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Bioaccumulation and trophic transfer of metals, As and Se through a freshwater food web affected by antrophic pollution in Córdoba, Argentina

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ABSTRACT

The concentration of metals (Al, Cr, Mn, Fe, Ni, Cu, Zn, Ag, Cd, Hg, Pb, U), As and Se in different ecosystem components (water, sediment, plankton, shrimp, and fish muscle) has been determined in a eutrophic reservoir in the Province of Córdoba (Argentina). Los Molinos Lake (LML) was sampled during the dry (DS) and wet seasons (WS) in order to examine the bioaccumulation and transfer of these inorganic elements through the food web. Stable nitrogen isotope ($\delta^{15}N$) was used to investigate trophic interactions. According to this, samples were divided into three categories: plankton, shrimp (*Palaemonetes argentinus*) and fish (Silverside, *Odontesthes bonariensis*). The bioaccumulation factor (BAF) was calculated for the organisms, and it was determined that the elements analyzed undergo bioaccumulation, especially in organisms such as plankton. The invertebrates were characterized by the highest BAF for Cu and Zn in both seasons, As (DS), and Cd and Hg (WS). The fish muscle was characterized by the highest BAF for Se (WS), Ag and Hg (DS). On the other hand, a significant decrease in Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and U concentrations through the analyzed trophic web during both seasons was observed. Moreover, a significant increase in Hg levels was observed with increasing trophic levels in the DS, indicating its biomagnification.

Despite the increasing impact of metals, As and Se pollution in the studied area due to urban growth and agricultural and livestock activities, no previous study has focused on the behavior and relationships of these pollutants with the biotic and abiotic components of this aquatic reservoir. We expect that these findings may be used for providing directions or guidance for future monitoring and environmental protection policies.

1. Introduction

An aquatic ecosystem is a habitat for aquatic organisms and also a reservoir of potential persistent chemicals (Achary et al., 2017). The advance of technology, the increasing amount of waste materials and a growing population have often resulted in the transformation of lakes, rivers and coastal waters into waste depots, where the natural balance is severely upset and, in cases, totally disrupted (Sharma, 2014). Some of the severe pollutants that have drawn more attention are metals and the metalloid As. They are a global concern, due to their potential toxic effect, persistence and ability to bioaccumulate in aquatic ecosystems (Hall, 2002; David et al., 2012; Batvari et al., 2015).

The introduction of these contaminants into the aquatic system derives from various sources; they can be present due to naturally occurring deposits or through anthropogenic activities (Ekeanyanwu et al., 2010; Merciai et al., 2014). The latter might be from smelting processes, fuel combustion entering the system via atmospheric fallout, effluents and dumping activities, from runoff of terrestrial systems, land application of sewage materials and leaching of garbage. Metals and As tend to be trapped in the aquatic environment and accumulate in sediment, being directly available to benthic fauna or released to the water column through different ways, increasing the dissolved concentration in the environment and threatening the ecosystem (Pekey et al., 2004). In addition to sediment and water, this kind of elements can enter the food web through organisms taken as part of the diet (zooplankton, phytoplankton, and benthos) or by uptake through the gills and skin, and be potentially accumulated in edible fish in aquatic ecosystems (Ahmed et al., 2015). This mobilization means that they can be accumulated in the body tissues of living organisms (bioaccumulation) and transferred through aquatic food webs, increasing the

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concentration as they pass from lower trophic levels to higher trophic levels (biomagnification). In contrast, a number of studies have documented biodilution, whereby metal/loids concentration in tissues decreases with increasing trophic position (van Hattum et al., 1991; Van Hattum et al., 1996; Besser et al., 2001; Farag et al., 1998; Quinn et al., 2003). The link between the elements and their accumulation or dilution in aquatic organisms also depends on the species, toxic and physicochemical conditions, and exposure routes (Croteau et al., 2005). There is also influence of the biological and ecological factors of the species that make up the food chain, such as eating habits, habitat, age, sex, health and the mechanisms of detoxification (Soto-Jiménez, 2011).

Naturally occurring stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) can be used as tracers to investigate the trophic relationships in foodwebs and any potential biomagnification of contaminants (Cui et al., 2011). A powerful tool to quantify the trophic position is $\delta^{15}N$, because its enrichment occurs incrementally across trophic levels with a constant rate (3–4‰). $\delta^{13}C$ is generally used to provide information on spatial habitat use and carbon sources in addition to trophic relationships, and it is enriched in consumer tissues to a minor degree, approx. 1‰ among different trophic levels (Dehn et al., 2006). Thus, $\delta^{13}C$ is also considered as a valuable biomarker for identifying different sources of primary production (Hobson et al., 2002; Hoekstra et al., 2003). Stable isotope analyses are widely used in ecotoxicological studies to elucidate contaminant behavior (e.g., bioconcentration and biomagnification) through the whole trophic chain (Cui et al., 2011).

Los Molinos Lake (LML) has been classified as mesotrophic to eutrophic, with recurrent cyanobacterial blooms and impaired water quality in summer and spring (Bazán et al., 2014). It was constructed for the purposes of providing drinking water, hydroelectrical power, irrigation, and flood control. In recent years, it has suffered natural impacts (fires and floods in the surrounding areas) and strong anthropogenic pressure by the growth of urban settlements and tourist facilities without planning or control. Currently, this water body represents a major touristic attraction for the region, and it is also used for recreational activities like fishing and water sports. The main activities performed in the catchment area are related to agriculture (soybean, corn and potato) and livestock, different animals (cows and horses) graze in the west coast of the reservoir and use it as a drinking trough (Rodriguez Reartes et al., 2016), providing a direct discharge of their manure into the water body. The treatment of domestic wastewater in LML is made through septic tanks and cesspools, which are insufficient due to the soil characteristics of the area, and the proximity of the dwellings to the reservoir (< 50 m from the coast for some buildings) (Rodriguez Reartes et al., 2016). Aditionally, around the lake there are hundreds of rafts that are inhabited in a permanent way, which produce different types of wastes, which are directly thrown into the reservoir. Therefore, there is a large direct discharge of domestic effluents, i.e. without previous treatment, into the lake.

While some studies have analyzed the behavior and relationships of metals in the biotic and abiotic components of aquatic environments (Aderinola et al., 2009; Jara-Marini et al., 2009; Mathews and Fisher, 2008), most of the research on these pollutants has focused on isolated components, e.g. sediments (Aprile and Bouvy, 2008), water (Melgar et al., 2008), plants (Bayen, 2012) or fish (Malik et al., 2010). The bioavailability and the potential for bioaccumulation and biomagnification of inorganic elements in all components of an ecosystem are high; hence the importance to understand the pollutant dynamics in the aquatic environments.

One of the major pathways of human exposure to metal/loids is fish consumption, reaching > 90% compared to other routes of exposure, like dermal contact and inhalation (Griboff et al., 2017). Silverside (*Odontesthes bonariensis*) is a characteristic fish from the central region of Argentina in South America, and it is considered by different authors (Sagretti and Bistoni, 2001; Vila and Soto, 1986) as an omnivorous species, which is known to shift its diet depending on the size of the individual. The small ones (< 25 cm length) feed on plankton and invertebrates, while the big ones (> 30 cm length) eat fish as primary food. This species is of economic importance, because it is widely used for commercial and sport fishing, being, for Argentina and Uruguay, the second most important fishery resource for local consumption as well as for exportation (Avigliano et al., 2015).

For all of the above, we consider it extremely important to evaluate the level of contamination in the reservoir, analyzing metals in abiotic and biotic samples. Therefore, the aims of this study are: 1) to determine metal, As and Se content in water, sediment, plankton, shrimp (*Palaemonetes argentinus*) and fish muscle (*Odontesthes bonariensis*) samples in LML to evaluate the influence of two contrasting climatic seasons (dry and rainy); and 2) to investigate the trophic transfer behavior of studied elements within an aquatic food web (water, plankton, shrimp and fish). Despite previous reports showing bioaccumulation or biomagnification of inorganic elements within aquatic ecosystems, our study aims to present the transfer of several elements (metals and metalloids) through a limited food web, showing similarities and discrepancies with previous reports, thus triggering the need for further research in this area.

2. Materials and methods

2.1. Study area

LML (31°43'30''S, 64°32'20''W) is an artificial water body located in the fault-bounded valleys of Calamuchita, located 65 km SW of Córdoba city (Argentina) (Fig. 1). It is confined by the Sierras Chicas (East) and Sierras Grandes (West). The main tributaries are the San Pedro River, Los Espinillos River, del Medio River and Los Reartes River. It has just one effluent, Los Molinos River. The lake has an area of 21.1 km^2, a maximum volume of 400 hm^3, and a maximum depth of 52 m. Its retention time has been estimated in 451 days. The rainfall regime of LML is characterized by two well-defined seasons, the dry season occurs between June and November, with frequent rains in the remaining months (wet season).

2.2. Sample collection and analysis

Samples were collected in the LML region (Fig. 1). The sampling area has approximately the same water quality as the rest of the lake (Bazán et al., 2014), with easy access for sampling. The samples were collected seasonally, in April 2014 (WS) and in August 2015 (DS), in this water reservoir. The organisms collected for this study were plankton, shrimp (*Palaemonetes argentinus*) and silverside fish (*Odontesthes bonariensis*). Simultaneously, water and sediment samples were taken. All samples were collected in the same sampling site. Concentration of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Ag, Cd, Hg, Pb and U were measured in these samples. Stable isotope compositions of $\delta^{13}C$ and $\delta^{15}N$ were measured in these samples. Superficial water samples ($n = 5$) were collected in previously cleaned polyethylene bottles and transported to the laboratory for analysis. They were acidified with ultrapure nitric acid (sub-boiling) and pre-filtered using nitrocellulose filters (0.45 µm pore size) (Sartorius, Göttingen, Germany). Sediment samples ($n = 3$) were collected at approximately 2 m from the shore and at 0–15 cm depth, using a plastic shovel and transferred into clean plastics bags. Subsequently, they were dried at 45 °C and sieved through acrylic meshes of 63 µm. Metals, As and Se fractionation was peformed by using a three-step sequential extraction procedure, which was discussed by Maiz et al. (2000). The following reagents were used: a) for the mobile fraction (A1) 0.01 M $CaCl_2$ solution, 2 h at room temperature, under agitation; b) for the mobilisable fraction (A2) 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M TEA aqueous solution at pH 7.3, 4 h at room temperature, under agitation; and c) for the residual fraction (A3) 1 mL of HNO_3 and 3 mL of HCl, overnight at room temperature. The sediment results were expressed as the sum of the concentrations obtained in the three fractions (A1 + A2 + A3).

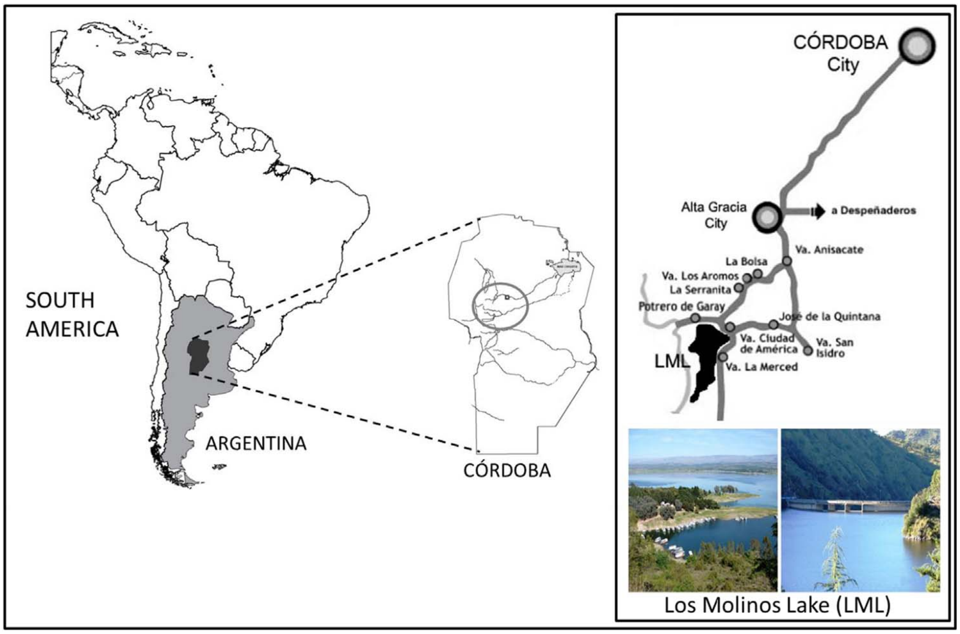

Fig. 1. Map of the Province of Córdoba - Argentina with indication of the studied area.

Plankton samples (n = 3) were collected filtering 20 L of water through a 50 µm nylon mesh. Shrimp (n = 7) (average length: 2.917 ± 0.032 cm in WS, and 2.815 ± 0.050 cm in DS) were captured using a plastic trawl, transported into 20 L containers using water from the capture site and keeping aeration by mechanical pump. Whole organisms were used for inorganic and isotopic determinations. Silverside individuals (n_{WS} = 10 and n_{DS} = 14) were captured with a fishing rod and were immediately iced and transferred to the laboratory. For each fish, weight (average weight: 63 ± 13 g in WS, and 190 ± 43 g in DS) and standard length (average length: 18 ± 2 cm in WS, and 24 ± 1 cm in DS) were recorded. They were dissected, separating the muscle. For the measurement of inorganic elements, biotic samples were dried at 40 °C until constant weight, stored at −20 °C until analysis. Biological samples were ground and homogenized with a mortar and pestle. About 0.02 g of each sample was digested with 8 mL of HNO_3 (sub-boiling) and 1 mL of hydrogen peroxide in teflon tubes according to Griboff et al. (2017). All samples were stored at 4 °C until analysis. The multi-elemental analysis in both abiotic and biotic samples was performed using a Mass Spectrometer Inductively Coupled Plasma (ICP-MS), (Q-ICPMS, Agilent Technology 7500 cx Series, California), equipped with an ASX-100 autosampler (CETAC Technologies, USA, Omaha, NE).

2.3. Quality assurance and quality control

All samples were digested in triplicate. Concentrations of studied elements were determined in triplicate; the repeatability of ICP-MS measurements was generally ≥97%. Quality assurance (QA) and quality control (QC) were performed using certified reference materials (CRMs): NIST 8414 (Bovine Muscle Powder) and NIST 1643e (Freshwater). The recoveries of the reference samples for tested elements were 102 ± 8% and 102 ± 7%, respectively. Spiked samples were also prepared. Variable amounts of mixed standard solutions, containing all elements analyzed, were added to 0.02 g of dried fish muscle, shrimp or plankton samples, prior to sample digestion. The rest of the procedure was the same as used for non-spiked samples. The average recoveries were 93 ± 9%, 94 ± 12% and 91 ± 7%, respectively.

2.4. Stable isotopes

The isotopic composition of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) in biological samples was measured using a Delza V Isotope Ratio Mass Spectrometer, connected with an elemental analyzer (both Thermo Fisher Scientific). Facility belonging to the Lehr und Forschungszentrum - Francisco Josephinum Wieselburg from Austria. Before measurement, the dried and homogenized samples were defatted, using a Soxhlet apparatus with petroleum ether. Between 0.95 and 1 mg of the remaining fat-free material was homogenized and introduced into tin capsules for analysis.

Stable isotope values (δ) were expressed in parts per thousand (‰) relative to the C and N reference materials (Vienna Pee Dee Belemnite (V-PDB) for ^{13}C, and on atmospheric N_2 (AIR) for ^{15}N), as follows:

$$\delta X‰ = ((\mathrm{R\ sample}/\mathrm{R\ standard}) - 1) \times 1000$$

where X is ^{13}C or ^{15}N and R is the ratio of $^{13}C/^{12}C$ or $^{15}N/^{14}N$ in each case. Replicate measurements of internal laboratory standards (glycine) show that the measurement errors for both carbon and nitrogen isotope analyses were better than ± 0.2‰.

2.5. Potential ecological risk assessment

In order to assess the degree of metals and As pollution in sediment, according to their toxicity and the response of the environment, the potential ecological risk assessment using the Hakanson factor (1980) was performed. It is based on eight parameters (PCB, Hg, Cd, As, Pb, Cu, Cr and Zn), but in this study we excluded PCB. It is calculated by the following equations:

$$R_I = \Sigma E_r^i$$

$$E_r^i = T_r^i C_f^i$$

$$C_f^i = C_o^i/C_n^i$$

where R_I is the sum of all risk factors for the elements tested in sediment, E_r^i is the monomial potential ecological risk factor, T_r^i is the toxicity coefficient which represents the toxic-response factor for a given metal. C_f^i is the contamination factor, C_o^i is the concentration of metals in sediment, and C_n^i is a reference value for metals. Depending on the values of E^ir and R_I obtained, the risk can be classified in the categories indicated in Table 1.

Table 1
Levels of ecological risk associated with an element (E_r^i) and total ecological risk level in sediments (R_I).

Scope of potential Ecological Risk Index (E_r^i)	Ecological risk level of single factor-pollution	Scope of potential toxicity index (R_I)	General level of potential ecological risk
$E_r^i < 40$	Low	$R_I < 95$	Low-grade
$40 \le E_r^i < 80$	Moderate	$95 \le R_I < 190$	Moderate
$80 \le E_r^i < 160$	Higher	$190 \le R_I < 380$	Severe
$160 \le E_r^i < 320$	High	$R_I \ge 380$	Serious
$E_r^i \ge 320$	Serious		

2.6. Bioaccumulation factor (BAF)

The bioaccumulation factor (BAF) was calculated according to the following equation for each species collected (Monferrán et al., 2016a):

$$BAF = Css/Cw$$

where Css is the element concentration in organisms at steady state (μg g^{-1}, dry weight), and Cw is the element concentration in water (μg mL^{-1}).

2.7. Statistical analysis

The values of the multi-elements concentration and stable isotopes are expressed as mean ± 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 $\delta^{15}N$ signature. When the p value is less than 0.0001, the linear regression between the heavy metal concentration and the trophic level is considered as significant. All statistical tests were performed using the InfoStat software (Argentina, 2008).

3. Results and discussion

3.1. Multi-element concentration in abiotic samples

In Table 2, concentrations of metals, As and Se in water (μg L^{-1}) and sediment (μg g^{-1} dw) samples in the DS and WS are shown. On a temporal scale, the concentration of the inorganic elements in water was different; Al, Mn, Fe, Cu and As had higher concentrations during the WS, Ni and U were higher during the DS, and Cr, Se, Ag, Cd and Hg were below the detection limit in both seasons. Localized inputs like river and backwater inputs, atmospheric fall-out as well as variation in different hydrological parameters play an important role in the variable concentration of elements observed (Achary et al., 2017). The correspondence between the WS and the higher concentrations of elements can be explained in terms of the increased quantity of eroded material and urban run-off expected while raining, considering that the samples were taken after a period of intense rains in Córdoba.

Our current results were compared with those of the San Roque Lake, another important lake of Córdoba, classified as a hypertrophic reservoir (Griboff et al., 2017). Concentrations of Al, Cr, Mn, Ni, Cu, Zn, Cd and Pb in LML were lower than those in water samples from the San Roque Lake, except Fe, which had similar concentrations in both lakes during the WS, and As was higher in the LML in the WS. In both lakes, Hg and Ag were not detected in water samples. Concentrations of As, Cd, Cr, Pb, Zn, Ni, and Cu in water samples were also lower than those reported by Zhang et al. (2016) in the Pontchartrain Lake (North America), which can be due to the different anthropic sources of contamination to which these reservoirs are subjected. For instance, Zhang et al. (2016) reported that the concentration of those elements in the Pontchartrain Lake water samples was highly influenced by the season and the distance from the highways (pollution effect of vehicular traffic). However, the concentrations of Pb and As in the LML were higher than those reported by Cui et al. (2011) for the Yellow River Delta in China, a region designated as a national nature reserve. In addition, the results obtained were compared with the established regulatory level for the protection of the aquatic wildlife in Argentina (AEWQG, 2003), observing that no threshhold was exceeded.

Concentrations of metals, As and Se in sediment were 1000–10,000 times higher than those in water. A number of studies have reported a similar phenomenon (Yi et al., 2011; Monferrán et al., 2011, 2016a, 2016b; Merlo et al., 2011). More than half of the analyzed elements in sediment samples were higher during the WS. There are still some exceptions like Cr, Fe and Zn, that were higher during the DS, and Al, Ni and As, which show no difference in concentrations between sampling seasons. It is worth to mention that when three fractions in separate way were analyzed (A1, A2 or A3), the same pattern is observed, being Ag, Al, Hg, Cd, Cu, Ni, Pb, Se and U (when quantification was possible) higher in WS than in DS (Supplemental material), while Cr, Fe and Zn higher in DS.

Concentrations of Al, Cr, Fe, Ni, As and Hg in the LML sediment were higher than those reported by Monferrán et al. (2016a) in the San Roque Lake in both sampling seasons. This may be due to the fact that the San Roque Lake is a hypertrophic lake with great anthropic pollution (Monferrán et al., 2016a). On the other hand, elements such as Mn, Cu, Ag, Cd and Pb were found in higher concentrations in sediment of the San Roque Lake during the DS, and in higher concentration in the LML during the WS. Concentrations of As, Cu, Pb and Zn were similar to those reported by Zhang et al. (2016) in sediment under the I-10 Bridge in Lake Pontchartrain (United States), but Cu, Zn, Cr, Ni, Cd, and Pb concentrations in the LML sediment were lower than those reported by Tao et al. (2012) in the Lake Taihu, China. It is known that the accumulation or bioavailability of metals in sediment depends on several factors such as pH, organic matter, redox conditions, salinity, oxides and hydroxides concentrations, among others (Nikinmaa, 2014). Looking at Table 2, we can see that, during the WS, the concentration of Al, As, Cu, Mn and Pb in sediment is higher than in the DS, this pattern was also observed in water samples for these same elements. These could indicate that, during the WS, there are physicochemical changes in the LML sediment, which lead to Al, As, Cu, Mn and Pb being more bioavailable, or there is a greater interchange of them between sediment and water, making them more bioavailable to the biota.

The results obtained were compared with those defined by the Canadian Guideline values for the Protection and Management of Aquatic Sediment Quality (Canadian Council of Ministers of the Environment, 2001). None of the element concentrations analyzed in this work exceed the risk levels reported by the legislation mentioned above.

The ecological risk indexes of metal/loids in the LML sediment, considering the DS and WS, were calculated, and are listed in Table 3. According to the risk classification proposed by Hakanson (1980) (Table 1), the ecological risk for the studied sediment is low in both seasons. However, the value for this index was higher during the WS. This is consistent with the fact that most of the elements involved in the index have the highest concentrations during the WS. The potential ecological risk index of a single element (E_r^i) showed that all elements measured exhibited a low ecological risk level. Hg showed a higher value of E_r^i during both seasons studied with respect to the other seven metal/loids measured in the sediment of the LML, mainly due to the high toxicity coefficient of this element.

3.2. Multi-element concentration in biotic samples

The accumulation of inorganic elements in organisms depends on various biotic and abiotic factors, such as the chemical elements and the biological species involved. It may be influenced by sex, age, size, life

Table 2
Concentrations of inorganic elements measured in water (μg L^{-1}), sediments and organisms (μg g^{-1} dry weight-DW) of Los Molinos Lake. Values are expressed as means ± SD. < LOD (below detection limit); < LOQ (below quantification limit). LODs: Cr-water 0,03 μg L^{-1}; Se-water 0,4 μg L^{-1}; Ag-water 0,13 μg L^{-1}; Cd-water 0,13 μg L^{-1}; Hg-water 0,4 μg L^{-1}; Ag-biota 0006 μg g^{-1}; Cd-biota 0,03 μg g^{-1}; U-biota 0,1 μg g^{-1}. LOQs: Ni-water 0,4 μg L^{-1}; Cu-biota 0,15 μg g^{-1}; Se-biota 0,6 μg g^{-1}; Pb-biota 0,03 μg g^{-1}. Different letters indicate statistically significant differences between the wet and dry season (DGC, P < 0.05).

Elements	Season	Water (μg L^{-1})	Sediment (μg g^{-1})	Plankton (μg g^{-1})	*P. argentinus* (μg g^{-1})	*O. bonariensis* (μg g^{-1})
Ag	Dry	< LOD	0.005 ± 0.001 [b]	< LOD	0.04 ± 0.01 [b]	0.12 ± 0.05 [a]
	Wet	< LOD	0.04 ± 0.01 [a]	0.27 ± 0.04 [a]	0.17 ± 0.01 [a]	0.04 ± 0.01 [b]
Al	Dry	10 ± 1 [b]	1375 ± 55 [a]	17,541 ± 1121 [a]	254 ± 50 [a]	3 ± 1 [b]
	Wet	14.4 ± 0.1 [a]	1411 ± 71 [a]	4887 ± 933 [b]	214 ± 24 [a]	4.3 ± 0.4 [a]
As	Dry	0.98 ± 0.05 [b]	1.57 ± 0.04 [a]	6.4 ± 0.5 [b]	7.1 ± 0.4 [b]	2.5 ± 0.4 [b]
	Wet	1.47 ± 0.04 [a]	1.9 ± 0.1 [a]	38 ± 8 [a]	9 ± 1 [a]	4.2 ± 0.8 [a]
Cd	Dry	< LOD	0.0305 ± 0.0001 [b]	0.077 ± 0.003 [a]	0.04 ± 0.01 [b]	< LOD
	Wet	< LOD	0.090 ± 0.001 [a]	0.060 ± 0.001 [b]	0.10 ± 0.01 [a]	< LOD
Cr	Dry	< LOD	2.9 ± 0.1 [a]	20 ± 1 [a]	0.53 ± 0.03 [b]	0.13 ± 0.03 [a]
	Wet	< LOD	2.1 ± 0.1 [b]	10 ± 1 [b]	3.4 ± 0.5 [a]	0.15 ± 0.03 [a]
Cu	Dry	0.048 ± 0.001 [b]	3.73 ± 0.02 [b]	15 ± 1 [a]	86 ± 8 [a]	0.5 ± 0.1 [a]
	Wet	1.3 ± 0.1 [a]	5.6 ± 0.1 [a]	9 ± 1 [b]	35 ± 2 [b]	< LOQ
Fe	Dry	23 ± 2 [b]	3597 ± 56 [a]	19,952 ± 1683 [a]	364 ± 73 [a]	11 ± 2 [b]
	Wet	51 ± 1 [a]	2858 ± 146 [b]	5556 ± 1087 [b]	271 ± 31 [b]	19 ± 3 [a]
Hg	Dry	< LOD	0.04 ± 0.01 [b]	0.12 ± 0.01 [b]	0.39 ± 0.04 [b]	1.7 ± 0.2 [a]
	Wet	< LOD	0.052 ± 0.005 [a]	1.4 ± 0.2 [a]	2.6 ± 0.4 [a]	0.5 ± 0.1 [b]
Mn	Dry	5.0 ± 0.1 [b]	75 ± 1 [b]	846 ± 63 [a]	31 ± 5 [a]	0.8 ± 0.2 [b]
	Wet	13.3 ± 0.2 [a]	165 ± 9 [a]	106 ± 30 [b]	26 ± 2 [a]	2.1 ± 0.5 [a]
Ni	Dry	0.56 ± 0.01 [a]	2.5 ± 0.1 [a]	13 ± 1 [a]	0.45 ± 0.04 [b]	0.18 ± 0.03 [a]
	Wet	< LOQ	2.8 ± 0.1 [a]	4 ± 1 [b]	1.6 ± 0.2 [a]	0.14 ± 0.03 [b]
Pb	Dry	0.05 ± 0.02 [a]	4.2 ± 0.1 [b]	10 ± 1 [a]	0.16 ± 0.03 [b]	0.05 ± 0.01 [a]
	Wet	0.08 ± 0.01 [a]	8.7 ± 0.1 [a]	5 ± 1 [b]	0.7 ± 0.2 [a]	< LOQ
Se	Dry	< LOD	0.81 ± 0.01 [b]	4.0 ± 0.1 [a]	1.9 ± 0.2 [a]	1 ± 0.1 [a]
	Wet	< LOD	1.1 ± 0.1 [a]	< LOQ	< LOQ	0.7 ± 0.1 [b]
U	Dry	0.36 ± 0.02 [a]	0.229 ± 0.005 [b]	1.7 ± 0.1 [a]	< LOD	< LOD
	Wet	0.119 ± 0.006 [b]	0.32 ± 0.01 [a]	< LOD	< LOD	< LOD
Zn	Dry	3.6 ± 0.4 [a]	10.8 ± 0.5 [a]	47 ± 4 [b]	72 ± 7 [b]	21 ± 2 [b]
	Wet	3.9 ± 0.2 [a]	8.8 ± 0.2 [b]	76 ± 16 [a]	172 ± 25 [a]	48 ± 5 [a]

Table 3
Ecological risk index of elements in Los Molinos Lake sediments on different seasons.

Season	E_r^i							RI
	As	Cu	Cd	Cr	Hg	Pb	Zn	
Dry	1.05	0.60	1.83	0.10	3.65	0.84	0.13	**8.2**
Wet	1.25	0.94	5.42	0.07	8.27	1.74	0.11	**17.8**

cycle and history, feeding habits, habitat preferences and water parameters (Heshmati et al., 2017), as well as by previous exposure to contaminants and consumer digestive physiology (Seebaugh and Wallace, 2009). Elements concentrations in the aquatic organisms from the LML (plankton, shrimp and fish) are presented in Table 2. Generally, during the DS, the concentration of the studied elements in plankton was higher than in the WS, with some exceptions (Zn, As, Ag and Hg). The accumulation of metal/oids in plankton depends on two main reasons: on the one hand, it depends on the productivity of the water body, the physiochemical properties of the water, and the quantitative and qualitative metals and metalloids present in environment (Mazej et al., 2010); and on the other, 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. A possible explanation for these results is that changes 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 DS and decreasing in the WS in the LML. This phenomenon can be extrapolated to higher trophic levels that feed on plankton (Monferrán et al., 2016a). During the DS, the highest levels of Al, Cr, Mn, Fe, Ni, Se, Cd, Pb and U were found in plankton in comparison with the accumulated elements in shrimp and fish muscle. Plankton can accumulate metals relatively rapidly from water, even from low concentrations (Mazej et al., 2010). According to the net mesh size used (50 μm), the collected plankton may consist of different varieties of unicellular algae, 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 environment (Monferrán et al., 2016a).

The concentration of most elements in plankton from the LML in the DS was higher than that reported by Monferrán et al. (2016a) in the DS but similar to the WS, both representing a hypertrophic reservoir, with high wastewater contamination. Previous studies have reported inhibition due to sewage effluent addition on plankton communities (Dunstan et al., 1975; Parker et al., 2012). A decrease in species diversity (Cooper and Brush, 1993; Sullivan, 1999) also has been observed in highly eutrophic systems. Therefore, this could be one of the reasons why the concentration of elements in plankton found in the LML is higher in comparison to the San Roque Lake during the DS.

All aquatic invertebrates, like shrimp, take up and accumulate metals and metalloids in their tissues from the surrounding aquatic medium or from food, no matter whether these elements are essential to metabolism or not. Unlike most fish in their feeding habits, shrimp is a scavenger that feeds on a wide range of materials including other bottom-dwelling animals and debris (Canli et al., 2001). In our study, concentrations of inorganic elements in shrimp showed great variability across elements and seasons. During the WS, shrimp had the highest concentration of Cr, Ni, Zn, As, Ag, Cd, Hg and Pb. On the other hand, Fe, Cu and Se were higher in the DS. There was no difference in Al and Mn concentrations between the sampling seasons.

Cu and Zn were presented in higher concentrations in shrimp than in plankton and fish muscle in both seasons. This is due to the fact that invertebrates like shrimp are known to be strong net metal accumulators for Cu and Zn (Cui et al., 2011; Hargreaves et al., 2011), because a certain quantity of each essential metal is required in the shrimp body to meet essential metabolic needs. For instance, Zn has been reported to be an important component of many enzymes including carbonic

Table 4
Bioaccumulation factors (BAFs) for studied elements in Los Molinos Lake. ND: not determined.

	Season	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	U	Zn
Plankton	Dry	ND	1,754,100	6531	592	666,667	312,500	867,478	300	169,200	23,214	200,000	10,000	4722	13,056
	Wet	2077	339,375	25,850	462	333,333	6923	108,941	3500	7970	10000	62,500	ND	ND	19487
P. argentinus	Dry	308	25,400	7245	308	17,667	1,791,667	15,826	975	6200	804	3200	4750	ND	20000
	Wet	1308	14,861	6122	769	113,333	26,923	5314	6500	1955	4000	8750	ND	ND	44103
O. Bonariensis	Dry	923	300	2551	ND	4333	10,417	478	4250	160	321	1000	2500	ND	5833
	Wet	308	299	2857	ND	5000	ND	373	1250	158	350	ND	1750	ND	12308

anhydrase, and Cu is a functional part of the hemocyanin protein 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). These results are similar to those obtained by Monferrán et al. (2016a), who showed that Cu and Zn were the elements most accumulated, in both seasons, by the same invertebrate species (*P. argentinus*).

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 (Monferrán et al., 2016a). 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 by humans.

Concentrations of metals, As and Se in the muscle of silverside (*O. bonariensis*) in the LML are presented in Table 2. Results demonstrate that, Al, Mn, Fe, Zn and As were found in higher concentrations during the WS, while the inverse behavior was observed for Ni, Cu, Se, Ag, Hg and Pb. Similar concentrations of Cr were found in both seasons. Cu and Pb could not be quantified in the fish muscle from this lake in the WS, and Cd and U were not detected in any of the two seasons studied. To our knowledge, our study is the first one that determines the concentration of uranium in fish from this lake, which is important because if this element reaches the human body, it can disrupt the normal functioning of the kidneys, liver, and lungs (Leggett and Pellmar, 2003).

Other studies also reported seasonal variation in the levels of metal accumulation in aquatic organisms (Salem et al., 2014; Jović and Stanković, 2014; Xiaobo et al., 2009). The mean concentration of Cr, Mn, Ni, and Zn in fish muscle found during this study in the WS and DS (0.14 $\mu g\ g^{-1}$, 1.45 $\mu g\ g^{-1}$, 0.16 $\mu g\ g^{-1}$ and 34 $\mu g\ g^{-1}$, respectively) is lower than that reported by Monferrán et al. (2016b), also in muscle of silverside from a hypertrophic reservoir, located 78 km north from the LML (3.1 $\mu g\ g^{-1}$, 3.8 $\mu g\ g^{-1}$, 0.75 $\mu g\ g^{-1}$ and 57 $\mu g\ g^{-1}$, respectively). A possible explanation for this is that the highest Cr, Mn, Ni and Zn concentrations were found in abiotic compartments (water and sediment) from the San Roque reservoir in comparison to those reported in the LML in this study. This means that the higher the metals concentration in abiotic media (exposure concentration), the higher the metals accumulation in biota, taking into account that the environment is one of the routes of exposure of this type of pollutants to the biota. On the other hand, Ag and Hg mean concentrations during both seasons (0.08 $\mu g\ g^{-1}$ and 1.1 $\mu g\ g^{-1}$, respectively) were higher than those reported by Monferrán et al. (2016b), (0.01 $\mu g\ g^{-1}$ and 0.07 $\mu g\ g^{-1}$, respectively). In this case, Ag and Hg concentrations in bioavailable sediment were higher in the LML than in the San Roque reservoir (Monferrán et al., 2016a, 2016b). Silver nanoparticles (AgNPs) are currently one of the nanomaterials most used in nanomedical devices, environmental remediation, cosmetics, homecare products, etc. Estimations indicate that a household could potentially release 470 µg of Ag into the sewage every day, coming from products containing AgNPs (Benn et al., 2010); Ag can accumulate in the aquatic environment like fish (Asharani et al., 2008; Cho et al., 2013; Rajkumar et al., 2016). This could explain the high concentrations of Ag in silverside muscle from the LML compared to other geographical regions (Monferrán et al., 2016a, 2016b; Avigliano et al., 2015).

Selenium (Se) concentration was also determined in silverside muscle from the LML to evaluate the potential impact of Hg on fish, since Se has a high chemical affinity for Hg in biological systems, and can form insoluble complexes, sequestering Hg and neutralizing its toxic effects (Arcagni et al., 2013). Se:Hg molar ratio was determined for fish muscle samples from the LML and the values obtained were 1,6 ± 0,3 (DS) and 4 ± 1 (WS), indicating that there is a molar excess of Se in the tissue, increasing the chance of participating in Hg detoxification (Se:Hg molar ratio˃1). The Se:Hg molar ratio could be an additional criterion, along with measured Hg concentrations, for assessing the risk of mercury exposure from the LML fish on humans.

Summing up, we found higher concentrations of Al, Cr, Mn, Fe, Ni, Se and Pb in plankton in both seasons, while As and Ag were found only in the WS. The highest levels of Cu and Zn were found in invertebrates (shrimp) in both seasons, and Hg in the WS, while Hg and Ag were found in highest concentration in fish muscle in the DS (Table 2). Similar concentrations of As were found in plankton and shrimp in the DS.

The bioaccumulation factor (BAF) indicates if the organism has a potential to accumulate chemicals from the aquatic environment, and it is generally not considered to be significant unless it exceeds 100 (USEPA, 1991). This value may vary, depending on several species-specific traits of the organisms, such as diet/uptake, feeding habit, habitat, body size, gender, metabolic capacity, and trophic levels (Peng et al., 2017). Results of BAF for studied elements and biota are reported in Table 4. To calculate BAF for those elements whose concentration in water was below the detection or quantification limits, LOD or LOQ, reported in Table 2, were used as Cw in the BAF equation. Based on the calculated BAF values, we observe a bioaccumulation of all elements analyzed in plankton samples, as BAFs exceed the 100 value. The same trend is observed for shrimp and fish samples. Assessment of BAF is a vital factor since the concentration of metals in such biota is used not only for the ecological risk assessment but it is required for the characterization of the biota under study as well as its consequent human health assessments (Jayaprakash et al., 2015).

BAFs of plankton were higher than those of shrimp and fish for most studied elements, in both seasons, with some exceptions. This could be due to the higher capability of plankton organisms to uptake inorganic elements directly from water, compared with shrimp and fish that use several uptake mechanisms, in addition to their stronger metabolic capability. In shrimp samples, Cu and Zn BAFs were the highest ones in both seasons, while As was also high in the DS, and Hg and Cd, in the WS. This agrees with the fact that Cu and Zn are essential elements for invertebrates (shrimp), as mentioned above. Fish muscle was characterized by the highest BAF for Ag and Hg in the DS, whereas in the WS, the highest BAF was for Se.

When we evaluated BAFs in plankton, we observed that the majority of the elements shows higher bioaccumulation in the DS, except for Zn, As, Ag and Hg, which present a higher BAF in the WS. In shrimp, the bioaccumulation factor of Cr, Ni, Zn, Ag, Cd, Hg and Pb tends to be higher during the WS; and in fish samples, Cr, Ni, Zn and As showed higher BAF values in the mentioned season.

Current BAF results for Al, Cr, Fe, Ni, Cu and Pb, recorded in the biota of the LML, were higher than the values reported by Monferrán et al. (2016a) and Cui et al. (2011), although both authors reported higher concentrations of these elements in water than those found in the LML. These results might indicate that the studied species present a high level of bioconcentration, which could have a higher environmental impact on the studied aquatic ecosystem.

3.3. Relationships between concentrations of inorganic elements and stable isotope ($\delta^{15}N$) values

Significant differences of stable carbon and nitrogen isotopes values among the different aquatic species in each season were found. $\delta^{15}N$ shows values of 6.1 ± 0.4‰; 10.8 ± 0.1‰ and 13.1 ± 0.4‰, for plankton, shrimp and fish, respectively, during the DS. On the other hand, $\delta^{15}N$ values were 9.5 ± 0.3‰; 10.7 ± 0.2‰ and 14 ± 1‰ for plankton, shrimp and fish, respectively, during the WS. $\delta^{13}C$ values were −18.9 ± 0.1‰; −19.2 ± 0.2‰ and −20.0 ± 0.4‰ for plankton, shrimp and fish, respectively, during the DS, whereas $\delta^{13}C$ values were −19.8 ± 0.1‰; −16.4 ± 0.3‰ and −18.0 ± 0.3‰ for plankton, shrimp and fish, respectively, during the WS.

$\delta^{13}C$ is useful for the identification of 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 $\delta^{13}C$ observed in the biota, during the DS, no statistically significant differences were found in plankton and shrimp, which presented higher values than fish. In the WS, it was observed that the highest values of this isotope were present in shrimp samples. Despite these observed differences, it was demonstrated that *P. argentinus* is considered as part of the diet (carbon source) for *O.bonariensis* (Sagretti and Bistoni, 2001) in the base of the food web. In general, in both seasons, the fish community presented the highest value of $\delta^{15}N$, shrimp had intermediate values, and plankton showed the lowest values of the food web. Considering the values obtained in the studied species and the fact that there is an increase in 3–5‰ of $\delta^{15}N$ per trophic level (Hobson et al., 2002), we suggest a food chain with increasing trophic levels as follows: plankton-shrimp-fish. This is consistent with what is already known about the dietary habits of silverside (Monferrán et al., 2016a).

We evaluated either biomagnification or biodilution of elements through the food web using $\delta^{15}N$ and the log-transformed concentration of metal/loids in biota (Table 5). For that, simple linear regressions were performed, where a significant and positive slope indicates accumulation through the food web (biomagnification), and a negative slope suggests the elimination of elements from the food web, or interrupted trophic transfer (biodilution) (Monferrán et al., 2016a). In the present study, we found no evidence of biomagnification of most of the elements analyzed in the lake. In general, the concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se and Cd in the reservoir food chain studied decreased significantly with increasing $\delta^{15}N$ ‰, in both seasons, showing a trophically dilution behavior in the analyzed food web (Fig. 2A). The biodilution of most of these elements in different food webs has been previously reported (Nfon et al., 2009; Campbell et al., 2005; Asante et al., 2008; Marín-Guirao et al., 2008) suggesting that elements might be partially biodiluted with increased trophic level or might be bioconcentrated by organisms, but they do not biomagnify in food chains. According to Nfon et al. (2009), this may be due to the homeostatic regulation of metal concentrations in organisms by metallothionein and metallothionein-like proteins found in vertebrates and invertebrates, which regulate the uptake, accumulation and excretion rates of these elements in biota, making food chain biomagnification unlikely.

In the particular case of As, previous studies showed that this metalloid is generally not biomagnified through different food chains. Asante et al. (2008) reported that there was no significant correlation between the As concentrations and the $\delta^{15}N$ ‰ values in fish from the East China Sea. Similarly, the concentrations of As in a pelagic Arctic marine food web (invertebrates, fish, birds, and mammals) were not significantly correlated with $\delta^{15}N$ ‰ values (Campbell et al., 2005). In addition, As was not significantly biomagnified through a pelagic food chain (phytoplankton, zooplankton, mysis, and herring) from the Baltic Sea (Nfon et al., 2009), and it did not exhibit any trend with the $\delta^{15}N$ ‰ values in aquatic organisms of the Sundarbans mangrove ecosystem in Bangladesh (Borrell et al., 2016). The decrease in As concentration along trophic levels may be the result of efficiency in eliminating the contaminant (Watanabe et al., 2008). For instance, Mogren et al. (2013) found that Chironomus riparius excretes arsenic to the exoskeleton between the larval and pupal stages, while Schaller et al. (2015) observed that Gammarus pulex accumulates arsenic in the cuticle. If arthropods deposit arsenic in the exoskeleton, subsequent ecdyses will eliminate the arsenic from food webs. If the process is efficient, then arsenic decreases through the food webs, and adults may transport little arsenic when leaving the aquatic environment. However, As was found to be significantly biomagnified in biota (zooplankton and fish) from Suruga Bay, Japan (Sakata et al., 2014) and in fish from the Sulu Sea (Asante et al., 2010).

Table 5
Regression parameters and p-values for $\delta^{15}N$ vs. inorganic element concentration (μg g^{-1} dry weight) in Los Molinos Lake. ND: not determined.

Element	Season	Regression of log [element] versus $\delta^{15}N$			
		Slope	Intercept	R^2	p-value
Ag	Dry	0.17	−3.16	0.66	0.0492
	Wet	−0.16	0.92	0.66	0.0002
Al	Dry	−0.57	8.04	0.94	< 0.0001
	Wet	−0.48	7.33	0.62	0.0002
As	Dry	−0.07	1.4	0.56	< 0.0001
	Wet	−0.12	2.38	0.29	0.0205
Cd	Dry	−0.07	−0.68	0.65	0.0049
	Wet	−0.4	2.9	0.95	< 0.0001
Cr	Dry	−0.31	3.14	0.99	< 0.0001
	Wet	−0.39	4.6	0.8	< 0.0001
Cu	Dry	−0.27	3.64	0.42	0.0011
	Wet	−0.48	6.12	1	< 0.0001
Fe	Dry	−0.48	7.43	0.97	< 0.0001
	Wet	−0.41	6.8	0.6	0.0003
Hg	Dry	0.18	−2.2	0.87	< 0.0001
	Wet	−0.19	2.28	0.91	< 0.0001
Mn	Dry	−0.45	5.92	0.95	< 0.0001
	Wet	−0.32	4.75	0.69	< 0.0001
Ni	Dry	−0.26	2.62	0.97	< 0.0001
	Wet	−0.3	3.3	0.75	< 0.0001
Pb	Dry	−0.32	2.86	0.97	< 0.0001
	Wet	0.69	−6.7	0.95	0.0001
Se	Dry	−0.09	1.19	0.92	< 0.0001
	Wet	ND	ND	ND	ND
U	Dry	ND	ND	ND	ND
	Wet	ND	ND	ND	ND
Zn	Dry	−0.07	2.27	0.4	0.0022
	Wet	−0.12	3.3	0.83	< 0.0001

On the other hand, we observed a significant positive relationship between $\delta^{15}N$ values and log-Hg concentrations during the DS (slope: 0.18, R^2 = 0.87, P-value < 0.0001) (Fig. 2B). It is worth to remark that the regression slope obtained is within the range of values reported for other food webs (with slopes ranging from 0.16 to 0.29) from different geographic locations (Campbell et al., 2003; Kidd et al., 2003; Guo et al., 2016). However, our regression slope was lower than that reported by Monferrán et al. (2016a) (0.36) in the San Roque Lake for the same food web (plankton, shrimp and silverside). A possible explanation for this could be that in the San Roque Lake, Hg concentration was determined in whole fish body, while, in this work, Hg was only determined in the silverside muscle. Arcagni et al. (2017) reported a trend towards biodilution of total Hg in a food web from the Nahuel Huapi Lake (Bariloche-Argentina), which is not consistent with our current

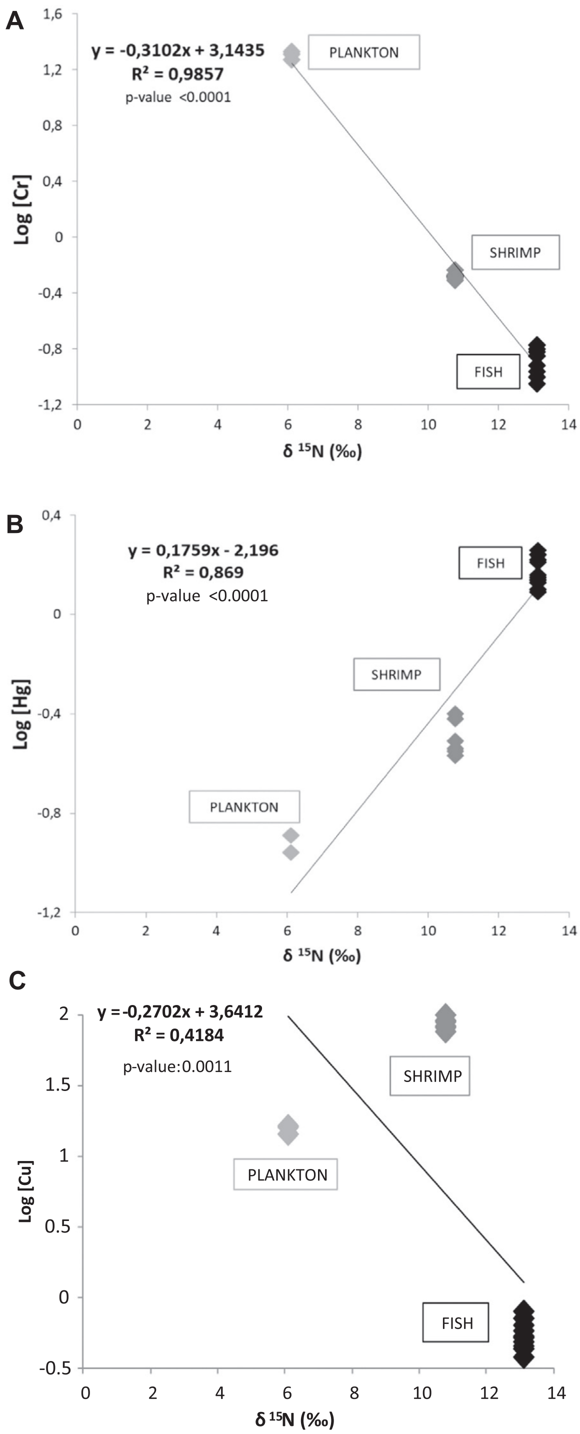

Fig. 2. Relationship between log [trace element concentration, μg g^{-1} dry weight] versus $\delta^{15}N$ for Cr (A); Hg (B) and Pb (C) in the studied food chain. Fig. A indicates an element that is biodiluted throughout the studied food web; Figure B shows an element that is biomagnified throughout the studied food web; Figure C shows an element transference throughout the studied food web.

results during the DS.

The accumulation of Hg through the aquatic food chain is especially problematic and consequently very well-documented (Monferrán et al., 2016a; Ofukany et al., 2014; Nfon et al., 2009). Mercury is classified as a non-essential metal and a highly toxic element that can be released into the global environment through a number of natural or anthropogenic processes. It has been demonstrated in many reports that the trophic transfer, from lower to higher trophic levels, is a predominant way of Hg accumulation in aquatic environments and can reach humans through edible fish. Recently, it was reported that the accumulation of Hg in *Odontesthes bonariensis* is a potential health risk for people who frequently consume these fish species from the LML, thus the consumption should be extremely limited to minimize health problems (Griboff et al., 2017). It is important to note that biomagnification of this element was not observed during the WS, which may be due to the fact that the specimens collected had a smaller size in the WS (18 ± 2) than those collected during the DS (24 ± 1). It is well-known that there exists a positive relationship between fish size/age and Hg concentrations; fish species with large sizes generally have higher levels of Hg accumuladated than those with smaller sizes (Bosch et al., 2016). In addition, positive but not significant slopes were found for Ag (DS) and Pb (WS) (Fig. 2C). It should be noted that Ag was not detected in plankton samples and neither was Pb in fish samples, so the transfer occurs from shrimp to fish and from plankton to shrimp, respectively. No evidence has been found to support biomagnification of Pb in different aquatic food webs (Campbell et al., 2005; Nfon et al., 2009; Sakata et al., 2014; Guo et al., 2016). Although our study did not show biomagnification of Pb (positive slope but, $p = 0.0001$), it is interesting to mention that there is a transfer of this element from plankton to shrimp, but from shrimp to fish Pb is biodiluted since the concentration of Pb was below < LOD in the silverside muscle. Very few studies exist about the trophic transfer of Ag through the trophic chain in the San Roque Lake (Córdoba, Argentina), the Ag level in aquatic organisms showed a significant decrease with increasing $\delta^{15}N$ values (Monferrán et al., 2016a). Although our study did not show biomagnification of Ag (positive slope but, $p = 0.0492$), a transfer of Ag from shrimp to silverside muscle is observed. The general absence of significant relations between elements and $\delta^{15}N$, as well as the lack of clear patterns given by the signs of the slopes of the regression equations, reflect the influence of the diet of organisms. The individuals collected feed on more than one trophic level, despite being progressively enriched with $\delta^{15}N$ with age (as given by length). Furthermore, most elements accumulate in certain organs, such as liver and gills, but are regulated to very low levels in fish muscle (Reinfelder et al., 1998). Besides, some elements are poorly absorbed from the diet or are absorbed from other routes of exposure, such as adsorption over the gills and uptake by way of ingested water (Pereira et al., 2010). Finally, the chemistry of metals, As and Se in food webs is very complex since (1) metals are naturally persistent in the environment, (2) both essential and non-essential metals are naturally bioaccumulated and internally regulated using different strategies (e.g., active excretion, storage) and this strategy changes according to the species studied, and (3) the toxicity of metals is highly influenced by geochemical factors that influence metal bioavailability.

4. Conclusions

The concentration of metals, As and Se in water and sediment samples from the LML did not appear to be exerting toxic effects on the aquatic biota, considering that their levels were below the limits established by the appropriate legislation. Our current results indicate a significant difference in the concentration of some elements within and between studied organisms, being bioaccumulated in all studied organisms, especially in plankton. Mercury showed biomagnification through the different components of the food web in the LML, during the DS, while Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and U showed an overall biodilution pattern. These behaviors, biomagnification or biodilution, can be expected considering the inorganic element handling strategy and the physiological requirements (e.g. sex, reproductive status, age and body condition), of the organisms. Additionally, evaluating elements that are biomagnified through the trophic chain or are present in concentrations higher than those allowed, serves as a guide to identify possible sources of pollution in this lake and with the consequent possibility of its control. These results trigger the need for more exhaustive studies to evaluate the transfer mechanisms through the food web, considering more trophic levels/species, and to have a more complete picture on the transfer of these pollutants during both seasons.

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Conflict of interest

The authors declare that there are no conflicts of interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2017.10.028.

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