^{B}$                 |  |  |
|     |                             |                                 |                             | (0.9–5.7)                 |  |  |
| Pb  | 48 <sup>A</sup> (0–634)     | 37*                             | 3 <sup>B</sup> (0–76)       | 9.5 <sup>c</sup> (0.4–39) |  |  |
| Sr  | 1665 <sup>A</sup>           | 2139 <sup>A</sup>               | 126 <sup>B</sup> (0–251)    | 21 <sup>C</sup> (10–47)   |  |  |
|     | (344-2229)                  | (769–7764)                      |                             |                           |  |  |
| Zn  | 179 <sup>A</sup> (0 - 2200) | 6120 <sup>B</sup><br>(0–75,870) | 162 <sup>C</sup> (45–1979)  | 81 <sup>D</sup> (59–142   |  |  |

P < 0.04). Considering the development of species, a negative correlation was identified of LT with the concentrations of Mn and Ba in muscle (P < 0.02) from both years sampled. Additionally, a negative correlation was also shown between LT and the concentrations of Cu, Sr and Zn in 2014; on the other hand, the concentration of Zn in the otoliths decreased significantly with the increase in LT (P > 0.02) in both years.

According to the results observed (Tables 2 and 3) and the BAF values calculated (Table 4), it may be suggested that Ba and Sr accumulate in the otoliths. Mn was primarily concentrated in the stomach

content and secondarily in muscle, with a decrease in concentration with age. The rest of elements (Pb, Zn, Cd, Cu) showed no clear trend of preferential accumulation between samples in any of the three tissues analyzed. Except for the magnification of Sr and Zn in the otoliths samples during both 2013 and 2014, the remaining elements showed dissimilar results in both years (Table 4). However,  $BMF_{food}$  values from both years showed a more consistent pattern of results, indicating that Cu seems to be magnified in the muscle. Ba, Mn, Pb and Zn displayed a very low frequency of magnification in this tissue, while Cd and Sr showed no tendency towards magnification (Table 5).

The noted values of BAF and BMF showed that the trace elements analyzed had been incorporated in the tissues of *O. argentinensis*. Since biomagnifications were determined under field conditions rather than under laboratory conditions, the biomagnification factors, BMF and BMF<sub>food</sub>, were inevitably the result of chemical uptake by all routes of chemical uptake. These routes include uptake via the dermis, respiratory surface, etc., rather than by dietary absorption alone (Boethling and Mackay 2000). The primary route of body intake of Sr and Ba is from water (Walther and Thorrold 2006), whereas that of Mn and Zn is mainly from the diet (Eisler 2010; Hogstrand 2012). Cd, Cu and Pb can be uptaken by either of the two routes. Higher uptake by one of the two routes depends on the environmental conditions, including salinity, pH, water hardness, and on the concentration of these elements in the water the fish inhabit (McGeer et al. 2012; Grosell 2012; Mager 2012).

Ba, Mn, Sr and Zn are among the most abundant elements in the earth's crust constituting between 0.1 and 0.02%. These elements are present at high concentrations in all environments, including seawater (Chowdhury and Blust 2012; Lucchini et al. 2015; Oskarsson 2015; Sandstead 2015). Ba, Sr and Zn are Ca-mimicry elements (chemically similar to Ca), therefore being able to interact with each other in a qualitatively similar way (i.e. competitively) (Walther and Thorrold

Table 4

Bioaccumulation factor (BAF) and Biomagnification factor (BMF) estimated for otoliths, muscle and stomach content of *O. argentinensis* during samplings from 2013 and 2014. (\*) Estimated from left-censored data. NE: not estimable because both variables were left-censored data.

|    | 2013     |      |        |      |                 |      | 2014     |       |        |       |                 |      |
|----|----------|------|--------|------|-----------------|------|----------|-------|--------|-------|-----------------|------|
|    | Otoliths |      | Muscle |      | Stomach content |      | Otoliths |       | Muscle |       | Stomach content |      |
|    | BAF      | BMF  | BAF    | BMF  | BAF             | BMF  | BAF      | BMF   | BAF    | BMF   | BAF             | BMF  |
| Ba | 142      | 0.6  | 13     | 0.05 | 21              | 0.08 | 10923*   | 7.11  | 35*    | 0.02  | 146*            | 0.1  |
| Cd | NE       | 86*  | 2*     | 0.4  | 0.4*            | 0.07 | NE       | NE    | NE     | NE    | NE              | NE   |
| Cu | NE       | 2.6* | 44*    | 0.2  | 8*              | 0.05 | NE       | 2.6*  | 41*    | 0.09  | 18*             | 0.04 |
| Mn | -        | 0.2* | -      | 0.01 | -               | 0.02 | -        | 0.09* | -      | 0.002 | -               | 0.02 |
| Pb | 265      | 7    | 2.3    | 0.06 | 2               | 0.05 | NE       | NE    | 34*    | 11    | 87*             | 29   |
| Sr | 287      | 15   | 4.5    | 0.2  | 1.3             | 0.07 | 372      | 11    | 0.54   | 0.02  | 2.9             | 0.1  |
| Zn | 277      | 15   | 42     | 2.3  | 41              | 2.2  | 8007     | 16    | 85     | 0.2   | 238             | 0.5  |

#### Table 5

Food Biomagnification factor (BMF<sub>food</sub>) median and range (in parentheses) estimated as the ratio between dry weight of trace elements in muscle and in stomach content of *O. argentinensis* during samplings from 2013 and 2014. NE: not estimable because both variables were left-censored data.

|    | 2013             | 2014             |
|----|------------------|------------------|
| Ba | 0.36 (0.05–1.9)  | 0.21 (0.08-0.4)  |
| Cd | 1.7 (0.03-2.3)   | NE               |
| Cu | 3.09 (0.1-62.7)  | 1.57 (0.24-5.98) |
| Mn | 0.34 (0.07-1)    | 0.09 (0.04-0.21) |
| Pb | 0.59 (0.01-0.81) | 0.33 (0.02-0.82) |
| Sr | 2.04 (0.01-4.4)  | 0.14 (0.06-0.33) |
| Zn | 0.60 (0.04–1.2)  | 0.26 (0.22-0.73) |

2006; Chowdhury and Blust 2012; Hogstrand 2012). For this reason, these elements are predominantly accumulated in hard bone tissues (Smith et al. 2005; Walther and Thorrold 2006; Yankovich 2009), including the aragonite matrix of otoliths, where the highest BMF values were determined. In addition, Mn is concentrated in hard tissues through substitution of Ca. It is found primarily in vertebrae and scaly skin (Eisler 2010), and tends to accumulate less in soft tissues such as muscles. This certainty is reflected in the lower  $BMF_{food}$  values of the latter (Table 5).

Elements with lower concentrations in tissue, water, and zooplankton (Cd, Cu and Pb) generally show lower concentrations in the geosphere (Mager 2012; Ellingsen et al. 2015; Nordberg et al. 2015). High concentrations of these elements have been associated with anthropogenic pollution (Baird 2001). Pb has a dysfunctional effect and is toxic even at low concentrations (Mager 2012). It can substitute Ca and therefore, be incorporated into hard tissues, and is scarcely found in muscle tissue masses (Mager 2012). This in agreement with the BAF and BMF values recorded in the present study (Tables 4 and 5). The correlation observed between Pb and Cu might be due to the two elements ability to provide access to each other (synergistic effect) during simultaneous exposure to both elements (Tao et al. 1999; Mager 2012). However, in agreement with that found in previous studies (Gray 2002), Cd concentrations were low in all samples so the trends were difficult to interpret.

Field results suggested that Cu and Sr were magnified in *O. argentinensis* muscle. Previous studies in fish, performed mostly under laboratory conditions, have indicated no biomagnification in the majority of the elements analyzed (including Cu and Sr). Moreover, these studies suggested that biomagnification was not the rule, but rather the exception (Reinfelder et al. 1998; Gray 2002; Wood et al. 2012a, 2012b). This difference between results under field and laboratory conditions suggests the importance of alternative routes of chemical uptake (like dermis and respiratory surface) for these essential elements. Furthermore, there is at least one recent field study that has suggested the possibility of biomagnification of Sr in muscle tissue of fish (for *Esox lucius*; Konovalenko et al. 2016). In this regard, it is important to carry out these types of studies in natural conditions, specifically in coastalestuarine species, that are more exposed to the presence of trace elements from continental discharges.

The correlations of Ba and Sr with age expand and corroborate the

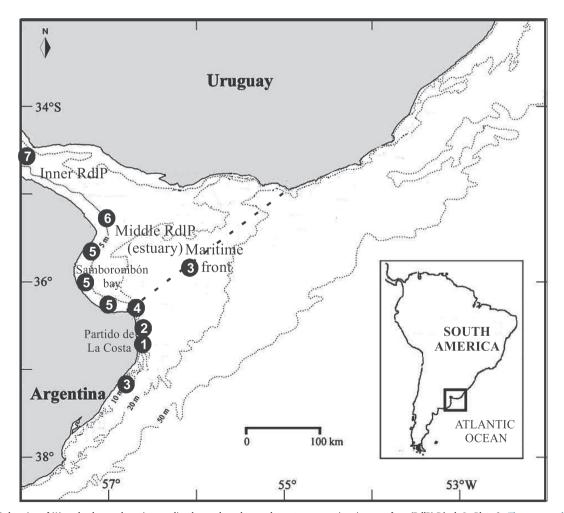


Fig. 1. Geographic location of (1) study place and previous studies that evaluated trace element concentrations in water from (RdlP) Río de La Plata 2 - Thompson and Sanchez de Bock (2007), 3 - Freeplata (2005), 4 - Schenone et al. (2007), 5 - Tatone et al. (2015), 6 - CARP (1990), 7 - Avigliano et al. (2015).

observations of Eisler (1984). Eisler ascertained that regardless of the tissue or species of teleost fish studied, the concentration of Cd and Pb increased with age, and that the concentration of Cu, Mn and Zn decreased with age in farming and development areas. These correlations are not fully understood and may be influenced by various factors which include changes in diet through the life cycle, the reproductive cycle, the fishes health, the bioavailability of chemical species, the interaction between trace elements and metallothioneins, and anthropogenic influence.

A possible source of trace elements in the study area is from the Río de la Plata (RdlP). The RdlP is the fifth largest river in the world, second only to the Amazon Basin in South America. The RdlP estuary located in Southeast South America is limited by the Argentinean coast in the South and Uruguayan coast in the North. The RdlP discharges significant amounts of organic matter and associated contaminants to the coastal waters, including heavy metals from petrochemical industries, tanneries, and meat processing facilities (Viana et al. 2005). There are numerous urban and industrial sites located along the Argentinean coast. The majority of waste from these sites is discharged either untreated, or has applied the most elemental treatment. Therefore, the RdlP estuary (Fig. 1) is a highly significant source of contaminants to the sea (Gerpe et al. 2002). The RdlP plume, which is freshwater flowing outside the bounds of the estuary, undergoes large seasonal and inter-annual changes related to river discharges and wind patterns (Piola et al., 2000; Soares, 2003; Gonzalez-Silvera et al. 2006). During the summer months, the plume is driven by preponderant easterly winds and expends southward along the Argentinean shore. Due to offshore Ekman transport, the plume tends to occupy a large portion of the shelf causing it to affect the study area. (Huret et al. 2005). Previous studies have showed trace element concentrations in the water in the of the RdlP estuary and in the area being researched (Avigliano et al. 2015; Tatone et al. 2015; Schenone et al., 2007; Thompson and Sanchez de Bock 2007; Freplata 2005; CARP 1990; Fig. 1, Table 6). In addition, any differences between trace element concentrations found in the stomach content between 2013 and 2014, could be related to the silversides primary source of diet, the megalopa larvae of decapods, during the latter year studied. Megalopa is a planktotrophic transitional stage of decapods that returns from the sea to the estuary (McConaugha 1992). It is difficult to classify megalopa larvae to the species level. However, if the adults live in the polluted estuarine environment, it is highly probably that their embryonic development stage, the eggs, had detectable concentrations of trace elements. This was previously discovered in studies conducted of the semiterrestrial burrowing crab, Neohelice granulate, and their eggs. Neohelice granulate is the sixth most studied species of crab and is widely distributed along the Argentine coast (Beltrame et al. 2010; Simonetti et al. 2012, 2013).

Only a few studies allow comparison of the content of metals in zooplankton. Scarlato et al. (1997) reported that zooplankton, on the coasts of Uruguay and Argentina (Buenos Aires), is highly contaminated with Cu, Pb, Mn, Zn. The concentrations recorded in the present study are similar to those reported by Scarlaro et al. for this study area (between 1 and 10  $\mu$ g g<sup>-1</sup> wet weight), except for the values for Zn and Mn

concentration, for which we recorded higher values.

To our knowledge, there have been no previous studies of the content of trace elements in O. argentinensis. However, several studies allow us to compare the content of metals with other Odontesthes species and other teleost fish in a nearby area. The values of Zn obtained for muscle of O. argentinensis were higher than the "high" values reported in tissues of Odontesthes by Viana et al. (2005) on the Uruguayan coast (10–75  $\mu$ g g<sup>-1</sup> dry weight), while values of Cu were similar in both of the studies. The concentrations of Zn recorded in muscle  $(7-42 \ \mu g \ g^{-1}$  wet weight) were similar to the Zn concentrations in the muscle of approximately 14 mostly carnivorous teleost fish obtained from the area of Samborombón Bay  $(5-50 \text{ mg g}^{-1} \text{ wet weight})$ Marcovecchio 2004: Marcovecchio and Moreno 1992). The concentrations of Ba, Cd, Mn, Pb, Sr and Zn recorded for muscle were predominantly greater in the present study than in the ones reported by Avigliano et al. (2015) for Odontesthes bonariensis in the RdlP and several shallow lakes of the Pampean plain region (Buenos Aires, Argentina). On the other hand, Mn and Zn concentrations in muscle were rather similar to the ones obtained by Vazquez et al. (2015) in the same shallow lakes. Furthermore, fish that feed on plankton accumulate Mn in bone tissues to a greater extent than those that feed on benthos (Petkevich 1967), and the concentration of Mn in muscle rarely exceeds  $0.5 \,\mu g \, g^{-1}$  wet weight (Eisler 2010). However, the results of this study indicate concentrations in muscle between 0.13 and 1.83  $\mu$ g g<sup>-1</sup> wet weight.

Concerning human consumption of this species, the concentrations of certain trace elements such as Zn in the tissues were lower than those established by the Argentine Food Code (100 ppm wet weight).The concentration limit of Mn in fish muscle acceptable for human consumption is not defined in the Argentine Food Code. Of the elements of possible anthropic origin, it should be noted that both Cu and Cd in muscle of *O. argentinensis* (average 1.10 and 0.04  $\mu$ g g<sup>-1</sup> wet weight, respectively) showed maximum values, which lie within the limits established by the Argentine Food Code. Pb exceeded the established limits in 8% of the samples studied (5.6  $\mu$ g g<sup>-1</sup> wet weight).

The information obtained in this study suggests an importance of both sources, water and diet, in the incorporation of trace elements in *O. argentinensis*. This incorporation constitutes a main issue of concern for the potential farming of this species in closed systems. In addition, specimens of *O. argentinensis* captured from the environment within the length range analyzed for muscle samples (LT < 21 cm), can be used for human consumption because the concentrations of trace elements agree within the standards established by the Argentine Food Code. It should be noted that, since the present study was conducted in the southern summer, additional prospective studies should be extended to different seasons of the year. This initiative would best assess the effect of temporal variation, mainly in stomach content, which could affect the estimation of BMF<sub>food</sub>.

### Acknowledgements

Financial support was provided by Universidad de Buenos Aires

### Table 6

Concentrations of Cd, Pb,Cu, Zn, Mn, Ba and Sr in surface water samples at the study site in this study and concentrations reported from previous studies. RdlP: Río de la Plata.

| Study site                            | Water body      | Trace element concentration (µg/l) |        |     |         |         |      |           | Reference                         |
|---------------------------------------|-----------------|------------------------------------|--------|-----|---------|---------|------|-----------|-----------------------------------|
|                                       |                 | Cd                                 | Pb     | Cu  | Zn      | Mn      | Ba   | Sr        |                                   |
| Partido de La Costa                   | Seawater        | ND                                 | 118    | ND  | 118-650 | 11–41   | 70   | 4429–6234 | This study                        |
| Partido de La Costa                   | Seawater        | < 2                                | 102    | 4   | 33      | -       | -    | -         | Thompson and Sanchez de Bock 2007 |
| Outer RdlP (maritime front and coast) | Seawater        | < 0.1                              | 2–4    | 2–4 | -       | -       | -    | -         | Freeplata 2005                    |
| Outer RdlP (coast)                    | Seawater        | 9                                  | 90-111 | 5   | 23-92   | 56-291  | -    | -         | Schenone et al. 2007              |
| Middle RdlP (Samborombón bay)         | Estuarine water |                                    |        |     |         | 0.3-3.3 |      |           | Tatone et al. 2015                |
| Middle RdlP (estuary)                 | Estuarine water | 0.2–5                              | 1.8-84 | 2–8 | -       | -       | -    | -         | CARP 1990                         |
| Inner RdlP                            | Freshwater      | 0.32                               | 2.48   | -   | 81.2    | 25.6    | 51.4 | 98.8      | Avigliano et al. 2015             |

(UBACYT 20020150100052BA), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET PIP 11220120100479CO) and Agencia Nacional de Promoción Científica y Tecnológica (PICT 2015-1823). We thank Natalia Turuelo and Sydney Forrester for help in the laboratory and Alejandro Ferrin (Muelle La Lucila) for assistance in the field.

#### References

- Antweiler, R.C., Taylor, H.E., 2008. Evaluation of statistical treatments of left-censored environmental data using coincident uncensored data sets: I. Summary statistics. Environ. Sci. Technol. 42, 3732–3738.
- APHA American Public Health Association, 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed. APHA, Washington, DC.
- Avigliano, E., Schenone, N.F., Volpedo, A.V., Goessler, W., Cirelli, A.F., 2015. Heavy metals and trace elements in muscle of silverside (*Odontesthes bonariensis*) and water from different environments (Argentina): aquatic pollution and consumption effect approach. Sci. Total Environ. 506, 102–108.
- Baird, C., 2001. Química ambiental. Reverté, Barcelona.
- Beltrame, M.O., De Marco, S.G., Marcovecchio, J.E., 2010. Influences of sex, habitat, and seasonality on heavy-metal concentrations in the burrowing crab (Neohelice granulata) from a coastal lagoon in Argentina. Arch. Environ. Contam. Toxicol. 58, 746–756.
- Boethling, R.S., Mackay, D., 2000. Handbook of Property Estimation Methods for Environmental Chemicals. CRC Press, Boca Raton, FL, USA.
- Campana, S.E., 1999. Chemistry and composition of fish otoliths: pathways, mechanisms and applications. Mar. Ecol. Prog. Ser. 188, 263–297.
- CARP Comisión Administradora del Río de La Plata, 1990. Estudio para la evaluación de la contaminación en el Río de La Plata. Informe de Avance 1989. Argentine Hydrographic Navy Service, Buenos Aires, Argentina.
- Chão, L.B., Pereira, L.E., Vieira, J.P., 1985. Estuarine fish community of the Patos Lagoon (Lagoa dos Patos, RS, Brazil)—a baseline study. In: Yánez-Arancibia, A. (Ed.), Fish Community Ecology in Estuaries and Coastal Lagoons: Towards an Ecosystem Integration. U.N.A.M. Press, México, pp. 429–450.
- Chowdhury, M.J., Blust, R., 2012. Strontium. In: Wood, C.M., Farrell, A.P., Brauner, C.J. (Eds.), Homeostasis and Toxicology of Non-Essential Metals. Fish Physiology Series 31B. Elsevier, New York, pp. 351–390.
- Connell, D.W., 1989. Biomagnification by aquatic organisms—a proposal. Chemosphere 19, 1573–1584.
- De Buen, F., 1953. Los pejerreyes (familia Atherinidae) en la fauna Uruguaya, con descripción de nuevas especies. Bol. Inst. Oceanogr. 4, 3–80.
- Di Dario, F., dos Santos, V.M., de Souza Pereira, M.M., 2014. Short communication range extension of *Odontesthes argentinensis* (Valenciennes, 1835) (Teleostei: Atherinopsidae) in the Southwestern Atlantic, with additional records in the Rio de Janeiro State, Brazil. J. Appl. Ichthyol. 30, 421–423.
- Dyer, B.S., 2000. Revisión sistemática de los pejerreyes de Chile (Teleostei, Atheriniformes). Estud. Oceanol. 19, 99–127.
- Eisler, R., 1984. Trace metal changes associated with age of marine vertebrates. Biol. Trace Elem. Res. 6, 165–180.
- Eisler, R., 2010. Compendium of Trace Metals and Marine Biota. Volume 2: Vertebrates Elsevier, Oxford.
- Ellingsen, D.G., Møller, L.B., Aaseth, J., 2015. Copper. In: Nordberg, G., Fowler, B., Nordberg, M. (Eds.), Handbook on the Toxicology of Metals. Specific Metals II. Amsterdam, Elsevier, pp. 765–786.
- FREPLATA, 2005. Análisis de Diagnóstico Transfronterizo del Río de la Plata y su Frente Marítimo. Documento Técnico. In: Proyecto Protección Ambiental del Río de la Plata y su Frente Marítimo: Prevención y Control de la Contaminación y Restauración de Hábitats, . http://www.freplata.org.
- Gerpe, M., Rodríguez, D., Moreno, V.J., Bastida, R.O., Moreno, J.D., 2002. Accumulation of heavy metals in the franciscana (*Pontoporia blainvillei*) from Buenos Aires Province, Argentina. LAJAM 1, 95–106.
- Gobas, F.A.P.C., Morrison, H.A., 2000. Bioconcentration and biomagnification in the aquatic environment. In: Boethling, R.S., Mackay, D. (Eds.), Handbook of Property Estimation Methods for Chemicals. CRC Press, Boca Raton, FL, USA.
- Gonzalez Silvera, A., Santamaria del Angel, E., Millán Núñez, R., 2006. Spatial and temporal variability of the Brazil-Malvinas Confluence and the La Plata Plume as seen by SeaWiFS and AVHRR imagery. J. Geophys. Res. Oceans 111, C06010.
- Gray, J.S., 2002. Biomagnification in marine systems: the perspective of an ecologist. Mar. Pollut. Bull. 45, 46–52.
- Grosell, M., 2012. Copper. In: Wood, C.M., Farrell, A.P., Brauner, C.J. (Eds.), Homeostasis and Toxicology of Essential Metals. Fish Physiology Series 31A. Elsevier, New York, pp. 54–135.
- Ho, T.Y., Wen, L.S., You, C.F., Lee, D.C., 2007. The trace metal composition of sizefractionated plankton in the South China Sea: biotic versus abiotic sources. Limnol. Oceanogr. 52, 1776–1788.
- Hogstrand, C., 2012. Zinc. In: Wood, C.M., Farrell, A.P., Brauner, C.J. (Eds.), Homeostasis and Toxicology of Non-Essential Metals. Fish Physiology Series 31A. Elsevier, New York, pp. 136–201.
- Huret, M., Dadou, I., Dumas, F., Lazure, P., Garçon, V., 2005. Coupling physical and biogeochemical processes in the Rio de la Plata plume. Cont. Shelf Res. 25, 629–653.
- Konovalenko, L., Bradshaw, C., Andersson, E., Lindqvist, D., Kautsky, U., 2016. Evaluation of factors influencing accumulation of stable Sr and Cs in lake and coastal fish. J. Environ. Radioact. 160, 64–79.
- Lucchini, R.G., Aschner, M., Kim, Y., Ŝarič, M., 2015. Manganese. In: Nordberg, G.,

Fowler, B., Nordberg, M. (Eds.), Handbook on the Toxicology of Metals. Specific Metals II. Amsterdam, Elsevier, pp. 975–1011.

- Mager, E.M., 2012. Lead. In: Wood, C.M., Farrell, A.P., Brauner, C.J. (Eds.), Homeostasis and Toxicology of Non-essential Metals. Fish Physiology Series 31B. Elsevier, New York, pp. 186–237.
- Marcovecchio, J.E., 2004. The use of *Micropogonias furnieri* and *Mugil liza* as bioindicators of heavy metals pollution in La Plata river estuary, Argentina. Sci. Total Environ. 323, 219–226.
- Marcovecchio, J.E., Moreno, V.J., 1992. Evaluación del contenido de metales pesados en peces de la Bahía Samborombón. Frente maritimo 12, 139–146.
- McConaugha, J.R., 1992. Decapod larvae: dispersal, mortality, and ecology. A working hypothesis. Am. Zool. 32, 512–523.
- McGeer, J.C., Niyogiand, S., Scott Smith, D., 2012. Cadmium. In: Wood, C.M., Farrell, A.P., Brauner, C.J. (Eds.), Homeostasis and Toxicology of Non-essential Metals. Fish Physiology Series 31B. Elsevier, New York, pp. 126–185.
- Medeiros, R.J., dos Santos, L.M.G., Freire, A.S., Santelli, R.E., Braga, A.M.C., Krauss, T.M., Jacob, S.D.C., 2012. Determination of inorganic trace elements in edible marine fish from Rio de Janeiro State, Brazil. Food Control 23, 535–541.
- Newman, M.C., 2015. Fundamentals of Ecotoxicology: The Science of Pollution. CRC Press.
- Ni, I.H., Wang, W.X., Tam, Y.K., 2000. The transfer of Cd, Cr, and Zn from zooplankton to mudskipper and glassy fishes. Mar. Ecol. Prog. Ser. 194, 203–210.
- Nordberg, G.F., Nogawa, K., Nordberg, M., 2015. Cadmium. In: Nordberg, G., Fowler, B., Nordberg, M. (Eds.), Handbook on the Toxicology of Metals. Specific Metals II. Amsterdam, Elsevier, pp. 667–716.
- Oskarsson, A., 2015. Barium. In: Nordberg, G., Fowler, B., Nordberg, M. (Eds.), Handbook on the Toxicology of Metals. Specific Metals II. Amsterdam, Elsevier, pp. 625–634.
- Petkevich, T.A., 1967. Elemental composition of bony tissues of plankton-feeding and benthos-feeding fish from the Northwest part of the Black Sea. Dopov. Nats. Akad. Nauk Ukr. 29, 142–146.
- Piola, A.R., Campos, E.J.D., Moller, O.O., Charo, M., Martinez, C., 2000. Subtropical shelf front off eastern South America. J. Geophys. Res. 105, 6565–6578.
- Reinfelder, J.R., Fisher, N.S., Luoma, S.N., Nichols, J.W., Wang, W.-X., 1998. Trace element trophic transfer in aquatic organisms: a critique of the kinetic model approach. Sci. Total Environ. 219, 117–135.
- Rodrigues, R.V., Freitas, L.S., Sampaio, L.A., 2009. Efeito da intensidade luminosa sobre a capacidade de predação de larvas do peixe-rei marinho Odontesthes argentinensis. Cienc. Rural 39, 246–249.
- Sampaio, L.A., 2006. Production of "pejerrey" Odontesthes argentinensis fingerlings: a review of current techniques. Biocell 30, 121–123.
- Sandstead, H., 2015. Zinc. In: Nordberg, G., Fowler, B., Nordberg, M. (Eds.), Handbook on the Toxicology of Metals. Specific Metals II. Elsevier, Amsterdam, pp. 1369–1385.
- Scarlato, N.A., Marcovecchio, J.E., Pucci, A.E., 1997. Heavy metal distribution in zooplankton from Buenos Aires coastal waters (Argentina). Chem. Speciat. Bioavailab. 9, 21–26.
- Schenone, N., Volpedo, A.V., Cirelli, A.F., 2007. Trace metal contents in water and sediments in Samborombón Bay wetland, Argentina. Wetl. Ecol. Manag. 15, 303–310.
- Simonetti, P., Botté, S.E., Fiori, S.M., Marcovecchio, J.E., 2012. Heavy-metal concentrations in soft tissues of the burrowing crab *Neohelice granulata* in Bahía Blanca Estuary, Argentina. Arch. Environ. Contam. Toxicol. 62, 243–253.
- Simonetti, P., Botté, S.E., Fiori, S.M., Marcovecchio, J.E., 2013. Burrowing crab (Neohelice granulata) as a potential bioindicator of heavy metals in the Bahía Blanca estuary, Argentina. Arch. Environ. Contam. Toxicol. 64, 110–118.
- Smith, J.T., Voitsekhovitch, O.V., Knoplov, A.V., Kudelsky, A.V., 2005. Radioactivity in aquatic system. In: Smith, J.T., Beresford, N.A. (Eds.), Chernobyl Catastrophe and Consequences. Springer/Praxis, Chichester, pp. 139–189.
- Soares, I., 2003. The Southern Brazilian Shelf Buoyancy-driven Currents. Ph.D. thesis. Univ. of Miami, Coral Gables, FLA.
- Tao, S., Liang, T., Cao, J., Dawson, R.W., Liu, C., 1999. Synergistic effect of copper and lead uptake by fish. Ecotoxicol. Environ. Saf. 44, 190–195.
- Tatone, L.M., Bilos, C., Skorupka, C.N., Colombo, J.C., 2015. Trace metal behavior along fluvio-marine gradients in the Samborombón Bay, outer Río de la Plata estuary, Argentina. Cont. Shelf Res. 96, 27–33.
- Tavares, R.A., Piedras, S.R.N., Fernandes, J.M., Pouey, J.L.O.F., Garcia, V.H., Moreira, H.L.M., Dionello, N.J.L., 2014. Growth performance of three pejerrey genetic groups in intensive culture system. Semina Cienc. Agrar. 35, 2749–2758.
- Thompson, G.A., Sanchez de Bock, M.F., 2007. Mortandad masiva de *Mesodesma mactroides* (Bivalvia: Mactracea) en el partido de la costa, Buenos Aires, Argentina, en Septiembre 2004. Atlantica 29, 115–120.
- Vazquez, F.J., Arellano, F.E., Cirelli, A.F., Volpedo, A.V., 2015. Monitoring of trace elements in silverside (*Odontesthes bonariensis*) from pampasic ponds, Argentina. Microchem. J. 120, 1–5.
- Velasco, C.A., Berasain, G.E., Oaci, M., 2008. Producción intensiva de juveniles de pejerrey (Odontesthes bonariensis). Biología Acuática 24, 53–58.
- Viana, F., Huertas, R., Danulat, E., 2005. Heavy metal levels in fish from coastal waters of Uruguay. Arch. Environ. Contam. Toxicol. 48, 530–537.
- Walther, B.D., Thorrold, S.R., 2006. Water, not food, contributes the majority of strontium and barium deposited in the otoliths of a marine fish. Mar. Ecol. Prog. Ser. 311, 125–130.
- Wood, C.M., Farrell, A.P., Brauner, C.J., 2012a. Homeostasis and Toxicology of Essential Metals. Fish Physiology Series 31A Elsevier, New York.
- Wood, C.M., Farrell, A.P., Brauner, C.J., 2012b. Homeostasis and Toxicology of Non-Essential Metals. Fish Physiology Series 31B Elsevier, New York.
- Yankovich, T.L., 2009. Mass balance approach to estimating radionuclide loads and concentrations in edible fish tissues using stable analogues. J. Environ. Radioact. 100, 795–801.