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Potential human health risks from metals and As via *Odontesthes bonariensis* consumption and ecological risk assessments in a eutrophic lake

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ABSTRACT

The concentration of Al, Cr, Fe, Mn, Ni, Cu, Zn, Hg, Sr, Mo, Ag, Cd, Pb and As was analyzed in water, sediment, and muscle of *Odontesthes bonariensis* from the eutrophic San Roque Lake (Córdoba-Argentina). The monitoring campaign was performed during the wet, dry and intermediate season. The concentration of Cr, Fe, Pb, Zn, Al and Cd in water exceeded the limits considered as hazardous for aquatic life. The highest metal concentrations were observed in sediment, intermediate concentrations, in fish muscle, and the lowest in water, with the exception of Cr, Zn, As and Hg, which were the highest in fish muscle. Potential ecological risk analysis of heavy metal concentrations in sediment indicated that the San Roque Lake posed a low ecological risk in all sampling periods.

The target hazard quotients (THQs) and carcinogenic risk (CR) for individual metals showed that As in muscle was particularly hazardous, posing a potential risk for fishermen and the general population during all sampling periods. Hg poses a potential risk for fishermen only in the intermediate season. It is important to highlight that none of these two elements exceeded the limits considered as hazardous for aquatic life in water and sediment. This result proves the importance of performing measurements of contaminants, in both abiotic and biotic compartments, to assess the quality of food resources. These results suggest that the consumption of this fish species from this reservoir is not completely safe for human health.

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1. Introduction

Metals and metalloids are naturally or anthropogenically present in the environment. In aquatic environments, metal pollution can result from waste disposal, smelter tacks, geological weathering or from the discharge of agricultural, municipal, residential or industrial waste products (Cui et al., 2011). Contamination of aquatic environments with this kind of pollutants is more dramatic within estuaries and semi-closed coastal zones. Metal/loids can be strongly accumulated and biomagnified in water, sediment, and along the aquatic food chain, and, under certain conditions, they may accumulate to a toxic concentration level that may lead to ecological damage (Yi et al., 2011). This phenomenon can also occur in freshwater bodies such as lakes.

Suspended sediments adsorb pollutants from water, thus lowering their concentration in the water column. Metals are inert in the sediment, and are often regarded as conservative pollutants (Olivares-Rieumont et al., 2005). However, they may be released into the water column in response to certain disturbances (Agarwal et al., 2005), causing a potential threat to ecosystems (Hope, 2006). Consequently, an analysis of the distribution of metals and As in sediments adjacent to populated areas could be used to investigate anthropogenic impacts on ecosystems, and would assist in the assessment of risks posed by human waste discharges (Hu et al., 2002; de Mora et al., 2004; Zheng et al., 2008).

Methods used to evaluate the ecological risk posed by heavy metals in sediments include the potential ecological risk index (Håkanson, 1980). Few studies have conducted ecological risk

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assessments in lentic environments, such as lakes, on a nationwide or regional scale. Therefore, providing a comprehensive risk assessment of lake sediments has become urgent to support environmental regulation.

In addition to chemical analysis, biological monitors are good means for controlling the status of natural water bodies (Ben Salem et al., 2014). Aquatic organisms have been reported to present higher concentrations of metals in their tissues compared to the levels in the surrounding environment (water and sediment) (Malik et al., 2010). Fish are considered one of the most susceptible aquatic organisms to toxic substances present in water (Jarić et al., 2011). It is known that muscle is not a target organ for accumulation during acute exposure; however, this tissue is a good indicator of chronic exposures. When pollutants exceed all defense barriers, the body begins to accumulate pollutants in this organ (Kalay et al., 1999). The accumulation of metals in muscle has a direct implication on the negative effect of fish consumption on humans.

Fish consumption has been identified as the major pathway of human exposure, accounting for $>90\%$ compared to other ways of exposure, such as inhalation and dermal contact (Bortey-Sam et al., 2015). The contamination of fish, vegetables, soil and water with metal/loids has reached unprecedented levels over the past decade in some parts of the word (Yabe et al., 2010). Consequently, human exposure to toxic metals has become a major health risk. Several methods have been proposed for the assessment of potential human health risks from metals and As exposure. Current non-cancer risk assessment methods are typically based on the use of the target hazard quotient (THQ), a ratio between the estimated dose of a contaminant and the reference dose below which there will not be any appreciable risk (USEPA, 2000).

In eutrophic lakes, the presence of metals and As is particularly relevant. The elevated concentrations of nutrients, warm temperatures and high biomass production are favorable conditions for the development of cyanobacterial blooms (Amé et al., 2003; Ruiz et al., 2013). Zeng et al. (2012) have described that metals are accumulated by the bloom-forming cyanobacterial cells. These intracellular metals would be released into surrounding waters when the cells decompose, leading to an increase in metal concentrations in the lake area.

The San Roque Reservoir, located in the province of Córdoba, (Argentina), has been classified as a eutrophic to hypereutrophic lake, with abundant cyanobacterial blooms in the warm periods (Amé et al., 2003; Ruiz et al., 2013). This reservoir is the main drinking water supply to Córdoba city, as well as a source of hydroelectric power. It is also an important recreational area, leading to an increase in the urbanization of the lake surroundings. Air pollution in the region, mainly by metals, is determined by human and industrial activities, registering sources of Co, Fe, Mn, Ni, Pb, Zn, and other metals (Carreras and Pignata, 2002; Pignata el al., 2007). In recent years, agricultural practices have also become potential sources of contamination due to the removal of soil and the use of fertilizers, which contain different metals (Bermudez et al., 2012).

At the San Roque Lake intake, silverside (*Odontesthes bonariensis*) is a very important resource for local and sport fishermen. *O. bonariensis* is a fish species native to South-America, which has been introduced in Europe and Asia (Brian and Dyer, 2006). It inhabits the sea as well as salty and fresh lentic inland water bodies (e.g. ponds and lagoons). The commercial and sport fishing of silverside makes it an economically important species, being the second most important fishery resource in Argentina and Uruguay, for both local consumption and exportation (Avigliano et al., 2015; Minagri, 2014).

The present study aims to analyze the presence of Al, Cr, Mn, Zn, Fe, Ni, Cu, As, Sr, Mo, Ag, Cd, Hg and Pb in muscle of silverside, and its relation to the concentration of these elements in water and sediment of the San Roque Lake, during three hydrological stations, and to assess the human health risk associated with fish consumption. At present, there is very little information published about contamination in water, sediment and edible fish from this eutrophic lake, as well as the extent of human exposure, and potential health consequences. Accordingly, there is a need for detailed information in order to know the health risks for fish consumers. The results of this study are useful for pollution control and risk management of heavy metals in similar areas around the world.

2. Materials and methods

2.1. Study site

The San Roque Reservoir is located in the west side of Sierras Chicas in the Punilla Valley, Province of Córdoba (Argentina), at 643 m above sea level (31°22′41″S–64°28′10″W) (Fig. 1). It is an artificial lake with an area of 16 km^2, maximum storage capacity of 180 hm^3, and maximum depth of 35.5 m. It has two main tributaries: the San Antonio River and the Cosquín River. It also has two minor tributaries: Los Chorrillos Brook and Las Mojarras Brook. The pluvial regime is characterized by biannual discontinuity. The dry season occurs between June and December, with frequent rains in the remaining months (wet season) (Vázquez et al., 1979). The San Roque Reservoir has been classified as eutrophic to hypereutrophic with elevated concentrations of nutrients, and high incidence of toxic cyanobacterial blooms (Amé et al., 2003).

2.2. Sample collection and analysis

Samples were collected in the San Roque region (Fig. 1). It is in this area where most silverside fishing occurs, and it has easy

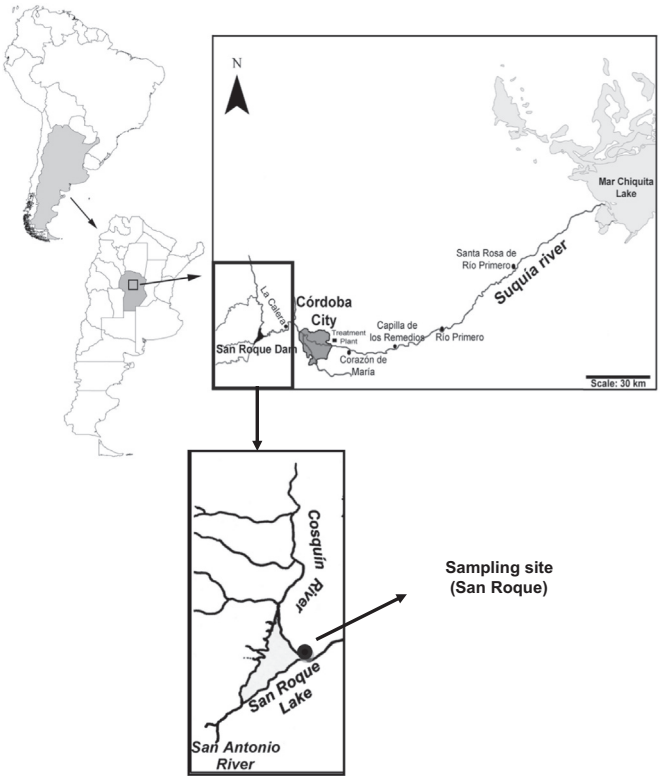

Fig. 1. Map of the Province of Córdoba – Argentina with indication of the studied area.

access for sampling. Three sampling campaigns were carried out during 2011–2012. Sampling dates were selected taking into account the seasonality and dimensions that characterize the lake, besides thermal variation. Therefore, we selected November 2011 as the end of the dry season (DS), February 2012 as the wet season (WS), and an intermediate month between the dry and wet seasons (August 2012) (IS). Al, Cr, Fe, Mn, Ni, Cu, Zn, Hg, Sr, Mo, Ag, Cd, Pb and As were measured in water, sediment and muscle of silverside.

Water and sediment samples were taken simultaneously with fish. Sample collection, containers, stabilization, and transportation to the laboratory as well as sample storage were done using previously described methods (Merlo et al., 2011). Water samples were collected into acid washed plastic bottles ($n=5$), acidified with ultrapure HNO_3, and stored at 4 °C 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 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 ultrapure HCl 0.5 N (Monferrán et al., 2011).

O. bonariensis (average length: November 2011 15.1 ± 0.5 cm; February 2012 16.5 ± 5.0 cm and August 2012 18.2 ± 4.1 cm) were captured by rod fishing. After capture, fish were sacrificed, ice-cooled, and transported to the laboratory, where they were dissected, separating the muscle. Only metals concentration in fish muscle (edible portion) was evaluated since in Argentina people do not habitually consume other parts of fish. The biological material was dried at 40 °C until constant weight, stored at −20 °C until analysis. Biological samples were grounded and homogenized with a mortar and pestle. Twenty milligrams of muscle sample were taken and digested with 8 mL nitric acid (sub boiling grade) and 1 mL of 30% H_2O_2 (ultrapure), in Teflon tubes on heating plates to 220 °C, during 8 h (Bertrand et al., 2013).

The analysis of metals and As in both abiotic and biotic samples was performed with a Mass Spectrometer Inductively Coupled Plasma (ICP-MS), X Series, Thermo-Elemental X7 series (Thermo Fisher Scientific, Bremen, Germany), equipped with an ASX-100 autosampler (CETAC Technologies, 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), United States Geological Survey Certificate of Analysis, Devonian Ohio Shale, SDO-1 and NIST 1643e (water).). Replicate analysis of these reference materials showed good accuracy, recoveries from CRMs are showed in. Table 1. Spiked samples were also prepared. Variable amounts of mixed standard solutions, containing all elements analyzed, were added to 0.02–0.04 g of fish sample (dried muscle) to double the starting concentration for each element. The rest of the procedure was the same as used for non-spiked samples. The average recovery was 98 ± 17%.

2.4. Assessment of potential ecological risk

Potential ecological risk was calculated using Håkanson (1980) methodology in which the sensitivity of the aquatic system depends on its productivity. The potential ecological risk index (RI) was introduced to assess the degree of heavy metal pollution in sediments, according to the toxicity of metal/loids pollution and the response of the environment. Sediments are reservoirs for metals, and the analysis and assessment of toxic metals contamination using tools such as pollution indices is imperative for monitoring aquatic environments.

Table 1
Trace element concentrations determined in three certified reference materials (all data as means ± SD. A) NIST 1646a (estuarine sediment) μg g^{-1} dry weight. B) SDO-1(United States Geological Survey Certificate of Analysis) μg g^{-1} dry weight. C) NIST 1643e (water) μg L^{-1}.

A

Metal	NIST 1646a		% Recovery
	Certified	Found	
Cr	40.9 ± 1.9	37.1 ± 2.3	90
Mn	234.5 ± 2.3	198.8 ± 1.5	84.8
Cu	10.01 ± 0.34	10.1 ± 0.29	101
Zn	48.9 ± 1.6	50.5 ± 2.9	103.3
As	6.23 ± 0.028	5.33 ± 0.83	85.6
Cd	0.148 ± 0.007	0.152 ± 0.013	103.1
Pb	11.7 ± 1.2	10.4 ± 0.1	88.9

B

Metal	SDO-1		% Recovery
	Certified	Found	
Cr	66.4 ± 7.6	61.3 ± 7.9	92.4
Ni	99.5 ± 9.9	95.4 ± 6.8	95.8
Cu	60.2 ± 9.6	57.6 ± 4.9	95.7
Zn	64.1 ± 6.9	57.5 ± 4.9	89.7
As	68.5 ± 8.6	64.2 ± 5.1	93.7
Sr	75.1 ± 11	73.2 ± 1.1	97.5
Mo	134 ± 21	140 ± 3.5	104.5
Hg	0.19 ± 0.08	0.21 ± 0.42	111.9
Pb	27.9 ± 5.2	29.7 ± 1.3	106.6

C

Metal	NIST 1643e		% Recovery
	Certified	Found	
Al	138.33 ± 8.4	132.46 ±	95.8
Cr	19.9 ± 0.23	18.8 ±	94.7
Mn	38.02 ± 0.44	40.13 ±	105.6
Fe	95.7 ± 1.4	95.10	100.0
Ni	60.89 ± 0.67	58.85 ±	96.7
Cu	22.2 ± 0.31	21.6 ±	97.2
Zn	76.5 ± 2.1	79.4 ±	103.8
As	58.98 ± 0.7	56.59 ±	96.0
Sr	315.2 ± 3.5	322.9 ±	102.4
Mo	118.5 ± 1.3	112.8	95.2
Ag	1.036 ± 0.073	1.050	101.4
Cd	6.408 ± 0.071	6.578	102.7
Pb	19.15 ± 0.20	18.33	95.7

The RI is calculated as indicated below:

$$R_I = \Sigma E_r^i \quad (1)$$

$$E_r^i = T_i^i C_f^i \quad (2)$$

$$C_f^i = C_o^i / C_n^i \quad (3)$$

The risk factor R_I proposed by Håkanson (1980) was based on eight parameters (PCB, Hg, Cd, As, Pb, Cu, Cr and Zn) measured in sediment. To calculate the Ecological risk assessment in the San Roque Lake, the PCB value was excluded because it was not measured during this work. R_I is calculated as the sum of all risk factors for metals measured in sediment during this work. E_r^i is the

Table 2
Standards of the potential ecological risk according to Eir and RI.

Scope of potential Ecological Risk Index (E_r^i)	Ecological risk level of single factor-pollution	Scope of potential toxicity Index(RI)	General level of potential ecological risk
$E_r^i < 40$	low	RI < 150	Low-grade
$40 \le E_r^i < 80$	moderate	$150 \le$ RI < 300	Moderate
$80 \le E_r^i < 160$	higher	$300 \le$ RI < 600	Severe
$160 \le E_r^i < 320$	high	$600 \le$ RI	Serious
$320 \le E_r^i$	serious		

monomial potential ecological risk factor, T_r^i is the toxic-response factor for a given substance, which accounts for the toxic and sensitivity requirements. The value of T_r^i for Hg, Cd, As, Cu, Pb, Cr, and Zn was 40, 30, 10, 5, 5, 2, and 1, respectively (Hilton et al., 1985). C_f^i is the contamination factor, C_o^i is the concentration of metal in the sediment of the San Roque Lake, and C_n^i is the background value of the heavy metal in coastal sediments (Li and Zheng, 1988) (Table 2).

2.5. Health risk assessment

2.5.1. Estimated daily intake of metal

The dietary exposure to trace metal was estimated using average concentrations of fish muscle. The estimated daily intake (EDI) of metal per fish consumption was made according to the equation used by Islam et al. (2014).

$$\text{EDI} = \text{FIR} \times C \quad (3)$$

where FIR is the food ingestion rate [g/person/day] (Fish consumption rate for adult residents were 200 g in this study), for FIR calculation RfDo is used, the RfD values (mg/kg/day) used in this study were as follows: Ag: 0.005; Sr: 0.6; Ni: 0.01; Mo: 0.005; Hg: 0.0001; Cu: 0.04; Cr: 0.003; Zn: 0.3; As: 0.0003; Cd: 0.1, provided by the USEPA's regional screening level (USEPA, 2015). An RfDo value for Pb does not exist because there is no evidence of a threshold below which a non-harmful intake could be allowed (USEPA, 2004), that's why values provided by JECFA (2011) were used. C is the metal concentration in fish [mg/kg, dry weight (dw)].

2.5.2. Non-carcinogenic and carcinogenic risk

In this study, the non-carcinogenic health risks associated with the consumption of silverside by the local inhabitants (fishermen and general population) were assessed based on the target hazard quotients (THQs). THQ was determined according to the USEPA (1989) method, and it is described by the following equation:

$$\text{THQ} = \frac{\text{EFr} \times \text{EDtot} \times \text{FIR} \times C}{\text{RfDo} \times \text{BWa} \times \text{ATn}} \times 10^{-3}$$

where THQ is the target hazard quotient; EFr is the exposure frequency; EDtot is the exposure duration (70 years) equivalent to the average lifetime (USEPA, 1991); FIR is the food ingestion rate (g/day); C is the concentration (μg/g); RfDo is the oral reference dose (mg/kg/day) based on USEPA (2009b), which indicates the quantity of the compound per kilogram weight that a human being could ingest per day without risk; BWa is the body weight (adult 70 kg); ATn is the averaging time for non-carcinogens 365 days/year × number of exposure years, assuming 70 years. The RfD values (mg/kg/day) used in this study were as follows: Ag: 0.005; Sr: 0.6; Ni: 0.01; Mo: 0.005; Hg: 0.0001; Cu: 0.04; Cr: 0.003; Zn: 0.3; As: 0.0003; Cd: 0.1, provided by the USEPA's regional screening level (USEPA 2015),

As it was mention in previous paragraph, RfDo value for Pb does not exist, therefore, the THQ for Pb was calculated using the following equation (Jovic and Stankovic 2014):

$$\text{THQ} = \frac{C}{\text{MRL}}$$

C: the metal concentration in fish muscle (μg/g dry weight); MRL (Maximum Residue Limit) set by the Regulation (EC) No. 1881/2006 (EC, 2006).

If such ratio exceeds unity, there may be a concern for potential health effects. We assumed that the ingestion dose is equal to the adsorbed contaminant dose, and that cooking has no effect on the contaminants according to USEPA (1989).

The health risks for fishermen and the general population were considered separately since the frequency of fish consumption is different. For fishermen, an exposure frequency of 48 days/year, once a week was set, while for the general population, it was 12 days/year, once per month.

It has been reported that exposure to two or more pollutants may result in additive and/or interactive effects (Hallenbeck, 1993). The total THQ is considered the arithmetic sum of the individual metal THQ values, derived from the method by Yi et al. (2011):

Total THQ (TTHQ)=THQ (toxicant 1)+THQ (toxicant 2)+THQ (toxicant 3)…

The carcinogens risk was estimated as the incremental probability of an individual to develop cancer over a lifetime exposure (USEPA, 1989).

Carcinogenic risk (CR) for As was calculated using the following equation:

$$\text{CR} = \frac{\text{EFr} \times \text{EDtot} \times \text{FIR} \times \text{CSFo}}{\text{BWa} \times \text{ATn}} \times 10^{-3}$$

CSFo is the oral carcinogenic slope factor from the Integrated Risk Information System (USEPA, 2010) database, which was 1.5 (mg/kg/day) for As. CR lower than 10^{-6} are considered to be negligible, between 10^{-6} and 10^{-4} are generally considered acceptable, and CR above 10^{-4} are considered unacceptable (USEPA, 1989, 2010; Islam et al., 2014).

2.6. Statistical analysis

Differences among concentration of metals and As in water, sediment and muscle of silverside among different samples were determined by a one-way analysis of variance (ANOVA), followed by a multiple comparison test (Tukey). When parametric assumptions were not fulfilled, Kruskal–Wallis followed by multicomparison Dunn's tests was used. Significance level was set at $p < 0.05$. We used the statistical software Infostat (2003).

Table 3
Water physico-chemical properties in the San Roque Reservoir.

Season	Temperature (°C)	pH	Dissolved Oxygen (mg L^{-1})	Conductivity (μS cm^{-1})	Lake level (m)[a]
Dry	27.4 ± 0.7	7.8 ± 0.2	9.9 ± 0.6	258 ± 10*	32.1
Wet	25.4 ± 1.1	7.4 ± 0.3	10.2 ± 0.3	189 ± 12	35.6
Intermediate	11.6 ± 0.9*	7.2 ± 0.2	12.1 ± 0.8	221 ± 6	33.0

Table 4
Concentrations of metals measured in water ($\mu g\ L^{-1}$) and sediments ($\mu g\ g^{-1}$ dry weight-DW) of the San Roque Reservoir. Values are expressed as means ± SD; sediments correspond to the fraction < 63 μm. < LOD (below detection limit); < LOQ (below quantification limit). LODs: Ag-water 0.006 $\mu g\ L^{-1}$; As – water 0.33 $\mu g\ L^{-1}$; Cr – water 0.06 $\mu g\ L^{-1}$.; Hg – water 0.006 $\mu g\ L^{-1}$.; Cd – water 0.03 $\mu g\ L^{-1}$.; Mo – water 0.048 $\mu g\ L^{-1}$; Pb – water 0.018 $\mu g\ L^{-1}$.; Mo – sediment 0.005 $\mu g\ g^{-1}$ LOQs: Hg – sediment 0.00002 $\mu g\ g^{-1}$. Different letters indicate significantly different values in the wet, dry and intermediate seasons (DMRT, $p \leq 0.05$).

	Season	Water ($\mu g\ L-^{1}$)	Sediment ($\mu g\ g^{-1}$ dw)
	dry	2434 ± 26^{b}	1051 ± 68^{b}
Al	wet	60 ± 2^{a}	780 ± 58^{a}
	Intermediate	56 ± 29^{a}	916 ± 5^{a}
	dry	2.6 ± 0.7^{a}	0.52 ± 0.02^{a}
Cr	wet	< LOD	0.41 ± 0.17^{a}
	Intermediate	< LOD	0.75 ± 0.01^{b}
	dry	224 ± 2^{c}	326 ± 25^{b}
Mn	wet	24 ± 4^{b}	109 ± 4^{a}
	Intermediate	11 ± 2^{c}	143 ± 15^{a}
	dry	2087 ± 10^{b}	724 ± 48^{b}
Fe	wet	51 ± 4^{a}	269 ± 1^{a}
	Intermediate	53 ± 17^{a}	1216 ± 65^{c}
	dry	5.5 ± 0.6^{a}	2.2 ± 0.1^{b}
Ni	wet	2.2 ± 0.6^{a}	1.3 ± 0.1^{a}
	Intermediate	5.5 ± 0.7^{a}	2.1 ± 0.1^{b}
	dry	5.5 ± 0.1^{c}	4.1 ± 0.1^{b}
Cu	wet	3.5 ± 0.6^{b}	2.5 ± 0.1^{a}
	Intermediate	1.8 ± 0.9^{a}	4.8 ± 0.4^{b}
	dry	17.8 ± 1.1^{a}	23.4 ± 0.2^{c}
Zn	wet	20.2 ± 0.8^{a}	8.9 ± 0.5^{b}
	Intermediate	14.9 ± 0.6^{a}	3.7 ± 0.6^{a}
	dry	3.8 ± 0.1^{a}	0.76 ± 0.11^{c}
As	wet	< LOD	0.34 ± 0.07^{a}
	Intermediate	< LOD	0.58 ± 0.01^{b}
	dry	105 ± 1^{b}	17 ± 1^{a}
Sr	wet	67 ± 2^{a}	15 ± 1^{a}
	Intermediate	85 ± 15^{a}	24 ± 1^{b}
	dry	9.1 ± 0.1^{a}	< LOD
Mo	wet	11.2 ± 0.6^{b}	< LOD
	Intermediate	< LOD	< LOD
	dry	< LOD	0.018 ± 0.007^{a}
Ag	wet	< LOD	0.014 ± 0.009^{a}
	Intermediate	< LOD	0.058 ± 0.008^{b}
	dry	< LOD	0.073 ± 0.014^{a}
Cd	wet	1.97 ± 0.08^{a}	0.059 ± 0.014^{a}
	Intermediate	< LOD	0.130 ± 0.008^{b}
	dry	< LOD	< LOQ
Hg	wet	< LOD	< LOQ
	Intermediate	< LOD	0.026 ± 0.012^{a}
	dry	2.35 ± 0.01^{b}	4.72 ± 0.06^{a}
Pb	wet	0.25 ± 0.02^{a}	7.85 ± 0.17^{b}
	Intermediate	< LOD	4.71 ± 0.29^{a}

3. Results and discussion

3.1. Chemical characterization of water sample

Results of chemical analysis in water samples are reported in Table 3. Significant seasonal variations in temperature were recorded between the three sampling dates, with the lowest temperature recorded in IS (11.6 °C), in agreement with winter time with no significant differences between DS and WS. The highest water levels were registered in WS, and the lowest in DS. Conductivity showed the highest values in the DS in agreement with the lowest water level record in the lake. No significant seasonal variations were recorded in pH values and the dissolved oxygen concentration (DO) of water samples.

3.2. Metals and As concentrations in abiotic and biotic matrixes

Concentrations of Al, Cr, Fe, Mn, Ni, Cu, Zn, Hg, Sr, Mo, Ag, Cd, Pb, and As were analyzed in water and sediment of the San Roque Lake (Table 4).

Generally, the highest concentrations of metals in water were detected during the DS. This could be explained by the low water volume at this time of the year. Some of the measured metals in water exceeded the limits considered as hazardous for aquatic life, according to the Argentinean Environmental Water Quality Guidelines (AEWQG, 2003), the US Environmental Quality Guidelines (USEPA, 2009a) and the Canadian Water Quality Guidelines (Canadian Council of Ministers of the Environment (CCME), 2002). For instance, values observed for Cr, Fe and Pb in water samples during the DS clearly exceed the regulated threshold value of 2.5 $\mu g\ L^{-1}$, 1370 $\mu g\ L^{-1}$ and 1.59 $\mu g\ L^{-1}$, respectively, established by AEWQG (2003). A similar situation is observed with Zn on the IS, which exceeds the threshold value (30 $\mu g\ L^{-1}$) established by CCME 2002, and with Al and Cd that exceed the threshold regulated value of 87 $\mu g\ L^{-1}$ and 0.25 $\mu g\ L^{-1}$), respectively (USEPA, 2009a).

Concentrations of metals and As in sediment were 1000–10,000 times higher than those in water. A number of studies have reported a similar phenomenon (Barak and Mason, 1989 and Yi et al., 2011, Monferran et al., 2011, Merlo et al., 2011). In the San Roque Lake, metal concentrations in sediment were significantly higher in the DS and IS, except for Pb which showed higher values in the WS (Table 4). A possible explanation for this is that the deposition of suspended material, due to slow water flow during the DS, leads to the deposition of finer grained sediments that contain more metals. This can explain the high metal concentration measured in sediment during the DS and IS, than in WS (Table 4).

Metal/loids concentrations measured in the San Roque sediments during the three sampling dates did not exceed the risk levels defined by the Canadian Guideline values for the Protection and Management of Aquatic Sediment Quality (Canadian Council of Ministers of the Environment, 2001). Argentinean regulations do not stipulate guideline values for inorganic elements in sediments.

Accumulation of metals in fish results primarily from surface contact with the water, from breathing, and via the food chain. Uptake by these three routes depends on the environmental levels of metals in the fish habitat.

Concentrations of metals and As in the muscle of silverside *(O. bonariensis)* in the San Roque Lake are presented in Table 5.

Most of the metals analyzed reached intermediate values in muscle with respect to water and sediment (sediment > fish > water). This is the expected behavior since metal/loids are not generally found in high concentrations in water, mainly due to deposition of metals in sediments, and to the uptake by plants and

Table 5
Concentrations of metals measured in fish muscle (μg g^{-1} dry weight-DW) of the San Roque Lake. Values are expressed as means ± SD. < LOD (below detection limit); LODs: Mo – 0.005 μg g^{-1}; Ag – 0.006 μg g^{-1}; Cd – 0.05 μg g^{-1}; Pb – 0.013 μg g^{-1}. Different letters indicate significantly different values in the wet, dry and intermediate seasons (DMRT, $p \leq 0.05$).

Season	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Sr	Mo	Ag	Cd	Hg	Pb
Dry	5.9 ± 0.9^{a} (4.5–6.5)	3.04 ± 0.60^{b} (2.21–3.58)	3.9 ± 0.8^{b} (3.4–5.2)	10 ± 2^{a} (7.5 – 13.6)	0.56 ± 0.08^{a} (0.49–0.63)	0.83 ± 0.06^{b} (0.76–0.91)	62 ± 7^{a} (50.9–67.8)	3.9 ± 0.4^{a} (3.6–4.3)	12 ± 5^{a} (8.5 – 19.1)	0.04 ± 0.07^{a} (0-0.15)	0.009 ± 0.004^{a} (0.007–0.015)	< LOD	0.04 ± 0.03^{a} (0–0.08)	0.07 ± 0.03^{a} (0.05–0.11)
Wet	37.8 ± 24.6^{b} (4.1–105.1)	3.32 ± 1.29^{b} (1.98–6.66)	3.6 ± 1.4^{b} (2.0–5.9)	29 ± 16^{a} (11.4–67.8)	1.04 ± 0.56^{b} (0.69–2.77)	0.86 ± 0.16^{b} (0.57 – 1.09)	52 ± 16^{a} (33.7–88.6)	2.6 ± 0.7^{a} (1.6–4.1)	9 ± 3^{a} (4.9–15.3)	0.08 ± 0.02^{a} (0.06–0.15)	0.012 ± 0.005^{a} (0.006–0.021)	< LOD	0.09 ± 0.06^{a} (0–0.18)	0.03 ± 0.04^{a} (0–0.13)
Intermediate	42.5 ± 26.6^{b} (1.3–93.9)	0.04 ± 0.07^{a} (0–0.19)	1.5 ± 1.6^{a} (0–4.95)	59 ± 38^{b} (1.1–134.5)	0.20 ± 0.40^{a} (0 – 1.1)	0.08 ± 0.19^{a} (0-0.5)	55 ± 14^{a} (36.7–72.1)	7.9 ± 2.1^{b} (4.8–12.1)	8 ± 6^{a} (0 – 19.8)	< LOD	< LOD	0.02 ± 0.08^{a} (0–0.29)	0.35 ± 0.07^{b} (0.26–0.46)	< LOD

animals (Yi et al., 2008). However, Cr, Zn and As showed higher concentrations in muscle than in sediments, and even though Hg was not registered in water and sediment, it showed high values in muscle. As it was mentioned before, muscle is not a target organ for accumulation during acute exposure, so these results demonstrate the chronic exposure to which the fish was subjected (Storelli, 2008; García et al., 2000). 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). The biomagnification of Hg from lower to higher trophic levels is well known. In many reports it was demonstrated that the trophic transfer is a predominant way of Hg accumulation in higher trophic levels in aquatic environments (Nfon et al., 2009; Blackmore and Wang, 2004; Kidd et al., 2003; Campbell et al., 2005). On the other hand, As has a considerable tendency to accumulate in bottom sediments (Smedley and Kinniburgh, 2002; Rosso et al., 2013). Essentially, fish assimilate metals (also As) by ingestion of particulate material suspended in water, feeding on contaminated preys, ion-exchange of dissolved metals across lipophilic membranes, e.g., the gills, and adsorption on tissue and membrane surfaces (Shah et al., 2009).

Cr, Mn, Ni, Mo, Ag, Pb and Cu were higher during both the WS and DS, while Zn and Sr concentration in fish muscle shows no difference between sampling seasons (Table 5).

In the Southern hemisphere, November and February stations (DS and WS) are characterized by higher temperature values. This phenomenon leads to an increase in water filtration and in the metabolism of aquatic organisms, increasing 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 change due to their short generation times. As environmental conditions change, the tolerance and optima of different taxa can be exceeded or shifted, causing changes to the relative abundance of the composition of plankton. This change in the composition of plankton due to environmental conditions can lead to a change in their ability to accumulate metals from the medium, increasing in the summer season and decreasing in winter in the San Roque Lake. This phenomenon can be extrapolated to higher trophic levels that feed on plankton, as is the case of the silverside fish (Sagretti and Bistoni, 2001; Rodrigues and Benvenuti, 2011).

On the other hand, As, Hg, Cd and Fe showed higher values during the IS (winter time). We did not find any explanation for the increase of these elements in muscle of Silverside in a season with lower temperatures. Other study also reported seasonal variation in the levels of metal accumulation in aquatic organisms (Ben Salem et al., 2014; Jovic′ and Stankovic′, 2014; Xiaobo et al., 2009).

3.3. Ecological risk

Based on Eqs. (1)–(3), ecological risk indexes of metal/loids in the San Roque Lake, considering the DS, WS and IS, were calculated and are listed in Table 6. The results indicate a low degree of ecological risk associated with toxic metal/loids present in the sediment of the San Roque Lake during the seasons studied. The potential ecological

Table 6
Potential metal ecological risk indexes of the sediment of the San Roque Lake.

	E_r^i							**RI**
Season	As	Cu	Cd	Cr	Pb	Zn	Hg	
Dry	0.51	0.68	4.38	0.02	0.94	0.29	0	**6.8**
Wet	0.23	0.42	3.54	0.01	1.57	0.11	0	**5.9**
Intermediate	0.39	0.80	7.80	0.03	0.94	0.05	4.16	**14.2**

Table 7
Estimated daily intake (EDI) from fish consumption by the general population and fishermen in the San Roque Lake. Pb[1]Chronic renal diseases: 0.63 μg/kg bw/day. Pb[2] Effects on the systolic blood pressure: 1.50 μg/kg bw/day.

	Elements											
	Cr	**Ni**	**Cu**	**Zn**	**As**	**Sr**	**Mo**	**Ag**	**Cd**	**Hg**	**Pb[1]**	**Pb[2]**
Daily allowed ingest for a 70 kg individual (mg)	0.21	0.7	2.8	21	0.021	42	0.35	0.35	0.07	0.007	0.044	0.105
Dry	0.608	0.112	0.166	12.3	**0.794**	2.48	0.008	0.002	ND	**0.008**	0.014	0.014
Wet	0.686	0.208	0.172	10.4	**0.512**	1.86	0.016	0.002	ND	**0.018**	0.006	0.006
Intermediate	0.008	0.04	0.016	11.1	**1.58**	1.59	ND	ND	0.004	**0.07**	ND	ND

Table 8
Estimated target hazard quotients (THQ) for individual metals and total THQ (TTHQ) from fish consumption by the general population and fishermen in the San Roque Lake.

Sampling	Exposure group	Elements											
		Cr	**Ni**	**Cu**	**Zn**	**As**	**Sr**	**Mo**	**Ag**	**Cd**	**Hg**	**Pb**	**TTHQ**
Dry	fisherman	0.381	0.004	0.008	0.077	**4.89**	0.008	0.003	0.001	0	0.15	0.233	5.75
	General population	0.095	0.001	0.002	0.019	**1.22**	0.002	0.001	0	0	0.04	0.233	1.61
Wet	fisherman	0.416	0.008	0.008	0.065	**3.26**	0.006	0.006	0.001	0	0.34	0.100	4.21
	General population	0.104	0.002	0.002	0.016	0.81	0.001	0.002	0	0	0.08	0.100	1.13
Intermediate	fisherman	0.005	0.002	0.001	0.070	**9.90**	0.005	0.000	0	0.008	**1.32**	0	11.31
	General population	0.001	0	0	0.017	**2.48**	0.001	0.000	0	0.002	0.33	0	2.83

risk index of a single element (E_r^i) showed that all elements measured exhibited a low ecological risk level. Cd showed a higher value of E_r^i during three seasons studied with respect to the seven metal/loids measured in the sediments of the San Roque Lake, mainly due to the high toxicity coefficient of this element.

3.4. Health risk assessment

The silverside (*O. bonariensis*) species from the studied lake is an important aquatic product in the Cordoba City region. Therefore, it is necessary to assess the health risks caused by the consumption of these fish species.

The estimated daily intake (EDI) of metal from fish consumption by the local inhabitants is presented in Table 7. It is interesting to mention that As and Hg exceeded the limits allowed in three sampling dates. Since this is the first study intensively monitoring trace metals in *O. bonariensis* in an eutrophic lake, it will be necessary to set up regulatory norms for dietary intake of this fish species.

The target hazard quotients (THQ) for an individual heavy metal through food consumption by the general population and fishermen are listed in Table 8. The THQ for most metals was less than 1, except for As and Hg. Arsenic exceeded the value of 1 for both fishermen and the general population during the three periods studied (except for the general population during the WS), while Hg showed values higher than 1 for fishermen only in the IS. The total metal THQ value for both consumer groups was higher than 1, indicating the potential health risks (Table 8).

The THQ for fishermen through fish consumption was about ten times higher than that of the general population. The highest average THQ value for these group suggests that they could experience adverse health effects, mainly associated with Hg and As, from fish consumption.

The carcinogenic risk (CR) caused by exposure of fish species to As is listed in Table 9. CR values obtained for As were not within the acceptable range. Therefore, the potential health risk for the inhabitants due to metal exposure through fish consumption in a eutrophic lake such as the San Roque Lake, should not be ignored.

The intake of these metals through food is associated with many diseases, because metals are rapidly distributed to different body systems, carried by erythrocytes which bind themselves to the hemoglobin. They join specific groups of certain proteins, thereby inhibiting the enzymatic activity of certain processes (Graeme and Pollack., 1998). The toxicity of As and Hg also involves the central nervous system (CNS), due to the ability of these elements to pass through the blood-brain barrier. The nervous system is exposed to them because they are excreted slowly and have a large storage capacity. The brain of adults and, in particular, of developing fetuses, is very sensitive to the neurotoxic effects of Hg (Fernandes Azevedo et al., 2012). On the other hand, it has been reported that As in adult humans produces several diseases including encephalopathy, convulsions and delirium (Graeme and PollacK., 1998; Moreno-Sánchez et al., 1999). These authors mention that other systems show early signs associated with exposure to Hg and As such as digestive disorders, hypotension and tachycardia. There are also other sources of metal exposures, such as consumption of other foodstuffs and dust inhalation, which were not included in this study. The constant monitoring of both elements in all food commodities is suggested in order to evaluate any potential health risk of the study area.

Table 9
Estimated carcinogenic risk (CR) of metals from fish consumption by the general population and fishermen in the San Roque Lake.

Exposure group	CR As
Fisherman	5.6E−04
General population	1.4E−04

Importantly, Arsenic was only detected in sediment and water in one sampling, and Hg was not detected in water and only detected in sediment in one season. None of the mentioned elements exceeded guidelines levels for the protection of aquatic biota in both matrixes (AEWQG, 2003; USEPA (2009a) and Canadian Council of Ministers of the Environment (2001)). However, both elements were present in the muscle of Silverside in concentrations greater than those allowed. This proves the importance of performing measurements of contaminants in abiotic and biotic compartments to assess the quality of food resources.

4. Conclusion

Concentrations of several metals measured in water exceed quality guideline values for the protection of the aquatic biota, particularly for Al, Cd, Cr, Fe, Pb and Zn in water. Conversely, levels of these elements in sediment were below such guidelines. The concentrations of most studied elements were higher in sediments, intermediate in muscle fish, and lower in the water, with the exception of Cr, Zn, As and Hg, that were higher in fish muscle. As and Hg did not exceed guidelines levels for the protection of aquatic biota in water or sediment. However, both elements were present in the muscle of Silverside in concentrations greater than those allowed. This proves the importance of performing measurements of contaminants in abiotic and biotic compartments to assess the quality of food resources.

From the human health perspective, THQ values showed that there was no health risk for consumers due to intake of an individual metal except for As, for both exposure groups during the wet, dry and intermediate season, and Hg in fishermen during the intermediate season. However, THQs for combined metals were higher than 1 for both exposure groups and in all sampling campaigns, indicating the potential health risk to the exposed consumers. There is evidence of cancer risk for fishermen and the general population (risk of developing cancer over a human lifetime is 5.6 in 10,000 and 1.4 in 10,000, respectively) who consume silverside only once per week or once per month.

Fish are a valuable and nutritious food, which should not be omitted from a balanced diet. Human health risks associated with fish consumption were not negligible, and the sources of heavy metal pollution in fish should clearly be controlled. According to these results we warn that fish consumption is a matter of risk. Clearly, there are benefits and risks associated with fish consumption, and the community should be provided with as much information as possible to allow them to maximize the positive health benefits, while minimizing the risks from contaminants. The availability of information on both the risks and benefits of specific fish species from particular areas is a key to making informed decisions about fish consumption.

Furthermore, in addition to metal studies, other organic contaminants such as pesticides and emergent contaminants of health concern should be evaluated in this fish species from the San Roque Lake.

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