



From water to edible fish. Transfer of metals and metalloids in the San Roque Reservoir (Córdoba, Argentina). Implications associated with fish consumption



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ABSTRACT

The concentration of Mn, Fe, Zn, Cu, Cd, Cr, Ni, Ag, Mo, Nd, Al, Ce, As, Sr, Pb, Pt and Hg was analysed in water, sediments, and aquatic organisms from the San Roque Reservoir (Córdoba-Argentina), sampled during the wet and dry season, to evaluate their transfer through the food web. Stable nitrogen ($\delta^{15}\text{N}$) isotopes were used to investigate trophic interactions. According to this, samples were divided into three trophic groups: plankton, shrimp (*Palaemonetes argentinus*) and fish (Silverside, *Odontesthes bonariensis*). Liver and gills are the main heavy metal storage tissues in fish. Hg and As concentrations in the muscle of *O. bonariensis* exceed the Oral Reference doses for metals established by USEPA (2009). Trophic magnification factors (TMFs) for each element were determined from the slope of the regression between trace element concentrations and $\delta^{15}\text{N}$. Calculated TMFs showed fundamental differences in the trophodynamics of the studied elements during the wet and dry season in the San Roque Reservoir. Concentrations of Ni, Cd, Cr, Al, Mn, Fe, Mo, Ce, Nd, Pt and Pb during both seasons, and Sr during the dry season, showed statistically significant decreases (TMF < 1) with increasing trophic levels. Thus these elements were trophically diluted in the San Roque food chain. Conversely, Cu, Ag and As (dry season) showed no significant relationships with trophic levels. Among the elements studied, Hg in the wet season, and Zn in the dry season were the only ones showing a statistically significant increase (TMF > 1) in concentration with trophic level. Current results trigger the need for further studies to establish differential behaviour with different species within the aquatic web, particularly when evaluating the transfer of toxic elements to edible organisms, which could pose health risks to humans.

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1. Introduction

Pollutants may have deleterious effects on the aquatic biota, directly or indirectly affecting aquatic ecosystems. Among the main pollutants, heavy metals are transported to aquatic ecosystems dissolved or suspended in domestic, industrial, and agricultural runoffs, and by atmospheric deposition (Megateli et al., 2009).

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Metals and the metalloid As are considered serious pollutants due to their persistence in the environment, bioaccumulation and high toxicity (Chen et al., 2011). The trophic transfer of these elements is an important mechanism for the accumulation of contaminants in higher organisms of the food web, representing the main way in which humans are exposed to environmental toxicants (Walton et al., 2010). Specifically, fish, when consumed as part of the diet because of their high nutritional quality, are one of the main vehicles that carry these pollutants from aquatic environments to human populations (Jiang et al., 2010; Sioen et al., 2007). Non-essential trace elements have been detected in edible tissues of fish due to their bioaccumulation, high persistence and non-biodegradable properties (Zhang and Wang, 2012). Fish are among the top consumers in an aquatic environment. The trophic transfer

(also referred to as trophodynamics) of elements along a food chain can result in an increase (biomagnification), a decrease (biodilution) or even no change in element concentrations from lower to upper components of the food web (Luoma and Rainbow, 2008). For instance, trophodynamics of elements such as mercury (Hg) have been well studied, showing consistent biomagnification trends. Conversely, there are discrepancies regarding the trophic transfer behaviour of others elements, such as Cd, Cr, As and Pb (Dietz et al., 2000; Nfon et al., 2009). Dietz et al. (2000) found that the concentration of Cd increased towards higher trophic levels in marine and freshwater ecosystems, with Cd concentrations in marine biota higher than those found in freshwater and terrestrial ecosystems, probably due to the presence of longer food chains. However, Pb showed the reverse pattern compared with Cd. In terms of biota samples, lead levels in terrestrial and freshwater ecosystems are higher than in the marine ecosystem. Nfon et al. (2009) reported that the regression coefficients of Pb and Cd indicated decreasing concentrations with increasing $\delta^{15}\text{N}$; i.e. these trace elements are trophically diluted (or biodiluted) in a marine food chain. Many factors, such as environmental conditions, contaminant levels, length of food chains, and physicochemical properties of contaminants can influence the trophic transfer behaviour of trace elements in the aquatic biota. More field research is necessary to fully understand these phenomena.

The evaluation of naturally occurring tracers consisting of stable isotope ratios, namely $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, are widely used in ecotoxicological studies to elucidate the behaviour of contaminants (e.g., biomagnification or biodilution) through the trophic web (McIntyre and Beauchamp, 2007; Bucci et al., 2007). $\delta^{15}\text{N}$ is effective for the assessment of the trophic position, mainly because the enrichment of the heavy nitrogen isotope occurs incrementally across trophic levels, with a constant rate (3–4‰) (Hobson et al., 2002). For $\delta^{13}\text{C}$, the enrichment of the heavy carbon isotope is not so obvious (approx. 1‰) among the different trophic levels. Thus, $\delta^{13}\text{C}$ is considered a valuable biomarker for identifying different sources of primary production (Hobson et al., 2002).

Heavy metals are concentrated at different levels in different fish organs (Bervoets et al., 2001). Essentially, fish assimilate metals by ingestion of particulate material suspended in the water, ingestion of contaminated food, ion exchange of dissolved metals across lipophilic membranes (e.g. gills), and also by adsorption on tissue and membrane surfaces. Metal distribution between different fish tissues depends on the mode of exposure, i.e. dietary and/or aqueous exposure, and can serve as a pollution indicator (Alam et al., 2002). Some metals, such as Fe, Cu, Zn and Mn, are essential metals since they play important roles in biological systems. Conversely, Hg, Pb and Cd are toxic, even in trace amounts.

At present, much research work focuses on the accumulation of different elements like Hg, As, Cd, Cr, Pb, Cu within the muscle tissue, which is the main edible part of fish (Storelli et al., 2006; Keskin et al., 2007; Avigliano et al., 2015). Because of metal absorption, regulation, storage and excretion mechanisms, diverse tissues differ in bioaccumulation rates (Jarić et al., 2011). Muscle is not always a good indicator of the whole fish contamination. Therefore, in addition to muscle, it is important to analyse other tissues to complete the picture of elements accumulation in fish (Hasson et al., 2006). Additionally, the analysis of toxic elements in different fish tissues is important, considering that these tissues can be used to produce fish meal, which is used for feeding other animals (pigs, poultry, etc.), including its use in aquaculture. The presence of metal-binding proteins in some fish tissues, such as metallothioneins in liver, can lead to higher metal accumulation in liver than in muscle (Uysal et al., 2009). Tissue distribution pattern depends both on the metal involved and on the animal species; consequently, the analysis of this problem deserves special attention (Jarić et al., 2011).

The silverside *Odontesthes bonariensis* is a native fish species of South-America, which has been introduced in Europe and Asia (Brian and Dyer, 2006). In Argentina, it can be found in the lower section of the Río de la Plata River Basin and in lentic inland water bodies (e.g. ponds and lagoons) (Avigliano et al., 2015). Sport fishing and the commercial use of silverside make it an economically important species (López et al., 2001), being the second most important fishery resource in Argentina and Uruguay, for both local consumption and exportation (Avigliano et al., 2015; Minagri, 2014). Moreover, the relatively high sensitivity of this species to pollutants (Carriquiriborde and Ronco, 2006), together with its availability from aquaculture research and commercial farms, has recently promoted its inclusion as test species in a standardised acute toxicity test method in Argentina (IRAM, 2007).

This work has three significant goals: (A) to study the distribution and seasonal variation of metals/metalloids (Mn, Fe, Zn, Cu, Cd, Cr, Ni, Ag, Sr, Mo, Nd, Al, Ce, As, Pb, Pt and Hg) in the San Roque Reservoir, including water, sediment and aquatic organisms; (B) to investigate the trophic transfer behaviour of studied elements within a limited aquatic food web (water, plankton, shrimp and fish (Silverside)); and (C) to estimate the associated health risks of toxic elements present in edible fish (Silverside). Despite previous reports showing bioaccumulation and even biomagnification of heavy metals within aquatic ecosystems, our study aims to present a more complete picture of the differential transfer (namely biomagnification and biodilution) of several elements (metals and metalloids) through a limited food web, showing similarities and discrepancies with previous reports and; thus, triggering the need for further research in this area.

2. Materials and methods

2.1. Study site

The San Roque Reservoir is located in the Punilla Valley, Province of Córdoba (Argentina) (31°22'41" S–64°28'10" W) (Fig. 1). It is an artificial lake characterised by marked seasonal changes in its water level, with a dry season from March to November, and a wet season with frequent rainfall from December to February. This reservoir has been classified as eutrophic to hypereutrophic with elevated concentrations of nutrients, and high incidence of toxic cyanobacterial blooms (Amé et al., 2003). The reservoir is the main drinking water supply for Córdoba city, and is used for irrigation, flood control, and recreational purposes (swimming, boating and fishing).

2.2. Sample collection and analysis

Samples were collected in the San Roque region (Fig. 1). The sampling area has approximately the same water quality as the rest of the lake (Amé et al., 2003), with easy access for sampling. There were two sampling campaigns. The first one was at the end of the dry season (October 2011), and the second one, at the end of the wet season (March 2012). Several elements (Mn, Fe, Zn, Cu, Cd, Cr, Ni, Ag, Sr, Mo, Nd, Al, Ce, As, Pb, Pt and Hg) were measured in water, sediments, plankton, shrimp (*Palaemonetes argentinus*) and various organs of silverside (*Odontesthes bonariensis* – Pisces, Atherinidae). Water and sediment samples were taken simultaneously with plankton, shrimp and fish. Sample collection, containers, stabilization, and transportation to the laboratory as well as sample storage were done using previously described methods (Monferrán et al., 2011).

Water samples were collected into acid washed plastic bottles ($n=5$), acidified with ultrapure HNO_3 , and stored at 4 °C

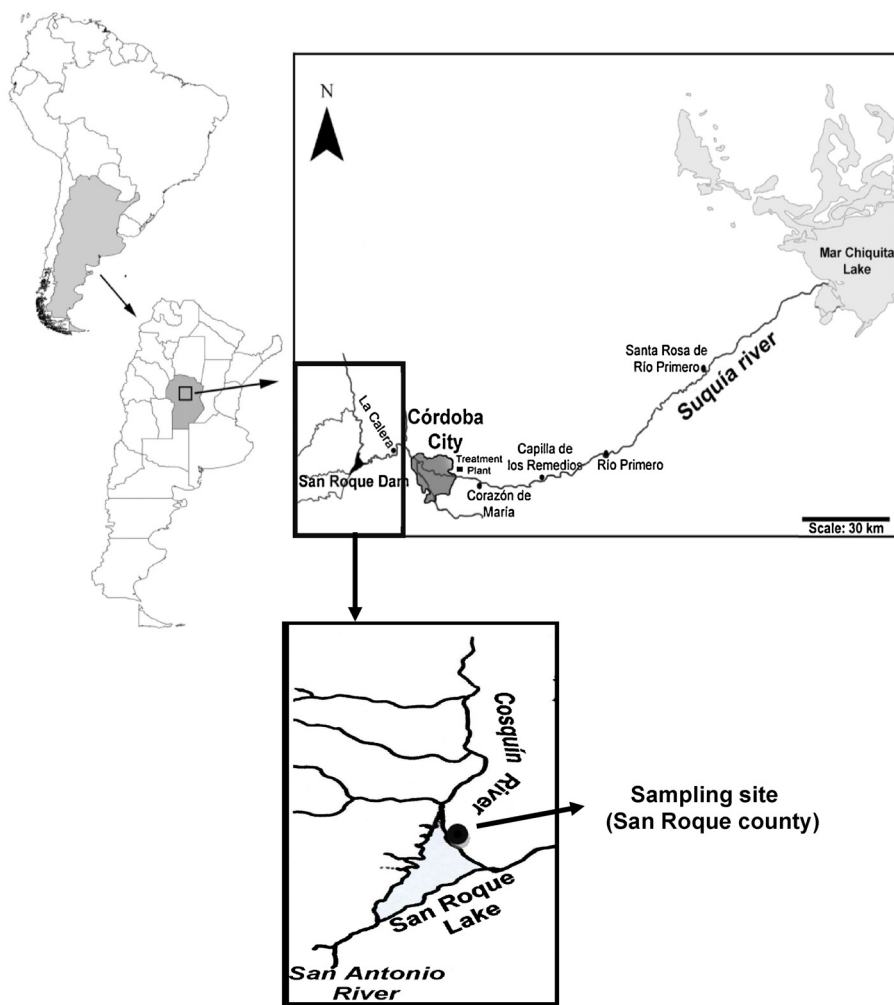


Fig. 1. Map of the Province of Córdoba – Argentina with indication of the studied area.

until analysis. Prior to measurements, samples were filtered using 0.45 μm nitrocellulose filters (Sartorius, Göttingen, Germany).

Sediment samples (0–15 cm depth interval) ($n=5$) were collected using a plastic shovel, transferred into clean 1-L plastic containers. Subsequently, sediments were dried at 40 °C, sieved to 63 μm using acrylic meshes. The analysis of total elements amounts in sediment was carried out from 200 mg sieved sediment, digested with nitric, hydrochloric and hydrofluoric acid in a heating plate, using a screw-closed PTFE container. The analyses of labile or bioavailable elements in sediments were performed from 1 g of the <63 μm dried material, which was processed by acid leaching, using ultra-pure HCl 0.5 N (Monferrán et al., 2011).

Plankton ($n=5$) was collected filtering 20L of water with a 50 μm nylon sieve. We did not discriminate between zoo and phytoplankton. Shrimp (*P. argentinus*) (average length: 2.917 ± 0.032 cm) were captured using plastic shrimp nets, transported into 20L containers using water from the capture site, keeping aeration by a mechanical pump.

O. bonariensis were captured with fishing rod (average weight: dry season 37.4 ± 7.2 g; $n=6$; wet season 32.7 ± 7.9 g; $n=12$; and average length: dry season 15.1 ± 0.5 cm; $n=6$; wet season 16.5 ± 5.0 cm; $n=12$). Once captured, fish were sacrificed, ice-cooled, and transported to the laboratory, where they were dissected, separating liver, gills, brain, gonads and muscle. The biological material was dried at 40 °C until constant weight, stored at –20 °C until analysis. Biological samples were ground and

homogenised with mortar and pestle. Twenty milligrams from each biological sample were taken (plankton, shrimp and different organs of fish), and digested with 8 mL nitric acid (sub boiling grade) and 1 mL of 30% H_2O_2 (ultrapure), using a microwave oven (MARS 3000; CEM Corporation) in Teflon tubes. The temperature program was: 1600 W 75%, 15 min ramp to 150 °C and 20 min at 150 °C. The total amount of elements in the whole fish was estimated from individual organs ($\mu\text{g g}^{-1}$ dry weight), considering the weight contribution of each organ to the total fish weight.

The multi-elemental analysis in both abiotic and biotic samples was performed using a Mass Spectrometer Inductively Coupled Plasma (ICP-MS), Thermo-Elemental X7 series (Thermo Fisher Scientific, Bremen, Germany), equipped with an ASX-100 autosampler (CETAC Technologies, USA, Omaha, NE).

2.3. Quality assurance and quality control

All samples were digested in triplicate. The concentrations of studied elements were determined in triplicate. Quality assurance (QA) and quality control (QC) were performed using certified reference materials (CRMs): NIST 1646a (estuarine sediment), NIST 1573a (tomato leaves), NIST1515 (apple leaves) and United States Geological Survey Certificate of Analysis, Devonian Ohio Shale, SDO-1. Recoveries from CRMs were $93 \pm 15\%$, $102 \pm 17\%$, $102 \pm 18\%$ and $98 \pm 11\%$, respectively. Spiked samples were also prepared. Variable amounts of mix standard solutions, containing all

elements analysed, were added to 0.02–0.04 g of fish sample (dried muscle and gills) to double the starting concentration for each element. The rest of the procedure was the same used for non-spiked samples. The average recovery was $98 \pm 17\%$.

2.4. Stable isotopes

Stable isotope ratios $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were measured in fish muscle and in total body homogenates from potential prey (plankton and shrimp), using an EA-IRMS (Costech Elemental Analyzer, ConFlo III interface, and Delta Plus Advantage MS) (Thermo Corporation, USA).

Before isotope analysis, dried samples (40°C) were further dried at 80°C for 2 h. Subsequently, a 0.9–2 mg sample was set in 8×5 mm Sn capsules for analysis.

The stable isotope abundance (d) is given by

$$\delta X \text{‰} = \left(\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right) \times 1000$$

where X is ^{13}C or ^{15}N and R is the ratio of $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$. Values of R standard can be determined based on the Vienna Pee Dee Belemnite (V-PDB) for ^{13}C , and on atmospheric N_2 (AIR) for ^{15}N . Replicate measurements of internal laboratory standards (glycine) show that the measurement errors for both carbon and nitrogen isotope analyses were $\pm 0.2\text{‰}$.

2.5. Calculations of bioaccumulation factors

For fish, invertebrates and plankton, trace element concentrations of total body homogenates were used for calculations. The bioaccumulation factor (BAF) is defined as:

$$\text{BAF} = \frac{C_{\text{ss}}}{C_{\text{w}}}$$

where C_{ss} is the element concentration in organisms at steady state ($\mu\text{g g}^{-1}$, dry weight), and C_{w} is the element concentration in water ($\mu\text{g mL}^{-1}$) (Pollman and Axelrad, 2014).

2.6. Statistical analysis

All values are expressed as mean(s) \pm standard deviation (SD). Normal distribution was checked by the Shapiro Wilks test. One way ANOVA was used to determine whether values were significantly different between seasons ($P < 0.05$). Regression analysis was used to examine the relationship between log metal concentration in tissues and $\delta^{15}\text{N}$ signature. InfoStat Software (V1.1) was used for all statistical calculations.

3. Results and discussion

3.1. Multi-element concentration in environmental compartments

Mean values for analysed elements in both water and sediment are given in Table 1. Generally, the highest concentrations in water were detected during the dry season. This could be the result of low water volume during the dry season (concentration). Conversely, during the wet season elements presented lower concentrations (dilution) (Table 1). These results are in agreement with previous reports measuring physical and chemical parameters (Wunderlin et al., 2001). Some measured elements exceed the maximum levels for the protection of the aquatic wildlife in Argentina (AEWQG, 2003). For instance, values observed for Al, Cu, Cr, Ni and Zn, during the dry season (Table 1), exceed regulatory levels (100, 2.87, 2.5, 4.2, $4.54 \mu\text{g L}^{-1}$, respectively). Similarly, Cu and Zn exceed the threshold limit during the wet season (2.87 and $4.54 \mu\text{g L}^{-1}$, respectively).

Water pollution has also affected the upper layer of sediment (0–15 cm), where highest concentrations were detected during the dry season ($P < 0.05$) (Table 1). Sediment samples presented different textures along the studied period (dry and wet season), varying from low to high silt sludge. It is noticeable that the deposition of suspended material, due to slow water flow during the dry season, leads to the deposition of finer grained sediments that contain more metals; this can explain the high metal concentration measured in sediment during the dry season in contrast with more sandy sediments typical of the wet season (Table 1). Our current results complement the few previous measurements of inorganic elements in sediments of the San Roque Reservoir. Current Cr, Cu, Ni and Fe concentrations in sediments are lower than those previously reported by Monferrán et al. (2010) in sediments of the Suquia River, close to the San Roque Dam (La Calera) (Fig. 1). Although Zn concentration presented higher values in the San Roque Reservoir than those previously found in La Calera, both concentrations do not exceed the risk levels defined by the Canadian Guideline values for the Protection and Management of Aquatic Sediment Quality ($315 \mu\text{g g}^{-1}$ Zn, dry weight) (Canadian Council of Ministers of the Environment, 2001). Argentinean regulations do not stipulate guideline values for inorganic elements in sediments.

Generally, the concentrations of studied elements in biota (plankton, shrimp and fish) were higher or similar during the wet season with respect to the dry season. However, the opposite trend was observed in water and sediment (Table 1, $P < 0.05$). This may be due to the increased water level temperature in the reservoir during the wet season, increasing the filtration of water and the metabolism in aquatic organisms, and, therefore, the accumulation of contaminants. Another possible explanation for this is that, in aquatic systems, plankton assemblages generally have strong relationships with environmental conditions, and rapidly respond to changes due to their short generation times. Different plankton assemblages may therefore characterise changes, driven by large-scale cycles such as the El Niño Southern Oscillation, seasonal changes, and pulse events like tsunamis and hurricanes (Nodine and Gaiser, 2015). As environmental conditions fluctuate, the tolerance ranges and optima of different taxa can shift or be exceeded, causing changes to the relative abundance of the composition of plankton. The change in plankton composition due to environmental conditions can lead to changes in the ability of plankton to accumulate metals from the medium, increasing in the wet season and decreasing in the dry season in San Roque Reservoir. This phenomenon can be extrapolated to higher trophic levels that feed on plankton. Schelske and Sicko-Goad (1990) showed that relatively small amounts of phosphorus and chelated trace metals may stimulate polyphosphate formation selectively in natural phytoplankton assemblages, thus trace metals present in eutrophic lakes with high anthropogenic loadings play an important role in phosphorus uptake and partitioning among phytoplankton populations, affecting therefore resource competition and succession among phytoplankton populations in waters that are influenced by high phosphorus loadings.

The highest levels of Ni, Al, Fe, Mo, Mn, Ce, Cr and Nd were found in plankton, while Cu, Ag and Zn presented highest concentration in shrimp, with Hg having highest values in fish, regardless of the season. Additionally, highest levels of As were found in plankton during the wet season. On the other hand, As levels were similar in fish and shrimp during both seasons, and in plankton during the dry season (Table 1). Cd concentration in plankton and shrimp ranged between 0.042 and $0.085 \mu\text{g g}^{-1}$ (dry weight) during both seasons, but Cd was not detected in fish (Table 1). According to the net mesh size used (50 μm), the collected plankton may consist of different varieties of unicellular algae (Tao et al., 2012), which are rich in oligoelements and major elements such as Fe, Al, Mn and Ni, as they have a great capacity to store elements from the surrounding

Table 1
Concentrations of metals measured in water ($\mu\text{g L}^{-1}$), sediments and organisms ($\mu\text{g g}^{-1}$ dry weight-DW) of the San Roque Reservoir. The total amount of elements in the whole fish was estimated from individual organs ($\mu\text{g g}^{-1}$ dry weight), considering the weight contribution of each organ to the total fish weight. Values are expressed as means \pm SD; sediments correspond to the fraction $< 63 \mu\text{m}$. $<\text{LOD}$ (below detection limit); $<\text{LOQ}$ (below quantification limit). LODs: Ag-water $0.006 \mu\text{g L}^{-1}$; As-water $0.33 \mu\text{g L}^{-1}$; Cr-water $0.06 \mu\text{g L}^{-1}$; Hg-water $0.006 \mu\text{g L}^{-1}$; Mo-biota $0.005 \mu\text{g g}^{-1}$ Pt-water $0.001 \mu\text{g L}^{-1}$; Pt-biota $0.00001 \mu\text{g g}^{-1}$ LOQs: Hg-biota $0.00002 \mu\text{g g}^{-1}$. Asterisks indicate statistically significant differences between the wet and dry season (DGC, $P \leq 0.05$).

Elements	Season	Water ($\mu\text{g L}^{-1}$)	Sediment ($\mu\text{g g}^{-1}$)	Plankton ($\mu\text{g g}^{-1}$)	<i>P. argentinus</i> ($\mu\text{g g}^{-1}$)	<i>O. bonariensis</i> ($\mu\text{g g}^{-1}$)
Ag	Dry	ND	0.018 ± 0.02	0.08 ± 0.01	0.19 ± 0.01	0.012 ± 0.003
	Wet	ND	0.014 ± 0.02	0.10 ± 0.05	0.20 ± 0.02	$0.023 \pm 0.020^*$
Al	Dry	$2434 \pm 26^*$	1051 ± 68	9052 ± 781	261 ± 45	8.1 ± 1.3
	Wet	60 ± 2	780 ± 58	8751 ± 2213	$415 \pm 120^*$	$74 \pm 82^*$
As	Dry	$3.8 \pm 0.1^*$	$0.76 \pm 0.11^*$	4.6 ± 0.7	4.6 ± 1.6	$5.4 \pm 0.8^*$
	Wet	$<\text{LOD}$	0.34 ± 0.07	$10.4 \pm 2.3^*$	5.2 ± 0.8	3.5 ± 1.3
Cd	Dry	$<\text{LOD}$	0.073 ± 0.014	0.085 ± 0.015	0.043 ± 0.009	$<\text{LOD}$
	Wet	$1.97 \pm 0.08^*$	0.059 ± 0.014	0.078 ± 0.018	0.068 ± 0.012	$<\text{LOD}$
Ce	Dry	0.62 ± 0.01	$12.5 \pm 0.1^*$	$42.8 \pm 5.1^*$	0.30 ± 0.11	0.011 ± 0.011
	Wet	$4.7 \pm 0.1^*$	7.8 ± 0.1	7.9 ± 1.9	$0.58 \pm 0.27^*$	$0.068 \pm 0.011^*$
Cr	Dry	$2.6 \pm 0.7^*$	0.52 ± 0.17	12.9 ± 2.5	2.2 ± 0.6	3.5 ± 0.4
	Wet	$<\text{LOD}$	0.41 ± 0.17	11.9 ± 2.4	$3.9 \pm 0.6^*$	5.5 ± 3.3
Cu	Dry	$5.5 \pm 0.1^*$	$4.1 \pm 0.1^*$	13.3 ± 0.9	54 ± 13	1.2 ± 0.1
	Wet	3.5 ± 0.6	2.5 ± 0.1	12.3 ± 1.2	$66 \pm 4^*$	$1.4 \pm 0.8^*$
Fe	Dry	$2087 \pm 10^*$	$724 \pm 48^*$	6718 ± 1213	160 ± 24	23 ± 4
	Wet	51 ± 4	269 ± 1	6277 ± 1432	$263 \pm 58^*$	76 ± 54
Hg	Dry	$<\text{LOD}$	$<\text{LOQ}$	$0.023 \pm 0.005^*$	$0.05 \pm 0.02^*$	0.035 ± 0.007
	Wet	$<\text{LOD}$	$<\text{LOQ}$	$<\text{LOQ}$	$<\text{LOQ}$	$0.07 \pm 0.03^*$
Mn	Dry	$224 \pm 2^*$	$326 \pm 25^*$	115 ± 30	42 ± 8	5.2 ± 0.6
	Wet	24 ± 4	109 ± 4	167 ± 29	50 ± 7	4.4 ± 1.3
Mo	Dry	9.1 ± 0.1	$<\text{LOD}$	$0.53 \pm 0.09^*$	0.25 ± 0.06	0.08 ± 0.03
	Wet	11.2 ± 0.6	$<\text{LOD}$	0.39 ± 0.06	$0.40 \pm 0.04^*$	$0.15 \pm 0.08^*$
Nd	Dry	$0.31 \pm 0.05^*$	$6.3 \pm 0.1^*$	$21.8 \pm 1.6^*$	0.15 ± 0.05	0.002 ± 0.001
	Wet	0.17 ± 0.01	4.4 ± 0.1	4.4 ± 0.9	$0.26 \pm 0.11^*$	$0.02 \pm 0.01^*$
Ni	Dry	$5.5 \pm 0.6^*$	$2.2 \pm 0.1^*$	9.4 ± 1.4	1.1 ± 0.2	0.65 ± 0.06
	Wet	2.2 ± 0.6	1.3 ± 0.1	8.6 ± 1.6	$1.3 \pm 0.4^*$	$1.7 \pm 1.1^*$
Pb	Dry	2.35 ± 0.01	4.72 ± 0.06	3.64 ± 1.02	0.14 ± 0.03	$0.08 \pm 0.03^*$
	Wet	2.53 ± 0.02	$7.85 \pm 0.17^*$	4.71 ± 2.42	0.42 ± 0.19	0.03 ± 0.02
Pt	Dry	$<\text{LOD}$	$<\text{LOD}$	$<\text{LOD}$	$<\text{LOD}$	$<\text{LOD}$
	Wet	$0.008 \pm 0.002^*$	$<\text{LOD}$	$<\text{LOD}$	$<\text{LOD}$	$<\text{LOD}$
Sr	Dry	$105 \pm 1^*$	17 ± 1	46 ± 15	82 ± 22	15 ± 4
	Wet	67 ± 2	15 ± 1	43 ± 10	108 ± 11	17 ± 10
Zn	Dry	17.8 ± 1.1	$23.4 \pm 0.2^*$	58 ± 3	70 ± 15	72 ± 9
	Wet	20.2 ± 0.8	8.9 ± 0.5	52 ± 8	$105 \pm 5^*$	57 ± 26

environment. Thus, these algae are usually selected as bioindicators of environmental pollution (Jun and Min, 2012). The concentration of elements in plankton from the San Roque Reservoir was similar to, or lower than, that reported by Tao et al. (2012) in lakes with low wastewater contamination.

Zn, Cu, Fe, Mn, Ni and Mo are essential elements with important metabolic functions. Thus, most organisms have biochemical mechanisms to regulate the amount of these elements within their cells. Instead, Cd is a non-essential element that competes with calcium for enzymatic sites (Regoli et al., 2012).

Our results could help interpreting the intraspecific differences in elements concentrations between both studied seasons. However, a great number of studies demonstrate that the bioaccumulation of metals in organisms depends on the particular element and species involved. The handling strategy of each species is determined by the metal assimilation efficiency, metal efflux rates and ingestion activity. Moreover, the physiological requirements of the organisms determine the final concentration of the element (Wang et al., 2011), which is in agreement with our results. For instance, invertebrates like shrimp are known to be strong net metal accumulators, especially Cu (Cui et al., 2011; Hargreaves et al., 2011). This is

because shrimp have a hemocyanin molecule in their hemolymph, whose function is to transport oxygen through the body, replacing hemoglobin, for which they have two Cu atoms instead of Fe (Giomi and Beltramini, 2007).

The concentration of Cu in fish found during this study ($1.2 \mu\text{g g}^{-1}$ dw and $1.4 \mu\text{g g}^{-1}$ dw in dry and wet season) is similar to that reported by Qiu et al. (2011) (about $1.6 \mu\text{g g}^{-1}$ dw in farmed fish), but lower than that reported by Chale (2002) (about $4 \mu\text{g g}^{-1}$ dw in pelagic fish). Considering the Cu concentration found in abiotic and biotic compartments of the San Roque Reservoir, it is surprising to find Cu in silverside from this lake in concentrations similar to those reported for farmed fish, where toxic exposure is supposed to be minimal. However, the accumulation of these elements could be attributed to lipid content in the farmed fish studied (pompano and snapper). It has been reported that significant positive relationships exist between the concentrations of Cu, Zn and As and lipid contents, indicating that lipid content may be an important factor regulating the bioaccumulation of these elements in farmed fish. Qiu et al. (2011)

Conversely, the levels of Hg in fish from the San Roque Reservoir ($0.035 \mu\text{g g}^{-1}$ dw, and $0.07 \mu\text{g g}^{-1}$ dw in dry and wet season,

respectively) were lower than those reported by Qiu et al. (2011) ($0.18 \mu\text{g g}^{-1}$ dw, and $0.22 \mu\text{g g}^{-1}$ dw in pompano and snapper, respectively). A possible explanation for this is that Hg concentrations found in water and sediment from Daya Bay and Hailing Bay, South China, are higher than the ones found in the San Roque Reservoir, meaning that the higher the Hg concentration in abiotic media (exposure concentration), the higher the Hg accumulation, among other factors. It is also worth to mention that concentrations of Zn ($72 \mu\text{g g}^{-1}$ dw, and $57 \mu\text{g g}^{-1}$ dw in dry and wet season, respectively) and Cr ($3.5 \mu\text{g g}^{-1}$ dw, and $5.5 \mu\text{g g}^{-1}$ dw in dry and wet season, respectively) in fish from the San Roque Reservoir were higher than those reported by Qiu et al. (2011) for farmed fish ($27.3 \mu\text{g g}^{-1}$ dw, and $0.54 \mu\text{g g}^{-1}$ dw in Zn and Cr, respectively). Moreover, the concentration of As found during this work ($5.4 \mu\text{g g}^{-1}$ dw, and $3.5 \mu\text{g g}^{-1}$ dw in dry and wet season, respectively) was higher than that reported by Ikemoto et al. (2008).

Summing up, we found higher concentrations of Ni, Al, Fe, Mo, Ce, Cr and Nd in plankton; with the highest levels of Cu, Ag, and Zn in invertebrates (shrimp), while Hg was the only element found in highest concentration in fish (Table 1). Farag et al. (2007) also reported higher levels of Ag, Cu, and Zn bioaccumulated in invertebrates, in comparison with fish from the Boulder River. In invertebrates, metal tolerance can be achieved by one or more possible physiological mechanisms: the reduction in metal uptake rates and/or enhancement of excretion rates, the incorporation of metals into insoluble deposits or granules, or the storage of accumulated metals in nontoxic physicochemical forms bound to cytosolic compounds including metallothioneins (MTs) or metallothionein-like proteins (MTLP), among others (Rainbow, 2007).

3.2. Trophic relationships

$\delta^{15}\text{N}$ shows values of $9.44 \pm 0.20\%$; $15.94 \pm 0.20\%$ and 17.22 ± 0.24 for plankton, shrimp and fish, respectively, during the dry season. On the other hand, $\delta^{15}\text{N}$ values were $9.92 \pm 0.20\%$; $15.03 \pm 0.20\%$ and $18.14 \pm 0.20\%$ for plankton, shrimp and fish, respectively, during the wet season. $\delta^{13}\text{C}$ values were $-18.97 \pm 0.20\%$; $-20.31 \pm 0.20\%$ and $-20.31 \pm 0.24\%$ for plankton, shrimp and fish, respectively, during the dry season; whereas $\delta^{13}\text{C}$ values were $-22.13 \pm 0.20\%$; $-16.72 \pm 0.20\%$ and $-18.63 \pm 0.22\%$ for plankton, shrimp and fish, respectively, during the wet season.

$\delta^{13}\text{C}$ is useful for the identification of the different sources of primary production (Hobson et al., 2002; Hoekstra et al., 2003). The values of this isotope in herbivores and carnivores correlate with those of their diet. According to the $\delta^{13}\text{C}$ observed in the biota of the San Roque Reservoir, no statistically significant differences were found in plankton, shrimp and fish during the wet season, while, in the dry season, silverside and shrimp presented higher $\delta^{13}\text{C}$ values than the plankton fractions. Despite these observed differences, plankton can be considered as part of their diet (carbon source for shrimp and silverside) in the base of the food web in the San Roque Lake.

Significant differences of $\delta^{15}\text{N}$ among different aquatic species were observed ($P < 0.05$) in both periods. Assuming that 9.44% is the lowest $\delta^{15}\text{N}$ value for plankton, the difference of $\delta^{15}\text{N}$ between plankton and *O. bonariensis*, which is the highest trophic level studied, was 7.78% and 8.57% in the dry and wet season, respectively. So far, the range of $\delta^{15}\text{N}$ values in studied species suggested a food chain with increasing trophic levels as follows: plankton-shrimp-fish, which is consistent with what is already known about the dietary habits of fish (Silverside). $\delta^{15}\text{N}$ showed a difference of 5.8% between plankton and shrimp, and approximately 3.0% between shrimp and fish. This is consistent with the $3\text{--}5\%$ increase

in $\delta^{15}\text{N}$ commonly proposed per trophic level (Hobson et al., 2002).

3.3. Bioaccumulation of studied elements

The bioaccumulation factor (BAF) is used to evaluate the ability of an aquatic organism to accumulate chemicals from the aquatic environment, indicating which organisms have a potential to accumulate chemicals. BAFs exceeding 100 are considered significant (USEPA, 1991). Results of BAF for studied elements and biota are reported in Table 2. For those elements where water had concentrations below the detection or quantification limit, LOD and LOQ, reported in the caption of Table 1, were used to calculate the value of BAF.

BAFs usually exceed 100 in plankton for most elements, with the exemption of Mo, Nd (dry season), Cd and Hg (wet season) (Table 2). Also, BAFs were higher than 100 in *P. argentinus* for most studied elements, with the exemption of Ce, Fe, Pb, Mo and Nd (dry season), Cd and Hg (wet season) (Table 2). Finally, BAFs were lower in fish (*O. Bonariensis*), with values lower than 100 for Al, Cd, Ce, Fe, Pb, Mn, Mo and Nd during the dry season, and for Cd, Ce, Pb, Mo and Nd during the wet season (Table 2).

When evaluating BAFs for the same element in different seasons, we observed that Ag, As, Cr, Cu, Ni and Zn were bioaccumulate throughout the studied period (dry and wet seasons) at all studied levels (plankton, shrimp and fish) (Table 2). The bioaccumulation of Al, Ce, Fe, Mo and Nd was lower in shrimp and fish, mainly during the dry season (Table 2), although water concentrations of these elements varied between both seasons studied. On the other hand, the bioaccumulation factor of Cd and Hg tends to be higher during the dry season, mainly in plankton and shrimp (Table 2), being Cd and Hg concentrations in water $< \text{LOD}$. These results reinforce the idea that metal concentrations in biota are a consequence of metal concentration in the environment (water and sediment) as well as in the diet of each species, among other factors. The highest values of BAFs correspond to essential elements (Zn, Cu, Fe, etc.), whereas lower BAFs link to non-essential ones (Cd, Hg, Pb etc.) in plankton, shrimp and fish. The accumulation of trace elements in the tissues of different kinds of organisms depends primarily on their concentrations in the aquatic environment. Other factors such as chemical speciation/bioavailability as well as organism growth cycle, age and trophic position can also influence the extent of accumulation of trace elements in organisms. Food quality and quantity may significantly affect the dietary assimilation and ingestion rate of fish. For fish, dietary uptake (highly associated with trophic transfer) is the most common way by which elements are accumulated, primarily because of the low dissolved uptake rate of metals (Qiu, 2015).

Generally, the BAFs of plankton were higher than those of shrimp and fish for most studied elements. This could be due to the higher capability of algae to uptake inorganic elements directly from water, compared with shrimp and fish that use several uptake mechanisms, in addition to their stronger metabolic capability. Furthermore, it was shown that dead algae could remain accumulating metals through adsorption to cell surfaces (Tao et al., 2012). So far, it is reasonable that algae (phytoplankton) presented higher BAFs during this work.

Current BAFs results for As, Cd, Cr, Hg and Zn, recorded in the biota of the San Roque Reservoir, were higher than the values reported by Cui et al. (2011), although they report higher concentrations of these elements in water than those found in San Roque Reservoir. These results indicate that the studied species present a high level of bioconcentration, which could have a higher environmental impact on the studied aquatic ecosystem.

Table 2
Bioaccumulation factors (BAFs) for studied elements in the San Roque Reservoir. ND: not detected.

	Season	Ag	Al	As	Cd	Ce	Cr	Cu	Fe	Hg	Mn	Mo	Nd	Ni	Pb	Pt	Sr	Zn
Plankton	Dry	16988	14398	8726	51598	8941	12486	3485	11651	3882	2297	59	70	3888	5795	ND	1982	6269
	Wet	16597	14570	9454	40	30316	148909	3531	124207	34	7012	346	26245	3849	1861	ND	642	2596
<i>P. argentinus</i>	Dry	31445	107	8724	14173	63	832	9775	76	9057	187	27	<1	181	59	ND	775	6953
	Wet	32972	6889	4703	35	2251	48510	18938	5200	34	2086	360	1536	574	168	ND	1622	5189
<i>O. Bonariensis</i>	Dry	1946	4	10080	<1	2	1346	220	11	7798	23	8	<1	118	34	ND	139	7150
	Wet	1946	135	4880	<1	43	44319	350	463	7798	219	67	6	294	31	ND	221	3564

3.4. Transfer of elements in the studied food chain

The trophic transfer of elements was estimated using relationships between the element concentration and $\delta^{15}\text{N}$ of studied species. Generally, a positive slope indicates accumulation through the food web, while a negative slope suggests the elimination of elements from the food web, or an interrupted trophic transfer. In the present study, we investigated relationships between concentrations of studied elements and $\delta^{15}\text{N}$.

The connection between $\delta^{15}\text{N}$ and metal concentrations shows a trophic level-dependent accumulation in the studied food web (Table 3). *O. bonariensis* is an omnivorous species, which is known to shift its diet according to the size of individuals. The small ones (<16 cm length) feed on plankton and invertebrates, while the big ones (>20 cm length) eat fish as primary food (Sagretti and Bistoni, 2001). Considering the size of studied fish (average of both samplings: 15.7 ± 0.7 cm), we consider it as a predator fish, preying on shrimp and plankton for feeding. Rodrigues and Bemvenuti (2011) demonstrated specifically that the prey found on the diet of *O. bonariensis* was *Palaemonetes argentines*. Positive slopes were found for Zn, As and Hg during the dry season, and for Hg throughout the wet season (Table 3). Only the regression for Hg showed a statistically significant positive slope ($P < 0.0001$), linked to the raise of $\delta^{15}\text{N}$ throughout the food chain (Table 3). Conversely, significant negative slopes ($P < 0.0001$) were found for Ni, Cd, Cr, Al, Mn, Fe, Mo, Ce, Nd, Pt and Pb during both seasons, and for Sr during the dry season, indicating decreasing concentration of these elements as $\delta^{15}\text{N}$ increases throughout the food chain (Fig. 2).

As mentioned before, only Hg was biomagnified to an appreciable extent in the food chain. Thus, the present study provides additional evidence of Hg biomagnification in aquatic food webs, as reported elsewhere (Atwell et al., 1998; Bargagli et al., 1998; Blackmore and Wang, 2004; Kidd et al., 2003; Campbell et al., 2005a). It is worth to remark that the regression slope of log Hg versus $\delta^{15}\text{N}$ (0.36) (Fig. 2A) is higher than values reported for other food webs (with slopes ranging from 0.16 to 0.29) (Campbell et al., 2003; Kidd et al., 2003). Hg is a metal released to the environment from both natural and anthropogenic sources (e.g., volcanos or waste incineration and coal burning plants), reaching aquatic reservoirs through river inputs and by atmospheric depositions (Drevnick et al., 2012). Hg does not have a known biological function; it is a non-essential element, toxic to all living organisms, including humans (Chouvelon et al., 2012). The biomagnification of Hg from lower to higher trophic levels is well known. Our current results show that the trophic transfer is a predominant way of Hg accumulation in higher trophic levels in the San Roque Reservoir, constituting a major source of contamination to humans, as the silverside is an edible fish.

Our current results do not show a significant correlation (element – $\delta^{15}\text{N}$) for Cu, Zn and Ag during either season, Sr during the wet season, or As during the dry season, suggesting neither biomagnification nor biodilution of these elements (Table 3, Fig. 2C). However, biomagnification of Cu and Zn could not be expected, as these metals are essential elements; thus, regulated by homeostasis being probably efficiently excreted by species belonging to higher trophic levels (e.g. Besser et al., 2001; Quinn et al., 2003).

Revenga et al. (2012) reported a trend towards biodilution of As in a food web from Moreno Lake (Bariloche–Argentina), which is not consistent with our current results during the dry season. Conversely, Ikemoto et al. (2008) and Cui et al. (2011) did not find a significant whole-food web relationship between As and $\delta^{15}\text{N}$, neither in the Mekong Delta (Vietnam) nor in the Yellow River Estuary Delta (China) food webs, respectively. Aquatic species bioconcentrate and bioaccumulate As by uptake from the surrounding water and feeding on contaminated preys. However,

Table 3
Regression parameters and *P* values for $\delta^{15}\text{N}$ vs. trace element concentration ($\mu\text{g g}^{-1}$ dry weight) in the San Roque Reservoir.

Element	season	Regression of log [trace element] versus $\delta^{15}\text{N}$			
		r^2	Slope	Intercept	<i>p</i> -value
Ag	Dry	0.02	-0.019	-0.7449	<0.5256
	Wet	0.28	-0.089	0.06	<0.0019
Al	Dry	0.9092	-0.3909	8.3203	<0.0001
	Wet	0.9294	-0.2534	6.349	<0.0001
As	Dry	0.0025	0.0016	0.6436	<0.8158
	Wet	0.6271	-0.0503	1.4427	<0.0001
Cd	Dry	0.4189	-0.2524	1.7331	<0.0001
	Wet	0.7356	-0.4181	3.4378	<0.0001
Ce	Dry	0.9352	-0.388	5.34	<0.0001
	Wet	0.8974	-0.2594	3.42	<0.0001
Cr	Dry	0.9095	-0.1573	2.9716	<0.0001
	Wet	0.3272	-0.0488	1.4628	<0.0001
Cu	Dry	0.0238	-0.0256	1.6112	<0.4721
	Wet	0.2632	-0.1142	2.5886	<0.027
Fe	Dry	0.9854	-0.3571	7.7713	<0.0001
	Wet	0.9499	-0.2269	5.8928	<0.0001
Hg	Dry	0.4285	0.076	-2.2706	<0.0288
	Wet	0.5461	0.3585	-8.5954	<0.0001
Mn	Dry	0.9026	-0.2051	4.6793	<0.0001
	Wet	0.8589	-0.1819	4.0854	<0.0001
Mo	Dry	0.5739	-0.0846	0.5541	<0.0001
	Wet	0.3738	-0.0546	0.2005	<0.0009
Nd	Dry	0.8886	-0.4152	5.3209	<0.0001
	Wet	0.834	-0.3287	3.9147	<0.0001
5Ni	Dry	0.9895	-0.2006	3.2181	<0.0001
	Wet	0.6159	-0.0875	1.6433	<0.0001
Pb	Dry	0.9873	-0.2963	4.0022	<0.0001
	Wet	0.9005	-0.2698	3.3509	<0.0001
Pt	Dry	0.9584	-0.1338	-1.8117	<0.0001
	Wet	ND	ND	ND	ND
Sr	Dry	0.6553	-0.0978	3.2575	<0.0001
	Wet	0.1933	-0.0502	2.3069	<0.0118
Zn	Dry	0.0889	0.0059	1.7436	<0.0001
	Wet	0.0003	-0.0001	1.8213	<0.0118

As compounds are efficiently excreted, reducing the possibility of accumulation and trophic transfer throughout food chains (Nfon et al., 2009).

Significant negative slopes for Pb, Ni, Cr, Al, Mn, Fe, Mo, Ce, Nd, Pt and Cd indicated decreasing concentrations with increasing $\delta^{15}\text{N}$ (biodilution) (Table 3, Fig. 2B). The biodilution of Al, Fe, Ni, Pb, Cr, Mn and Cd in freshwater and marine species has been previously reported (Winterbourn et al., 2000; Colaço et al., 2006). Similarly, Campbell et al. (2005a) concluded that Al, Fe, Ni, Pb and Cd were biodiluted in a pelagic Arctic marine food web. Watanabea et al., 2008 tested whether biodilution of some elements was a consequence of higher trophic levels having a larger body size, with the lower surface:mass ratio, resulting in reduced uptake of metals. They found that body mass was negatively correlated with tissue metal concentration in many cases, body size did not increase with trophic level (as $\delta^{15}\text{N}$ did). Thus, biodilution was not a consequence of larger body size with higher trophic position, but they find the possibility of increasingly efficient excretion (or reduced assimilation) of elements for macroinvertebrates at higher trophic levels. A probable hypothesis to explain biodilution of these trace elements could be related to the influence of homeostatic regulation in superior organisms, added to potential mechanisms including increased metabolism and reduced absorption of highly hydrophobic compounds in the gut in higher trophic levels (McLachlan,

1996). Further studies will be necessary to determine these mechanisms.

Generally, the concentration of elements like Cd, Fe, Mn, Ni, Pb and Al is regulated by metallothionein and metallothionein-like proteins, found in both vertebrates and invertebrates (Newman and Unger, 2003). Additionally, Ni, Cd and Pb are present in forms that are poorly absorbed in aquatic media and aquatic invertebrates (e.g. Ni in aquatic media is mostly present as hexahydrate ion, which is poorly absorbed from the diet); thus, these elements are generally stored in muscle tissues and bones. Consequently, concentrations of the previously mentioned elements are reduced during trophic transfer by growth dilution (Campbell et al., 2005a,b).

Although our results show biodilution throughout the studied food chain for Nd, Pt and Ce, we did not find previous reports on bioconcentration/biodilution of these elements. So far, our results seem to be the first on the transfer of these elements (Ce, Nd and Pt) throughout the limited aquatic food web used for this study.

3.5. Distribution of elements in different organs of *O. bonariensis*

Results of element accumulation in fish tissues are shown in Table 4, showing differential distribution among studied tissues for all studied elements ($P < 0.05$). Cu and Mo showed the highest concentrations in fish liver during both seasons, while As, Fe, and

Table 4
Metal and metalloid concentrations in different tissues of *Odontesthes bonariensis* expressed as mean \pm standard deviation (minimum and maximum values). Concentrations are expressed as $\mu\text{g g}^{-1}$ dry weight; <LOD below the detection threshold. Different letters indicate statistically significant differences between organs (DGC, $P \leq 0.05$).

Elements	Season	Muscle	Gill	Liver	Gonad	Brain
Ag	Dry	0.009 \pm 0.004 ^b (0.008–0.015)	0.014 \pm 0.008 ^b (0.006–0.023)	0.04 \pm 0.03 ^a (0.019–0.087)	0.014 \pm 0.04 ^b (0.008–0.016)	0.007 \pm 0.002 ^b (0.006–0.008)
	Wet	0.012 \pm 0.005 ^a (0.006–0.021)	0.018 \pm 0.011 ^a (0.004–0.043)	0.160 \pm 0.240 ^a (0.011–0.690)	0.091 \pm 0.131 ^a (0.015–0.410)	0.021 \pm 0.008 ^a (0.012–0.041)
Al	Dry	6 \pm 1 ^b (4–6)	47 \pm 20 ^a (11–93)	13 \pm 5 ^b (7–20)	8 \pm 4 ^b (4–13)	3 \pm 5 ^b (0.01–8)
	Wet	39 \pm 25 ^b (5–105)	467 \pm 373 ^a (63–1063)	102 \pm 174 ^b (3–661)	27 \pm 25 ^b (6–92)	33 \pm 35 ^b (5–132)
As	Dry	3.9 \pm 0.1 ^b (3.6–4.3)	17.3 \pm 3.0 ^a (13.9–20.7)	17.5 \pm 4.5 ^a (11.2–22.1)	5.4 \pm 1.1 ^b (4.5–6.5)	2.9 \pm 0.5 ^b (2.3–3.3)
	Wet	2.6 \pm 0.1 ^c (1.6–4.1)	9.9 \pm 2.3 ^b (5.0–13.3)	17.1 \pm 5.1 ^a (9.8–25.1)	7.3 \pm 2.9 ^b (3.5–13.9)	3.2 \pm 2.0 ^c (0.8–7.5)
Cd	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
Ce	Dry	0.013 \pm 0.08 (0.005–0.009)	0.090 \pm 0.068 [*] (0.040–0.200)	0.042 \pm 0.041 [*] (0.006–0.102)	0.009 \pm 0.006 (0.004–0.024)	0.032 \pm 0.040 (0–0.080)
	Wet	0.032 \pm 0.018 ^b (0.004–0.073)	0.210 \pm 0.140 ^a (0.055–0.475)	0.122 \pm 0.203 ^b (0.004–0.760)	0.041 \pm 0.040 ^b (0.003–0.128)	0.051 \pm 0.072 ^b (0.003–0.231)
Cr	Dry	3.0 \pm 0.6 ^a (2.2–3.6)	4.1 \pm 1.8 ^a (2.7–6.8)	5.7 \pm 2.0 ^a (3.6–8.6)	4.6 \pm 1.0 ^a (3.3–5.7)	4.9 \pm 0.8 ^a (4.3–5.5)
	Wet	3.4 \pm 1.3 ^b (1.9–6.7)	6.0 \pm 3.0 ^b (2.6–12.0)	9.2 \pm 5.4 ^a (1.9–16.2)	6.9 \pm 4.5 ^b (2.5–17.7)	14.1 \pm 4.4 ^a (5.6–19.4)
Cu	Dry	0.8 \pm 0.1 ^b (0.7–0.9)	1.4 \pm 0.4 ^b (1.1–2.1)	5.6 \pm 2.1 ^a (3.8–8.5)	2.5 \pm 0.6 ^b (1.8–3.1)	4.2 \pm 0.2 ^a (3.9–4.5)
	Wet	0.8 \pm 0.2 ^c (0.6–1.1)	1.8 \pm 0.5 ^c (1.2–3.1)	9.2 \pm 4.7 ^a (5.1–21.3)	3.6 \pm 1.1 ^b (2.1–6.1)	4.2 \pm 1.1 ^b (3.2–7.4)
Fe	Dry	10 \pm 3 ^b (7–14)	141 \pm 53 ^a (96–208)	166 \pm 67 ^a (110–258)	44 \pm 17 ^b (30–67)	65 \pm 16 ^b (46–79)
	Wet	29 \pm 16 ^c (11–68)	358 \pm 258 ^b (61–1014)	619 \pm 285 ^a (366–1347)	111 \pm 47 ^c (49–224)	77 \pm 13 ^c (53–94)
Hg	Dry	0.038 \pm 0.033 ^a (0.029–0.080)	<LOD	<LOQ	<LOQ	<LOD
	Wet	0.094 \pm 0.062 ^a (0–0.181)	0.029 \pm 0.033 ^b (0–0.081)	0.013 \pm 0.031 ^b (0–0.094)	0.007 \pm 0.017 ^b (0–0.048)	<LOD
Mn	Dry	3.9 \pm 0.8 ^b (3.4–5.2)	28.6 \pm 10.2 ^a (21.8–43.8)	6.3 \pm 3.9 ^b (3.8–12.1)	3.5 \pm 1.3 ^b (2.1–3.8)	1.6 \pm 0.4 ^b (1.3–2.0)
	Wet	3.6 \pm 1.4 ^c (2.0–5.9)	29.3 \pm 10.4 ^a (5.6–42.3)	9.1 \pm 5.9 ^b (3.7–25.3)	3.7 \pm 1.2 ^c (1.8–6.8)	3.5 \pm 2.8 ^c (1.8–12.6)
Mo	Dry	<LOQ	0.27 \pm 0.04 ^b (0.23–0.31)	0.61 \pm 0.14 ^a (0.48–0.76)	0.36 \pm 0.12 ^b (0.28–0.45)	<LOD
	Wet	0.08 \pm 0.24 ^b (0.06–0.15)	0.22 \pm 0.06 ^b (0.09–0.31)	1.31 \pm 0.97 ^a (0.53–3.72)	0.41 \pm 0.14 ^b (0.25–0.83)	0.32 \pm 0.24 ^b (0.15–1.13)
Nd	Dry	<LOD	0.027 \pm 0.036 ^a (0–0.075)	<LOD	<LOD	<LOD
	Wet	0.004 \pm 0.001 ^b (0–0.038)	0.120 \pm 0.079 ^a (0.031–0.271)	0.019 \pm 0.033 ^b (0–0.085)	0.007 \pm 0.019 ^b (0–0.056)	<LOD
Ni	Dry	0.6 \pm 0.1 ^c (0.5–0.6)	1.6 \pm 0.3 ^a (1.2–1.9)	0.8 \pm 0.4 ^c (0.5–1.3)	0.5 \pm 0.1 ^c (0.4–0.6)	1.2 \pm 0.1 ^b (1.1–1.3)
	Wet	1.0 \pm 0.6 ^b (0.7–2.8)	3.1 \pm 1.2 ^a (0.8–5.6)	1.8 \pm 1.7 ^b (0.4–5.8)	2.2 \pm 2.8 ^b (0.3–8.8)	2.4 \pm 0.1 ^b (0.9–6.3)
Pb	Dry	0.07 \pm 0.03 ^b (0.05–0.11)	0.187 \pm 0.057 ^a (0.14–0.25)	0.061 \pm 0.03 ^b (0.03–0.09)	0.065 \pm 0.019 ^b (0.05–0.09)	<LOD

Table 4 (Continued)

Elements	Season	Muscle	Gill	Liver	Gonad	Brain
	Wet	0.027 ± 0.036 ^b (0–0.126)	0.22 ± 0.11 ^a (0.11–0.42)	0.029 ± 0.067 ^b (0–0.22)	0.022 ± 0.037 ^b (0–0.103)	0.021 ± 0.08 ^b (0–0.301)
Pt	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
Sr	Dry	12.3 ± 4.9 ^b (8.5–19.1)	76 ± 16 ^a (61–95)	4.4 ± 5.6 ^b (0.9–12.6)	4.0 ± 2.8 ^b (1.3–6.0)	1.00 ± 0.04 ^b (0.97–1.03)
	Wet	9.3 ± 3.3 ^b (4.9–15.3)	111 ± 24 ^a (76–158)	1.03 ± 0.87 ^b (0.43–3.34)	3.23 ± 2.00 ^b (1.25–6.68)	2.14 ± 2.00 ^b (0.65–6.67)
Zn	Dry	61 ± 7 ^b (51–68)	113 ± 22 ^a (90–131)	98 ± 22 ^a (78–118)	95 ± 26 ^a (65–125)	158 ± 30 ^a (123–180)
	Wet	52 ± 16 ^c (34–89)	133 ± 22 ^a (78–158)	94 ± 32 ^b (58–183)	130 ± 26 ^b (98–162)	64 ± 14 ^c (4–98)

Cr presented high concentrations during the wet season and Ag during the dry season. Looking at Table 1 we can see that, during the wet season, the concentration of As was higher in plankton, while concentrations of Fe and Cr were higher in shrimp. These could indicate that the transfer of these elements (As, Fe and Cr) is mainly occurring from food to fish, not from water (environment) to fish. This last result triggers the need to evaluate differential pathways for the transfer of diverse elements through the aquatic web, considering changes in the food chain. This result reinforces previous reports, demonstrating that *P. argentinus* is a component of the diet of *O. bonariensis* (Sagretti and Bistoni, 2001; Rodrigues and Bemvenuti, 2011). Concentrations of Al, Ni, Zn, Mn, Nd and Ce were highest in gills during both studied seasons, in agreement with a previous report on the Pontic shad (*Alosa immaculata*) from the Danube River (Visnjic-Jeftic et al., 2010).

Overall, the highest concentrations of most analysed elements were recorded in liver and gills, while the lowest ones were observed in the brain, with some exceptions as Ni, Cu and Cr. Such pattern has been observed in other fish species (Dural et al., 2006; Storelli et al., 2006; Ploetz et al., 2007). Muscles have low accumulative potential (Jarić et al., 2011). Conversely, the high accumulative ability of the liver is the result of the activity of metallothioneins (Ploetz et al., 2007; Messaoudi et al., 2009). So far, many authors have recommended the liver as the best environmental indicator of both water pollution and chronic exposure to heavy metals (Jarić et al., 2011; Messaoudi et al., 2009; Agah et al., 2009). Gills could be important as they present a site for direct contact with metals and other elements dissolved or suspended in the water. High metal concentrations in gills can point out to water as the main source of pollution (Jarić et al., 2011). According to Dural et al. (2006) and Erdoğan and Erbilir, (2007), levels of total metals in gills can be influenced by the absorption of metals onto the gill surface, but also by the element complexation with the mucous. It is known that muscle is not a target organ for the accumulation during acute exposure; however, this tissue is a good indicator of chronic exposures. When pollutants exceed all defence barriers, the body begins to accumulate pollutants in this organ (Kalay et al., 2000). The accumulation of metals in muscle has a direct implication on the negative effect of fish consumption by humans.

The dominant concentration of Cu in the liver of *O. bonariensis* in the San Roque Reservoir agrees with the results published by Carriquiriborde and Ronco (2008), where they show that the essential element Cu was quickly stabilised and little retained in the gill, but rapidly and highly accumulated by the liver of this species on sub-chronic laboratory experiments. This differs from other species findings, suggesting that gills are the centre for the accumulation of this metal in *Scarus gibbus* (El-Moselhy et al., 2014).

Zn, Ni, As and Al showed highest concentrations in fish gills. A possible explanation for the accumulation of these elements in gills may be related to a progressive bioaccumulation by fish, which can be incorporated from the water or sediment. It is also necessary to emphasize that gills showed high concentrations of trace elements due to their close association with the environment and hence the incorporation of elements from the environment. Our current results are in good agreement with other studies that determined the highest concentration of Zn in fish gills (Dural et al., 2006; Storelli et al., 2006; Rashed, 2001), but opposite to results reported by Jarić et al. (2011), who found maximum concentration of nickel in fish liver, and by Has-Schon et al. (2006), who found the highest concentration of As in the muscle of different fish species from River Neretva, Croatia.

Cr, Ag, Fe and Mo showed highest concentrations in fish liver, which is in line with previous findings by Jarić et al. (2011). As mentioned before, the high accumulative ability of the liver is the result of the activity of metallothioneins, which may explain the higher concentration of these elements in this organ (Ploetz et al., 2007; Messaoudi et al., 2009), although Carriquiriborde and Ronco, 2008 found that silverside quickly and evenly accumulated Cr in liver and gills on sub-chronic laboratory experiments. Chromium concentrations, ranging from 5.00 to 7.60 $\mu\text{g g}^{-1}$, were reported in fish liver from the South Platte River basin, USA (Heiny and Tate, 1997). Other authors found Cr concentrations in edible tissue of *S. glanis*, at lower levels than our current findings (Mendil and Uluzlu, 2007; Matasin et al., 2011).

The highest content of Hg found during this study was in fish muscle (Table 4), although no Hg concentrations were found in water or were <LOQ in sediment from the San Roque Reservoir. This result was similar to that observed in *O. bonariensis* from the Titicaca Lake, where values of Hg were also <LOD in water (Monroy et al., 2014), but opposite to those found in *Myleus rubripinnis* and *Semaprochilodus vari*, where liver was the main organ accumulating Hg (Regine et al., 2006). This also could be due to the differences in the amount of metallothionein (like proteins) contents in the similar tissues of different species and the types of sulfur amino acids (e.g., methionine and cysteine) in liver of *Myleus rubripinnis* and *Semaprochilodus vari*, because tissues with higher amounts of metallothionein reportedly absorb more Hg (Khoshnamvand et al., 2013).

We did not find measurable concentrations of Pt and Cd in any of the studied fish organs.

As, Cr, Fe, Mn and Zn concentrations in muscle of *O. bonariensis* from the San Roque Reservoir were higher than those reported for the same species in other Argentinian lakes and lagoons (Avigliano

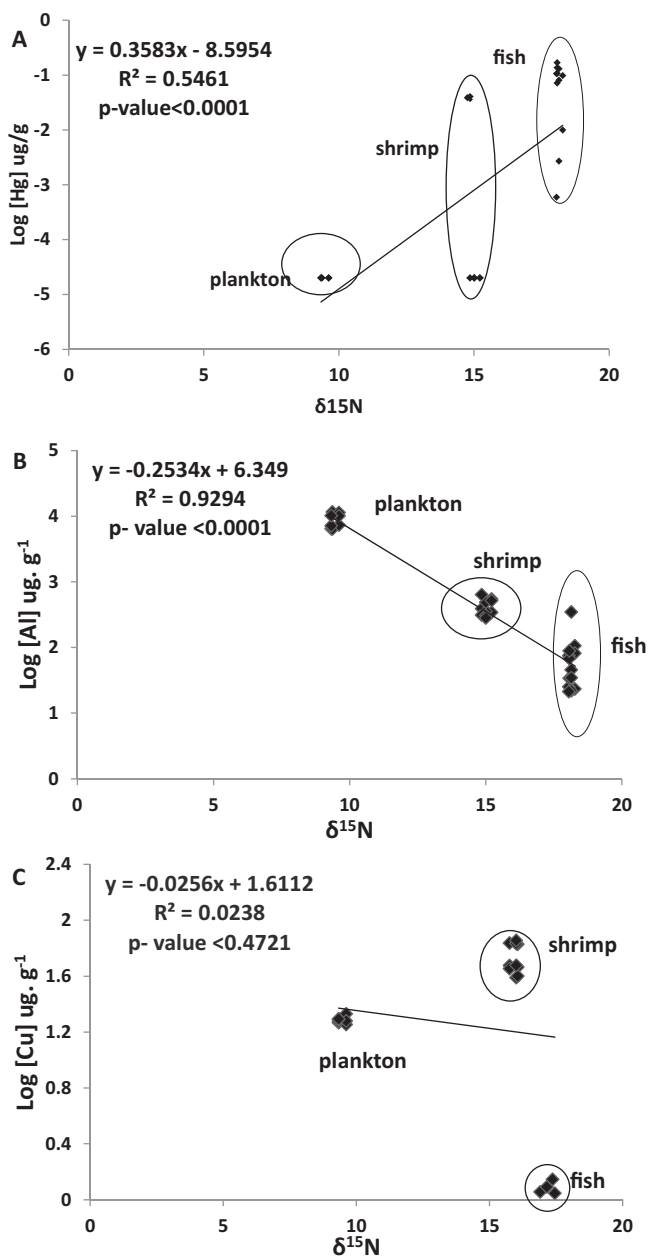


Fig. 2. Relationship between log [trace element concentration, µg g⁻¹ dry weight] versus δ¹⁵N for mercury, Hg (A) wet season; aluminium, Al (B) wet season and Copper Cu (C) dry season in the studied food chain. (A) A trace element that is biomagnified throughout the studied food web; (B) a trace element that is biodiluted throughout the studied food web; (C) a trace element without significant change throughout the studied food web.

et al., 2015). However, Hg, Ni and Cd concentrations were in agreement with results reported by Avigliano et al. (2015).

3.6. Implications for fish consumers

Considering the average value for Hg, As and Cr, found during this study in muscle of *O. bonariensis*, and assuming that a 70 kg person eats 150 g of fish muscle per day; a simple calculation reveals an average consumption of 11.2 µg Hg per day (wet season). Also, a year-average daily intake of 21 µg As and 210 µg Cr, exceeds the Oral Reference doses for heavy metals recommended by USEPA (2009), which are 0.16; 0.3 and 3.0 µg kg⁻¹ body weight per day for Hg, As and Cr, respectively. So far, the risk of consuming contaminated fish increases during the wet season (summer),

where the highest concentrations of contaminants in fish muscle were observed (Table 4). Fish is a valuable and nutritious food, which should not be omitted from a balanced diet. Human health risks associated with fish consumption are not negligible, and the sources of metal pollution in fish should clearly be controlled.

4. Conclusions

Concentrations of several metals-metalloids measured in water exceed quality guideline values for the protection of the aquatic biota, particularly for Al, Cu, Cr, Fe, Ni and Zn in water. Conversely, levels of these elements in sediment were below such guidelines.

Our current results indicate a significant difference in the concentration of some trace elements within and between studied organisms. Only Hg showed a consistent biomagnification throughout different components of the food web, while most studied elements, with the exemption of Mo, Nd (dry season) and Cd and Hg (wet season), were bioconcentrated from water to plankton with further biodilution from plankton to higher levels (shrimp and fish). Other trace elements (e.g. Cu, Zn, Ag, Sr and As) did not evidence bioconcentration or biodilution as might be expected considering homeostatic regulation and/or biochemical processes.

The present study revealed a differential accumulation of the studied elements among five analysed tissues of *O. bonariensis*. Liver and gills were the main storage tissues for studied elements, with Hg and As in muscle exceeding the Oral Reference dose established by USEPA. It is worth to mention that some elements are mainly accumulated from fish food (As, Fe and Cr), raising question on the presence of differential pathway for the accumulation of diverse elements through different aquatic webs.

These results trigger the need for more exhaustive studies to evaluate the transfer mechanisms through the food web, considering not only bioaccumulation but also biodilution factors, which may be applicable to toxic metals-metalloids and also to other toxic pollutants present in the food web.

Additionally, levels of toxic metals-metalloids found in muscle of *O. bonariensis* during this study suggest that frequent fish consumers could have a chronic exposure to As and Hg. This last result suggests the need for evaluating and controlling pollution sources within this basin. The current study could also be used as a leading case to demonstrate the “boomerang concept”, meaning “what you freely put into your sewage can be back into your food if a non-appropriate wastewater treatment is applied”.

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