Ecotoxicology and Environmental Safety 163 (2018) 492–501

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Assessment of exposure to metals, As and Se in water and sediment of a freshwater reservoir and their bioaccumulation in fish species of different feeding and habitat preferences

Paola L. Garnero[a], Magdalena V. Monferran[b], Germán A. González[a], Julieta Griboff[b], Bistoni María de los Ángeles[a,*]

[a] IDEA – Instituto de Diversidad y Ecología Animal (CONICET) and Facultad de Ciencias Exactas Físicas y Naturales, Universidad Nacional de Córdoba, Av. Vélez Sarsfield 299 (X5000JJC), Córdoba, Argentina

[b] ICYTAC – Instituto de Ciencia y Tecnología de Alimentos Córdoba (CONICET) and Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Bv. Dr. Juan Filloy s/n, Ciudad Universitaria, 5000 Córdoba, Argentina

ARTICLE INFO

Keywords:
Multi-element
Río Tercero Reservoir
Abiotic matrices
Ichthyofauna
Feeding

ABSTRACT

The concentrations of metals (Ag, Al, Ba, B, Be, Bi, Cd, Co, Cr, Cu, Fe, Ga, Hg, Li, Mn, Mo, Ni, Pb, Rb, Sr, Tl, U, V, Zn), As and Se were analyzed in water and sediments from three sites of Río Tercero Reservoir (Córdoba, Argentina) during the wet and the dry season. The dynamics of metals in six fish species (*Hoplias malabaricus, Oligosarcus jenynsii, Rhamdia quelen, Bryconamericus iheringii, Astyanax fasciatus* and *Odontesthes bonariensis)* from the reservoir were investigated to discover the possible differential influence of habitat and diet on metal accumulation in the fish. In the abiotic matrix, the highest heavy metal concentrations were observed in sediment. The concentrations of Al, Cu and Pb in water exceeded the limits considered as hazardous for aquatic life. Potential ecological risk analysis of metal concentrations in sediment indicated a low ecological risk in Río Tercero Reservoir in all sampling periods. The enrichment factor indicated that Cu, Pb, Zn and Hg come from anthropogenic sources. Among five different organs, the highest metal levels were found in gills and intestine. *Rhamdia quelen* and *Oligosarcus jenynsii* were the species with the highest values of metal accumulation in the whole body. Our study showed that the accumulation pattern of these multi-elements in the different fish species did not respond to diet or habitat, but seemed to be related to the detoxification mechanisms and the metabolism of each organism.

1. Introduction

The steady increase in metals concentrations in the environment from anthropogenic activities means that they have become main pollutants (Orozco Barrenetxea et al., 2003; Newman and Unger, 2002). Low concentrations of some metallic elements are essential for organisms, but others can be available in the environment without any associated biological activity, and the heavy metals are the most well-known of these. The highest levels of metals in the environment have been recorded in areas with a high density of human settlement and of industrial and agricultural activities (Tao et al., 2012). These elements persist in the environment because they are not degraded and can be bioaccumulated in organisms, and some of them are highly toxic (Ye et al., 2011).

The metals enter water bodies and are adsorbed by sediments, which are an excellent trap and sink for heavy metals in the aquatic environment (Shafie et al., 2014; Praveena et al., 2012; Luoma and Bryan, 1981). The ability of sediments to adsorb organic and inorganic contaminants makes sediment analysis a valuable tool to assess and monitor water quality. However, when disturbed or when the physical-chemical conditions are altered, the contaminants may be released into the water column causing a potential threat to ecosystems (Shafie et al., 2014). They may also provide a habitat and food source for benthic fauna. Contaminants present in this matrix may thus be directly or indirectly toxic to aquatic organisms (Yi et al., 2011).

Aquatic organisms have been reported to have higher concentrations of metals in their tissues than the levels in the surrounding environment (water and sediment) (Malik et al., 2010). Fish are suitable bioindicators for metal pollution because they occupy a range of trophic levels and they have a known ability to concentrate pollutants (e.g.

* Corresponding author.
E-mail address: mbistoni@unc.edu.ar (B.M. de los Ángeles).

https://doi.org/10.1016/j.ecoenv.2018.07.023
Received 30 March 2018; Received in revised form 22 June 2018; Accepted 5 July 2018

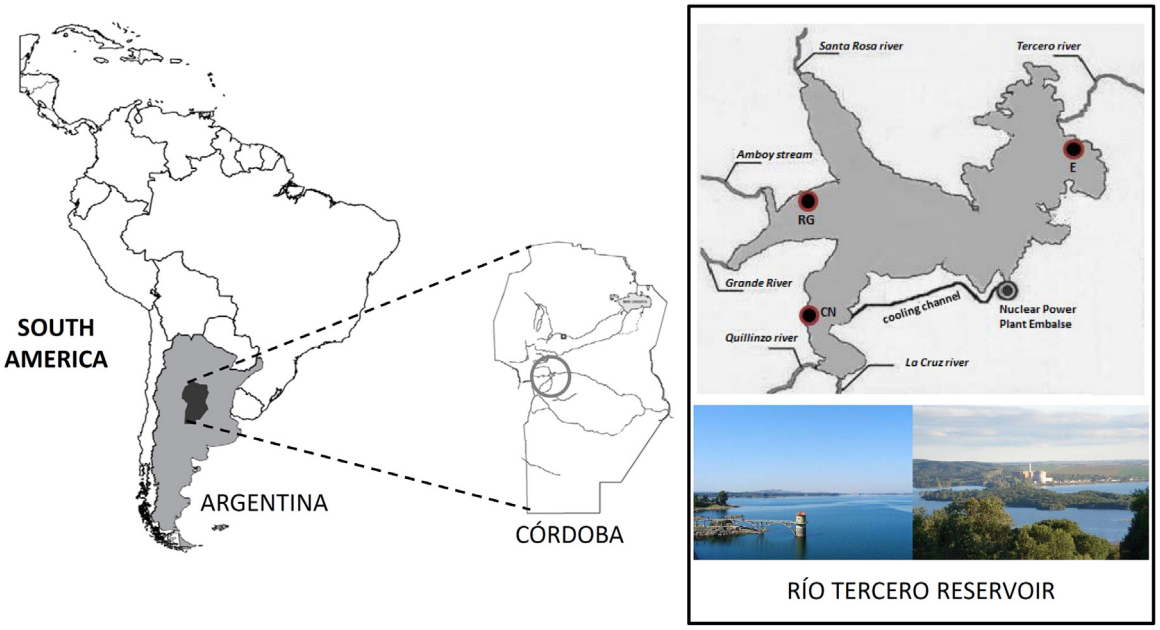

Fig. 1. Map of the Province of Córdoba, Argentina with their study areas. Río Grande (RG), Embalse (E) and Central Nuclear (CN).

pesticides, biphenyls, heavy metals) (Monroy et al., 2014; Agarwal et al., 2007; Manirakiza et al., 2002). Heavy metal concentration in fish tissues reflects past or present exposure (Henry et al., 2004). Thus, in addition to chemical analysis, monitoring contamination through fish tissues helps to assess the quality of aquatic ecosystems (Monferran et al., 2016; Weber et al., 2013).

Bioaccumulation of metals in fish occurs mainly through water and food, involving dietary routes (digestive tract) and non-dietary routes (skin and gills) (Oost et al., 2003). The degree of metal accumulation depends on the pollutant type, the species, their eating habits and trophic level in the food chain, as well as on physical and chemical characteristics of the system (Weber et al., 2013; Oost et al., 2003; Farkas et al., 2002). The top predator fish (upper food web position) are prone to accumulate more metals than species at a lower trophic level, because they are exposed to comparatively greater contamination due to magnification through the trophic chain (Has-Schön et al., 2006; Peakall and Burger, 2003; Al-Yousuf et al., 2000). Aversely, Yousafzai et al. (2010) showed that omnivorous fishes accumulated more metals than carnivorous fishes and Weber et al. (2013) found that higher metal accumulation occurred in detritivorous species than in carnivorous species.

Another factor that may be involved in metal accumulation in the organism is the habitat of the fish. Several studies have suggested that metal concentration is higher in species living close to the sediment than in those living in free waters (Monroy et al., 2014; Kojadinovic et al., 2007; Mason et al., 2000). However, other authors suggest that the processes by which metals accumulate in the tissues and organs of living organisms are species-dependent and are related more to mechanisms of detoxification and metabolism (Jakimska et al., 2011) than to food or habitat.

In the province of Córdoba, Argentina, several studies have found high heavy metal levels in air and soil (Bermudez et al., 2012, 2010; Carreras and Pignata, 2002; Pignata et al., 2002), with human, agricultural and industrial activities as significant sources of metals. Río Tercero Reservoir (RTR), the largest artificial water body in the province, is used for hydroelectricity, irrigation and drinking water, supplying the local inhabitants. Many sources near the lake can affect the quality of the water: it has the only nuclear power plant in the province, human settlements, agricultural crops and tourist sites on its margins. It provides various suitable habitats and different diets for many fish species, some of which are used for sport fishing and are consumed by local people (Mariazzi et al., 1992).

There are some limnological studies of the RTR (Mariñelarena et al., 2014; Mariazzi et al., 1992), and a population study of the fish *Odontesthes bonariensis* (Mancini and Grosman, 1998), but there is no information about metals in the water and sediments, or on the accumulation of metals in the organs of fish. In recent years, there has been an increase in fields cultivated around the reservoir and a greater influx of tourists in the area (Ledesma et al., 2013); therefore, joint studies are needed on abiotic and biotic elements to characterize the degree of contamination of the reservoir and the dynamics of the contaminants in the fish that inhabit it.

The aim of this study was to determine the concentration of metals in the water and sediments of the RTR and to investigate the dynamics of metals in fish species from the reservoir, to understand whether the habitat and diet determine differential metal accumulation.

Six fish species in RTR were studied: *Hoplias malabaricus*, an ichthyophagous, top predator fish, of quiet vegetated waters; *Oligosarcus jenynsii,* a carnivore which uses the water column; *Rhamdia quelen*, an omnivore, closely related to the substrate and benthopelagic in its natural habitat; *Bryconamericus iheringii* and *Astyanax fasciatus*, omnivores of quiet vegetated waters; and *Odontesthes bonariensis*, a planktophage, which feeds in free water (Haro and Bistoni, 2007).

We tested the hypothesis that the top predator is prone to accumulate metals due to the biomagnification of these elements along the trophic chain and that the bottom level fish accumulate more metals because they are in direct contact with the sediment.

2. Materials and methods

2.1. Study area

The RTR is in the Calamuchita valley of the Province of Córdoba, Argentina (32°11′S, 64°25′W) (Fig. 1), with a surface area of 46 km^2, an average depth of 12 m, a maximum depth of 46 m and a volume of 560 hm^3. The hydrological regime is pluvial, with a single maximum period of rainfall (from October to March), and a single minimum period (from April to September). The mean annual rainfall is about 630 mm. The RTR is multipurpose, used for hydroelectricity, drinking water and irrigation (Mariazzi et al., 1992).

2.2. Sample collection and metals analysis

Two sampling campaigns were carried out in the RTR, one in the dry season (July 2014; winter) and the other in the wet season (March 2015; summer). Three sampling sites with different contamination sources were selected (Fig. 1): Río Grande (RG), surrounded by crops, mainly soybeans; Embalse (E), a tourist area with human settlements; and Central Nuclear (CN), an area near the water cooling channel of the Embalse Nuclear Plant and agricultural practices.

At each sampling station, water temperature, pH, dissolved oxygen and conductivity were measured in situ using multiparametric equipment (WTW Multiline F/Set 3). Water samples were collected in acid washed plastic bottles (n = 6), acidified with ultrapure HNO3, and stored at 4 °C until analysis. Prior to measurement, samples were filtered using 0.45 mm nitrocellulose filters.

The sediments were collected using a plastic shovel (n = 6) to take the first 0–15 cm depth, and placed in clean plastic bags. They were dried at room temperature and sieved through 63 µm acrylic meshes. The sediment was digested following the method developed by Maiz et al. (1997). 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 mobilizable 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. Based on this, the pseudototal sediment was analyzed, which consisted of the sum of the three fractions ($A_1 + A_2 + A_3$), and also the sediment corresponding to the movable fractions ($A_1 + A_2$), which was named the bioavailable fraction. All samples were stored at 4 °C until analysis.

Rod fishing and trawling were used to collect the fish, simultaneously with water and sediment samples. The following species of fish were weighed and measured (standard length): *Hoplias malabaricus* (n = 7, average length: 22.8 ± 9.9 cm, average weight: 220.0 ± 103.3 g); *Oligosarcus jenynsii* (n = 27, average length: 11.3 ± 3.3 cm, average weight: 26.6 ± 24.0 g); *Rhamdia quelen* (n = 12, average length: 24.1 ± 5.3 cm, average weight: 285.4 ± 195.9 g); *Bryconamericus iheringii* (n = 19, average length: 7.8 ± 1.7 cm, average weight: 7.3 ± 5.4 g); *Astyanax fasciatus* (n = 5, average length: 9.5 ± 2.7 cm, average weight: 16.6 ± 9.5 g) and *Odontesthes bonariensis* (n = 23, average length: 18.5 ± 5.7 cm, average weight: 91.7 ± 90.9 g). At the laboratory, the fish were dissected to obtain gills, liver, intestine, brain, and muscle. Biological samples were dried at 40 °C to constant weight and homogenized with a mortar. For the measurement of inorganic elements, about 25 mg for each organ 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, for 12 h. All samples were stored at 4 °C until analysis.

The metals Ag, Al, Ba, B, Be, Bi, Cd, Co, Cr, Cu, Fe, Ga, Hg, Li, Mn, Mo, Ni, Pb, Rb, Sr, Tl, U, V, Zn, and As and Se were analyzed in water and sediment. Only the elements with neurotoxic, hepatotoxic or gastrotoxic action (Hg, As, Pb, Al, Ni, Cd, Sr and Se) were measured in the organs of the different species of fish (Repetto and Repetto, 2000).

Before the analysis, all samples were diluted with 2% v/v sub-boiled nitric acid. In both abiotic and biotic samples, the analysis of the metals As and Se was performed with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS), X Series, Thermo-Elemental X7 (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. Quality assurance (QA) and quality control (QC) were performed using certified reference material (CRMs): NIST 1643e (Freshwater). The recoveries of the reference samples for tested elements are shown in Table S.1 (Supplementary material). Spiked samples were also prepared. Variable amounts of mixed standard solutions, containing all elements analyzed, were added to 0.02 g of fish samples (dried gills, intestine, liver, muscle and brain), prior to sample digestion. The rest of the procedure was the same as used for non-spiked samples. The average recoveries were 83.5 ± 19.2%, 94.7 ± 17.4%, 88.1 ± 10.4%, 103.9 ± 11.6% and 104.1 ± 17.6%, respectively.

2.4. Enrichment factor in sediments

Enrichment factor (EF) indicates the dynamics of an inorganic pollutant or chemical element of the earth's crust that can be transported by rain, wind, or anthropogenic sources. In the present study, EF was used to deduce the origin (natural or anthropogenic) of the metals in the sediment of the RTR.

The EF is defined following the equation (Loska et al., 1997):

$$EF = (M/X)sample/(M/X)background$$

where: *(M/X) sample* is the ratio of metal and reference element (X) concentrations of the sample, and *(M/X) background* is the ratio of metal and reference element (X) concentrations of a background.

The reference elements are assumed to have little variability of occurrence, and they are present in trace concentrations in the environment examined.

According to Zhang and Liu (2002), EF values lower than 1.5 indicate that the metal comes entirely from crustal materials or natural processes, whereas EF values greater than 1.5 suggest that the sources are probably of anthropogenic origin.

The EF for each of the elements was calculated only in the pseudototal sediments. The EF was based, on the one hand, on the background values of the metals taken from a river tributary of RTR with pseudo-pristine characteristics (Río Grande) (Harguinteguy et al., 2016) and, on the other, on the values of the upper continental crust (Rundnick and Gao, 2003). The reference elements were Mn and Cd, which were selected due to their low occurrence variability at the study sites.

2.5. Potential ecological risk assessment

The potential ecological risk index (R_I) was determined to assess the degree of heavy metal pollution in the sediments, according to the toxicity of metal pollution and the response of the environment. Potential ecological risk was calculated according to Håkanson (1980):

$$R_I = \Sigma E_r^i$$

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

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

The risk factor R_I proposed by Håkanson (1980) is based on eight parameters (PCB, Hg, Cd, As, Pb, Cu, Cr and Zn) measured in sediment. To calculate the ecological risk in the **RTR**, R_I was calculated as the sum of all the risk factors for metals measured in sediment, excluding PCB because this was not measured during this work. E_r^i is the monomial potential ecological risk factor, and T_r^i the toxic-response factor for a given substance, which accounts for the toxic and sensitivity requirements. The values of T_r^i for Hg, Cd, As, Cu, Pb, Cr, and Zn were 40, 30, 10, 5, 5, 2, and 1, respectively (Hilton et al., 1985). C_f^i is the contamination factor, C_o^i the concentration of metal in the sediment of the RTR, and C_n^i is the background value of the heavy metal in coastal sediments. The values of C_n^i for Hg, Cd, As, Cu, Pb, Cr, and Zn were 0.2, 0.5, 15, 30, 25, 60 and 80, respectively (Li and Zheng, 1988). The potential ecological risk indices E_r^i and R_I were calculated for both sediments (pseudototal and bioavailable).

Depending on the values obtained of E^ir and R_I, the risk is classified in different categories: Low ($E_r^i < 40$), Moderate ($40 \leq E_r^i < 80$),

Considerable ($80 \leq E_r^i < 160$), High ($160 \leq E_r^i < 320$), Very high ($E_r^i \geq 320$) and Low-grade ($R_I < 95$), Moderate ($95 \leq R_I < 190$), Considerable ($190 \leq R_I < 380$), Very high ($R_I \geq 380$).

2.6. Statistical analysis

The concentration of the elements in water and sediment was analyzed by means of the Fisher-Pitman permutation test, which is a robust alternative for cases where the assumptions of normality and homoscedasticity are not met (Neuhäuser and Manly, 2004; Boik, 1987).

To know whether the habitat and feeding influence metal accumulation in the species, the metals in the fish were analyzed regardless of the sampling site. Because there were differences in the metal concentration only in water between sites and seasons, the Bioaccumulation Factor (BAF) was used, to standardize the variability contributed by the capture site and thus be able to compare the levels of metal accumulation among all the species collected. The BAF values are calculated as the ratio between the element concentration in organisms at steady state ($\mu g\, g^{-1}$, dry weight) and the element concentration in water ($\mu g\, mL^{-1}$) (Authman and Abbas, 2007). The measurements taken in each fish were thus divided by the measurement in water corresponding to the site where the fish was captured. Values below the limit of detection (LOD) were estimated as LOD/√2, as recommended by Verbovsek (2011), and the same criterion was applied for the limit of quantification (LOQ). Metals with more than 40% of observations below the limit were discarded from subsequent analyses.

BAF values were logarithmically transformed to meet the assumptions of normality and homogeneity of variance. Mixed linear models and Tukey's HSD were used to analyze the accumulation of each metal per organ per species, the total metal accumulation between organs of the same species and the total metal accumulation between species. Individual fish were considered as a random factor to correct repeated measures. All analyses were performed in R 3.3.1 (R Core Team, 2016). The influence of fish body length (measured in mm) and sex on metal accumulation was tested using the models described above. No significant effect was found ($F = 3.61$, p-value = 0.061).

3. Results and discussion

3.1. Physico-chemical parameters in water samples

Seasonal variations of the physico-chemical water parameters were not registered at all sites and seasons. Only the highest temperature values for all sites were recorded in the wet season, which is the summer season (Table S.2).

3.2. Element concentrations in water and sediments

There were no significant differences among sites in element concentrations in water in the dry season. In the wet season, the highest concentrations for most metals (Li, Al, V, Cr, Mn, Fe, Co, Ga, Rb, Sr, Ba and U) were at the CN site (Table 1). The main disturbances at this site are the nuclear plant and agricultural activities. Elements probably enter the reservoir from the nuclear power station, but further studies are needed to confirm the exact sources. Agricultural practices are known to be a main source of metals through impurities from fertilizers and pesticides (Weber et al., 2013) and these agrochemicals have been identified as potential sources of heavy metals in air and soil in Córdoba province (Pignata et al., 2002). High concentrations of heavy metals have been found in agricultural soils of other basins of the province (Harguinteguy et al., 2013; Bermudez et al., 2012). There are also crops at the RG site but the concentration of metals there is lower than at CN. More metals may enter the aquatic environment at CN by the increased runoff velocity due to the greater slope at CN (2.25%) than at RG (1.16%) (González del Tánago del Río and García de Jalón Lastra, 1998).

The comparison between seasons of metal/As/Se concentrations in the water showed the highest concentrations in the wet season at RG and CN, but no significant differences between seasons at E (Table S.3). Since RG and CN are surrounded by crops to which pesticides are applied in the wet season, these contaminants may enter the aquatic system by air as a result of spraying, or by precipitation, or by runoff from the fields (Ballesteros et al., 2014).

Only three of the metals measured in water exceeded the limits considered by the different regulatory agencies as hazardous for aquatic life. During the dry season, Pb (Site RG) exceeded the limit of $1.59\ \mu g\, L^{-1}$ established by the Argentine Environmental Water Quality Guidelines (Argentinean Environmental Water Quality Guidelines AEWQG Niveles Guía Nacionales de Calidad de Agua Ambiente, 2003), and Cu (Site RG), the limit values of $4.1\ \mu g\, L^{-1}$ established by the Canadian Water Quality Guidelines (Canadian Council of Ministers of the Environment, 2002). In the wet season, Al (site CN) exceeded the limits of $100\ \mu g\, L^{-1}$ and $87\ \mu g\, L^{-1}$ established by Canadian Water Quality Guidelines and the US Environmental Quality Guidelines (USEPA (US Environmental Protection Agency), 2009), respectively.

We compared the highest concentrations of elements recorded in our study (at site CN – wet season) with those in two large lakes in the province of Córdoba (Los Molinos Lake and San Roque Lake) that are characterized by pollution sources similar to those of our study site: agriculture and an important urban development in the lakeshore area, as well as tourism growth (Griboff et al., 2017). Except for Pb, Zn and Cu, the concentrations of Al, As, Fe, Mn and U were higher in the RTR than in the Los Molinos Lake (Griboff et al., 2018). Compared with those of San Roque Lake, concentrations of Al, As, Fe, Mn, Cr and Sr were also higher in the RTR, while Cd, Cu, Mo, Ni, Pb and Zn were lower than those recorded for San Roque. Hg was not detected in water samples from any of the water bodies.

As expected, the concentrations of most of the elements in sediment were higher than those in water. Elements tend to be adsorbed in sediments as they are poorly soluble in water (Weber et al., 2013; Jakimska et al., 2011; Yi et al., 2011).

In contrast to the pseudototal sediments, the concentrations of most of the elements measured in the bioavailable fraction were below the LOD (detection limit), both in the dry season and in the wet season. There were no significant differences between sites in concentrations of elements in sediment (pseudototal and bioavailable) for either hydrological season. Similarly, there were no significant differences between hydrological seasons from the same site (Table S.3). Similar values were observed in RTR as in Los Molinos Lake (Griboff et al., 2018), except for Pb, Hg and U, which showed higher concentrations in the RTR. In contrast, in San Roque Lake most of the values were lower than in RTR (Monferran et al., 2016). San Roque Lake, however, is a hypertrophic lake with sewage pollution (Griboff et al., 2018), while RTR and Los Molinos Lake are surrounded by crops, and thus the higher concentrations observed in these lakes appear to be influenced by the contribution of agricultural practices.

Our study indicated a low degree of ecological risk from the metals present in both sediments (Table 2). The potential monomial ecological risk index of a single element (E^ir) show that all elements measured exhibited a low ecological risk level.

EF showed that Cu, Pb and Zn come from anthropogenic sources compared with the concentration registered in a pseudo-pristine river (Fig. 2(A)), while Fe, Co and Ni are contributed by the materials of the crust and natural processes. When compared with the upper continental crust, only Hg greatly exceeds the value of 1.5, showing its entry to the reservoir from anthropogenic sources (Fig. 2(B)).

Hg and Pb are emitted into the atmosphere and can travel thousands of kilometers, since they have the capacity to join suspended particles in the air and finally be deposited by rains in aquatic and terrestrial ecosystems (Gioia et al., 2017; Wang et al., 2012). Consequently, many aquatic systems that have never received direct discharges of Hg may register high levels of these metals. On the other hand, Cu and Zn are

Table 1
Concentrations of metals As and Se measured in water (μg L^{-1}) and sediments (μg g^{-1}) of Río Tercero Reservoir. Values are expressed as means ± SD. < LOD: below detection limit. LOD_S water (μg L^{-1}): Ag 0.04; Al 6.91; As 0.51; B 15.02; Be 0.04; Bi 0.07; Cd 0.01; Co 0.04; Cr 0.12; Cu 0.47; Fe 7.81; Ga 0.08; Hg 0.02; Li 0.11; Mo 0.11; Ni 0.31; Pb 0.04; Rb 0.04; Se 0.94; Tl 0.32; Zn 1.59. LOD_S sediment (μg g^{-1}): Ag 0.003; Al 0.631; As 0.046; B 1.371; Be 0.003; Bi 0.007; Co 0.003; Cr 0.011; Hg 0.002; Mo 0.010; Pb 0.004; Rb 0.003; Se 0.086; Tl 0.029; U 0.013; V 0.008; Zn 0.145. Different letters indicate statistically significant differences between the sites for each hydrological season ($P < 0.05$).

Elements	*Sites*	*Season*											
		Dry ***Water***		**Wet**		**Dry** ***S. Bioavailable***		**Wet**		**Dry** ***S. Seudototal***		**Wet**	
Ag	*CN*	< LOD		< LOD		< LOD		< LOD		0.05 ± 0.01	**a**	0.02 ± 0.01	**a**
	Em	< LOD		< LOD		< LOD		< LOD		0.11 ± 0.03	**a**	0.02 ± 0.01	**a**
	RG	< LOD		< LOD		< LOD		< LOD		0.02 ± 0.01	**a**	0.01 ± 0.01	**a**
Al	*CN*	< LOD		800 ± 8	**a**	< LOD	**a**	< LOD		1346 ± 198	**a**	124 ± 79	**a**
	Em	< LOD		< LOD		< LOD	**a**	< LOD		1600 ± 317	**a**	138 ± 56	**a**
	RG	< LOD		< LOD		11 ± 0.04	**a**	< LOD		1361 ± 191	**a**	219 ± 2	**a**
As	*CN*	< LOD		3.85 ± 0.01	**a**	< LOD		< LOD		1.86 ± 0.32	**a**	< LOD	
	Em	< LOD		3.67 ± 0.05	**b**	< LOD		< LOD		1.33 ± 0.46	**a**	< LOD	
	RG	< LOD		3.72 ± 0.17	**ab**	< LOD		< LOD		0.24 ± 0.02	**a**	< LOD	
Ba	*CN*	15.9 ± 0.2	**a**	31.9 ± 0.4	**a**	2.07 ± 0.09	**a**	4.21 ± 0.02	**a**	55 ± 12	**a**	31 ± 6	**a**
	Em	15.2 ± 1.5	**a**	13.6 ± 0.1	**b**	5.56 ± 0.95	**a**	2.20 ± 0.10	**a**	75 ± 1	**a**	35 ± 12	**a**
	RG	6.7 ± 1.0	**a**	12.5 ± 0.1	**c**	4.45 ± 0.01	**a**	3.81 ± 0.05	**a**	33 ± 1	**a**	33 ± 2	**a**
B	*CN*	< LOD		< LOD		< LOD		< LOD		< LOD		< LOD	
	Em	< LOD		< LOD		< LOD		< LOD		< LOD		< LOD	
	RG	< LOD		< LOD		< LOD		< LOD		< LOD		< LOD	
Be	*CN*	< LOD		< LOD		< LOD		< LOD		0.08 ± 0.01	**a**	0.02 ± 0.02	**a**
	Em	< LOD		< LOD		< LOD		< LOD		0.10 ± 0.03	**a**	< LOD	
	RG	< LOD		< LOD		< LOD		< LOD		0.08 ± 0.01	**a**	0.01 ± 0.02	**a**
Bi	*CN*	< LOD		< LOD		< LOD		1.1 ± 0.2	**a**	0.13 ± 0.01	**a**	0.04 ± 0.03	**a**
	Em	< LOD		< LOD		< LOD		< LOD	**a**	< LOD		0.04 ± 0.02	**a**
	RG	< LOD		< LOD		< LOD		< LOD	**a**	< LOD		< LOD	
Cd	*CN*	< LOD		< LOD		0.02 ± 0.01	**a**	0.03 ± 0.01	**a**	0.06 ± 0.01	**a**	0.05 ± 0.01	**a**
	Em	< LOD		< LOD		0.03 ± 0.01	**a**	0.03 ± 0.01	**a**	0.08 ± 0.08	**a**	0.06 ± 0.01	**a**
	RG	0.04 ± 0.05	**a**	< LOD		0.02 ± 0.01	**a**	0.02 ± 0.01	**a**	0.04 ± 0.01	**a**	0.02 ± 0.01	**a**
Co	*CN*	< LOD		0.77 ± 0.01	**a**	< LOD	**a**	0.04 ± 0.01	**a**	1.3 ± 0.2	**a**	0.14 ± 0.06	**a**
	Em	< LOD		< LOD		0.15 ± 0.01	**a**	0.05 ± 0.01	**a**	2.2 ± 0.5	**a**	0.27 ± 0.10	**a**
	RG	< LOD		< LOD		0.03 ± 0.01	**a**	0.03 ± 0.01	**a**	0.9 ± 0.1	**a**	0.21 ± 0.01	**a**
Cr	*CN*	< LOD		1.03 ± 0.04	**a**	< LOD		< LOD		2.1 ± 0.3	**a**	0.13 ± 0.08	**a**
	Em	< LOD		< LOD		< LOD		< LOD		4.2 ± 0.9	**a**	0.47 ± 0.20	**a**
	RG	< LOD		0.29 ± 0.51	**b**	< LOD		< LOD		2.5 ± 0.5	**a**	0.47 ± 0.01	**a**
Cu	*CN*	< LOD		< LOD		3.1 ± 0.2	**a**	0.17 ± 0.02	**a**	6.9 ± 0.4	**a**	0.48 ± 0.18	**a**
	Em	< LOD		< LOD		2.1 ± 0.2	**a**	2.47 ± 0.35	**a**	11.2 ± 3.3	**a**	3.40 ± 0.74	**a**
	RG	10 ± 9	**a**	< LOD		0.4 ± 0.1	**a**	0.14 ± 0.01	**a**	3.8 ± 0.4	**a**	0.61 ± 0.01	**a**
Fe	*CN*	< LOD		680 ± 3	**a**	11.5 ± 0.2	**a**	9.3 ± 1.6	**a**	3027 ± 459	**a**	203 ± 111	**a**
	Em	< LOD		< LOD		22.7 ± 1.8	**a**	29.9 ± 4.3	**a**	3361 ± 803	**a**	466 ± 130	**a**
	RG	< LOD		170 ± 4	**b**	57.1 ± 9.9	**a**	13.2 ± 0.2	**a**	2134 ± 339	**a**	411 ± 4	**a**
Ga	*CN*	< LOD		3.09 ± 0.03	**a**	0.16 ± 0.01	**a**	0.31 ± 0.01	**a**	2.3 ± 0.4	**a**	0.66 ± 0.19	**a**
	Em	< LOD		1.46 ± 0.03	**b**	0.43 ± 0.07	**a**	0.19 ± 0.02	**a**	4.5 ± 1.4	**a**	0.53 ± 0.16	**a**
	RG	< LOD		1.40 ± 0.01	**b**	0.36 ± 0.02	**a**	0.30 ± 0.01	**a**	2.4 ± 0.2	**a**	0.77 ± 0.01	**a**
Hg	*CN*	< LOD		< LOD		< LOD		< LOD		0.86 ± 0.11	**a**	0.05 ± 0.05	**a**
	Em	< LOD		< LOD		< LOD		< LOD		1.98 ± 2.55	**a**	0.06 ± 0.01	**a**
	RG	< LOD		< LOD		< LOD		< LOD		0.03 ± 0.02	**a**	0.09 ± 0.06	**a**
Li	*CN*	1.0 ± 1.0	**a**	1.62 ± 0.02	**a**	0.05 ± 0.01	**a**	0.04 ± 0.05	**a**	1.5 ± 0.2	**a**	0.21 ± 0.08	**a**
	Em	1.5 ± 0.1	**a**	< LOD		0.04 ± 0.01	**a**	0.01 ± 0.01	**a**	1.3 ± 0.2	**a**	0.26 ± 0.10	**a**
	RG	0.6 ± 0.1	**a**	< LOD		0.16 ± 0.01	**a**	0.06 ± 0.01	**a**	1.2 ± 0.2	**a**	0.35 ± 0.01	**a**
Mn	*CN*	11 ± 2	**a**	72.1 ± 0.1	**a**	3.7 ± 0.1	**a**	12.34 ± 0.66	**a**	74.4 ± 11.3	**a**	16.4 ± 2.7	**a**
	Em	7 ± 3	**a**	12.8 ± 0.2	**b**	7.6 ± 0.3	**a**	2.79 ± 0.43	**a**	70.2 ± 17.6	**a**	8.5 ± 2.9	**a**
	RG	9 ± 3	**a**	37.1 ± 0.4	**c**	7.4 ± 0.2	**a**	5.35 ± 0.01	**a**	29.2 ± 1.1	**a**	9.4 ± 0.1	**a**
Mo	*CN*	< LOD		< LOD		< LOD		< LOD		< LOD		0.09 ± 0.02	**a**
	Em	< LOD		< LOD		< LOD		< LOD		< LOD		0.11 ± 0.04	**a**
	RG	< LOD		< LOD		< LOD		< LOD		< LOD		0.10 ± 0.01	**a**
Ni	*CN*	< LOD		< LOD		0.11 ± 0.01	**a**	0.05 ± 0.01	**a**	2.0 ± 0.3	**a**	0.18 ± 0.09	**a**
	Em	< LOD		< LOD		0.22 ± 0.02	**a**	0.17 ± 0.03	**a**	5.1 ± 1.0	**a**	0.85 ± 0.29	**a**
	RG	0.6 ± 0.6	**a**	< LOD		0.10 ± 0.03	**a**	0.04 ± 0.01	**a**	2.3 ± 0.4	**a**	0.36 ± 0.01	**a**
Pb	*CN*	< LOD		< LOD		1.02 ± 0.03	**a**	< LOD	**a**	6.1 ± 1.2	**a**	3.06 ± 0.02	**a**
	Em	0.5 ± 0.6	**a**	< LOD		4.92 ± 0.28	**a**	7.14 ± 0.35	**a**	21.4 ± 0.5	**a**	20.16 ± 5.54	**a**
	RG	2.0 ± 2.8	**a**	< LOD		0.17 ± 0.01	**a**	0.35 ± 0.01	**a**	2.2 ± 0.8	**a**	2.34 ± 0.19	**a**
Rb	*CN*	< LOD		3.25 ± 0.04	**a**	0.06 ± 0.01	**a**	0.07 ± 0.01	**a**	5.2 ± 1.3	**a**	0.39 ± 0.25	**a**
	Em	< LOD		1.42 ± 0.01	**b**	0.05 ± 0.01	**a**	< LOD	**a**	5.0 ± 0.5	**a**	0.34 ± 0.15	**a**
	RG	0.3 ± 0.4	**a**	1.29 ± 0.03	**c**	0.08 ± 0.02	**a**	0.05 ± 0.01	**a**	5.9 ± 0.4	**a**	0.85 ± 0.01	**a**
Se	*CN*	< LOD		< LOD		< LOD		0.04 ± 0.01	**a**	< LOD		0.04 ± 0.01	**a**
	Em	< LOD		< LOD		< LOD		0.04 ± 0.01	**a**	0.31 ± 0.44		0.12 ± 0.04	**a**
	RG	< LOD		< LOD		< LOD		0.03 ± 0.01	**a**	0.07 ± 0.03		0.03 ± 0.01	**a**
Sr	*CN*	81.2 ± 0.1	**a**	98 ± 1	**a**	5.7 ± 0.3	**a**	2.72 ± 0.02	**a**	49 ± 10	**a**	3.7 ± 0.5	**a**
	Em	70.7 ± 8.1	**a**	67 ± 1	**b**	8.1 ± 0.7	**a**	3.61 ± 0.41	**a**	36 ± 2	**a**	4.9 ± 0.9	**a**
	RG	38.9 ± 3.4	**a**	62 ± 1	**c**	4.3 ± 0.1	**a**	3.04 ± 0.11	**a**	15 ± 3	**a**	4.5 ± 0.2	**a**

(*continued on next page*)

Table 1 (*continued*)

Elements	*Sites*	*Season*											
		Dry ***Water***		**Wet**		**Dry** ***S. Bioavailable***		**Wet**		**Dry** ***S. Seudototal***		**Wet**	
Tl	*CN*	< LOD		< LOD		< LOD		< LOD		0.06 ± 0.01	**a**	< LOD	
	Em	< LOD		< LOD		< LOD		< LOD		0.04 ± 0.01	**a**	< LOD	
	RG	< LOD		< LOD		< LOD		< LOD		0.04 ± 0.02	**a**	< LOD	
U	*CN*	0.58 ± 0.01	**a**	0.87 ± 0.01	**a**	0.02 ± 0.01	**a**	0.04 ± 0.01	**a**	0.69 ± 0.15	**a**	0.15 ± 0.01	**a**
	Em	0.38 ± 0.02	**a**	0.49 ± 0.01	**b**	0.02 ± 0.02	**a**	< LOD	**a**	0.74 ± 0.02	**a**	0.30 ± 0.12	**a**
	RG	0.10 ± 0.04	**a**	0.40 ± 0.01	**c**	0.01 ± 0.01	**a**	< LOD	**a**	0.29 ± 0.06	**a**	0.19 ± 0.02	**a**
V	*CN*	1.8 ± 2.4	**a**	5.90 ± 0.02	**a**	0.73 ± 0.03	**a**	< LOD		12 ± 2	**a**	0.50 ± 0.27	**a**
	Em	2.4 ± 0.4	**a**	2.83 ± 0.05	**b**	0.38 ± 0.03	**a**	< LOD		12 ± 3	**a**	1.03 ± 0.43	**a**
	RG	2.1 ± 1.6	**a**	2.34 ± 0.08	**c**	0.04 ± 0.01	**a**	< LOD		6 ± 1	**a**	1.36 ± 0.01	**a**
Zn	*CN*	< LOD		< LOD		1.63 ± 0.05	**a**	< LOD	**a**	11 ± 1	**a**	< LOD	
	Em	< LOD		< LOD		7.60 ± 0.58	**a**	3.3 ± 0.5	**a**	49 ± 13	**a**	5.4 ± 1.4	**a**
	RG	7.9 ± 1.7	**a**	< LOD		0.92 ± 0.02	**a**	< LOD	**a**	9 ± 1	**a**	< LOD	

Table 2
Ecological risk index of elements in Río Tercero Reservoir sediments.

	E_r^i							R_I
	Cd	Hg	As	Cu	Pb	Cr	Zn	
PSEUDOTOTAL sediment	3	14	0.1	0.6	0.9	0.04	0.1	19
BIOAVAILABLE sediment	1	0	0	0.2	0.1	0	0.02	2

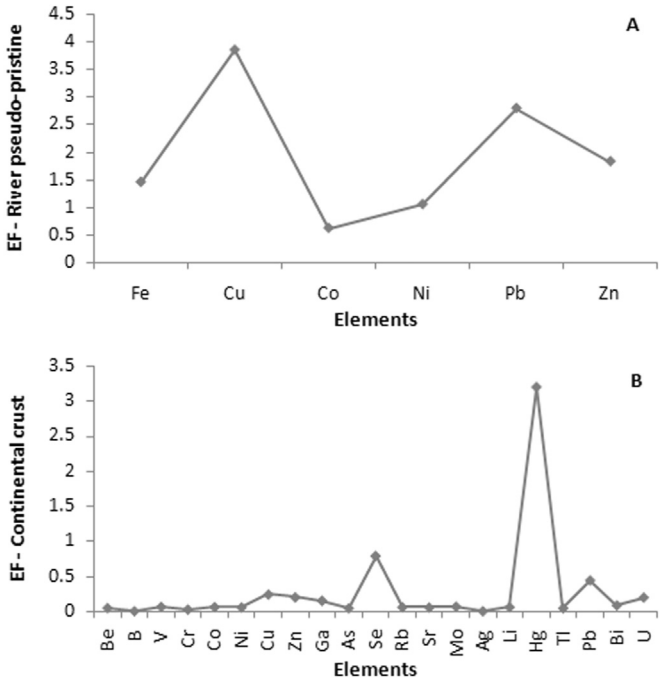

Fig. 2. Enrichment factor for each metal in relation to (A) a river with pseudo-pristine characteristics (Rio Grande) and (B) the values of the Continental Crust.

part of the commercial formulations of pesticides (Bertrand et al., 2015), and can enter the system through these, which matches the agricultural activity in the surrounding area.

3.3. Element bioaccumulation in fish tissues

The values given by the BAF for the different elements in fish organs are presented in Table 3. The concentrations (μg g^{-1}, dry weight) of the different elements in the fish organs used to calculate the factors are shown in Table S.4.

Pollutants were rarely distributed uniformly in the body tissues but were accumulated by a particular target organ. The BAF for Al showed the highest values in the intestine of *R. quelen, B. iheringii* and *O. bonariensis*. The BAF for Al was also highest among organs in the intestine of *A. fasciatus, O. jenynsii* and *H. malabaricus*, but there was no significant difference.

The highest BAF values for As were registered in the intestine in all species except for *O. bonariensis* and for *O. jenynsii*, which had the highest BAF value for this element in liver and in brain, respectively. However, the highest values of BAF for intestine were statistically significant only for *A. fasciatus* and *B. iheringii*. Some authors have shown that As causes behavioral changes (aggression) in fish, fragmentation of chromosomal DNA in the liver, alterations in the expression of certain proteins, as well as damage to the immune system (Hermann and Kim, 2005).

The highest BAF results for *Cr* were mainly in the intestine and gills in *B. iheringii*, *O. jenynsii* and *R. quelen.* The difference in the BAF values between these organs was significant only for *B. iheringii.* In *O. bonariensis*, the highest values were in the intestine, with no significant differences between this tissue and liver and gills. In *H. malabaricus* and *A. fasciatus*, there were no significant differences in factor values between organs. None of the species showed significant differences between their organs for Ni, except *O. bonariensis*, where the BAF showed their highest values mainly in the gills, intestine and liver. It should be noted that *O. bonariensis* had the lowest value of BAF for Ni in brain for all analyzed species. The highest values of Sr were in the gills in all species.

There is no clear pattern with respect to the BAF value for Se in the organs of the different species. However, it can be observed that the values tend to be higher in the liver than in the other organs. Similar results have been reported by other studies (Ciardullo et al., 2008). The liver is the primary storage site of Se in fish, as well as other organs such as the kidney and ovaries (Swift, 2002). The high concentration of Se in the liver reflects dietary uptake (Jasonsmith et al., 2008).

It should be noted that the BAF for *Hg* was higher in the muscle of all species, except for *H. malabaricus and R. quelen.* In the former, there were no significant differences between the studied organs, and in the latter, differences were not significant among muscle and gills, liver and intestine. It is known that muscle is not a target organ for accumulation during acute exposure, so this tissue is a good indicator of chronic exposure. When pollutants overcome the defense barriers, they begin to accumulate in muscle (Kalay et al., 1999). This was also mentioned by Arcagni et al. (2017), who registered higher total Hg concentrations in muscle than in liver in two fish species native to Nahuel Huapi Lake (Argentina). Most Hg in fish liver is in inorganic form and this organ is where demethylation occurs. So, inorganic Hg accumulates in the liver and may be sequestered by binding proteins or accumulated in Se-Hg stable compounds (Khan and Wang, 2009).

It should be noted that Hg was registered in the brain for all species. Some authors have detected changes in behavior in fish due to the

Table 3
Bioaccumulation Factor (BAF) values for the metals As and Se in the organs of the fish. Different letters indicate statistically significant differences of BAF values between organs ($P < 0.05$).

Species	*Organs*	*Elements*													
		Al		As		Cr		Hg		Ni		Se		Sr	
A. fasciatus	*Muscle*	1	a	0.1	a	33,127	a	20,579.1	c	644	a	672	a	37	ab
	Gill	272,796	b	0.1	a	17,712	a	0.1	a	1840	a	4182	b	643	b
	Brain	324,139	b	0.1	a	38,693	a	0.3	b	2074	a	2181	ab	33	a
	Liver	892,150	b	0.1	a	73,711	a	0.2	b	977	a	5001	b	28	a
	Intestine	1,630,015	b	193.9	b	72,589	a	0.1	a	2587	a	1740	ab	146	ab
R. quelen	*Muscle*	25,236	a	272	a	2751	a	89,050	b	968	a	727	a	29	a
	Gill	36,597	a	313	a	6255	ab	64,653	b	1764	a	2453	b	966	b
	Brain	56,391	a	429	a	6047	ab	2742	a	576	a	2637	bc	47	a
	Liver	35,550	a	274	a	3894	a	67,338	b	1294	a	6243	c	18	a
	Intestine	1,796,185	b	619	a	16,368	b	46,555	b	3371	a	2057	b	366	b
B. iheringii	*Muscle*	594	a	329	a	897	a	44,216	b	1197	a	1527	ab	73	a
	Gill	4660	b	384	a	3128	b	9663	a	1207	a	2616	abc	837	b
	Brain	831	ab	287	a	2151	ab	10,998	a	1131	a	1418	a	79	a
	Liver	1292	ab	522	a	2321	ab	11,628	a	1885	a	3535	c	34	a
	Intestine	62,995	c	3350	b	9942	c	7036	a	843	a	2928	bc	82	a
O. jenynsii	*Muscle*	104,349	a	111	bc	5574	a	78,043	b	438	a	744	a	49	ab
	Gill	564,600	a	104	b	17,999	c	42,482	ab	1029	a	2180	bc	1576	c
	Brain	143,175	a	274	c	5812	b	20,562	a	466	a	1680	b	39	ab
	Liver	180,462	a	42	a	9156	b	47,995	ab	547	a	3864	c	25	a
	Intestine	605,824	a	177	bc	17,454	bc	26,519	ab	1091	a	2060	b	65	b
O. bonariensis	*Muscle*	1621	b	508	a	894	a	91,474	c	433	ab	1567	a	39	b
	Gill	6321	bc	1051	a	2821	b	34,405	bc	1877	b	1741	ab	914	c
	Brain	44	a	440	a	873	a	9193	a	30	a	1618	ab	23	ab
	Liver	1661	b	7597	b	2872	b	36,466	bc	1241	b	5640	c	11	a
	Intestine	30,533	c	3800	b	4133	b	16,810	ab	1013	b	3053	bc	41	b
H. malabaricus	*Muscle*	237,480	a	53	a	7159	a	41,697	a	652	a	883	a	58	a
	Gill	181,744	a	132	ab	8132	a	18,246	a	1557	a	2155	ab	957	b
	Brain	506,975	a	65	a	10,258	a	15,535	a	2925	a	1824	ab	40	a
	Liver	130,463	a	104	a	5276	a	21,481	a	886	a	3653	b	22	a
	Intestine	879,888	a	618	b	9758	a	16,351	a	769	a	2547	ab	66	a

presence of Hg in the brain (Monteiro et al., 2010). Moreover, changes in the concentration of metallothioneins, histological damage and even mortality have been observed in fish with Hg in their organs (Giari et al., 2008; Vieira et al., 2011). The incorporation of this metal into organs in humans through their food is associated with pathologies. Hg is rapidly distributed by erythrocytes by binding to hemoglobin, thus reaching the different systems of the organism, where it joins specific groups of proteins, inhibiting the enzyme activity of certain processes (Graeme and Pollack, 1998). Hg may also cross the blood-brain barrier and cause neurotoxic effects, especially in the brains of the elderly and of fetuses (Moreno-Sánchez et al., 1999; Graeme and Pollack, 1998). *Cd* and *Pb* are toxic metals that can be assimilated, stored, and concentrated by organisms through the food chain (Weber et al., 2013). However, in more than 40% of observations in our study, these metals were registered below limit of detection (LOD) and were, therefore, discarded from analysis.

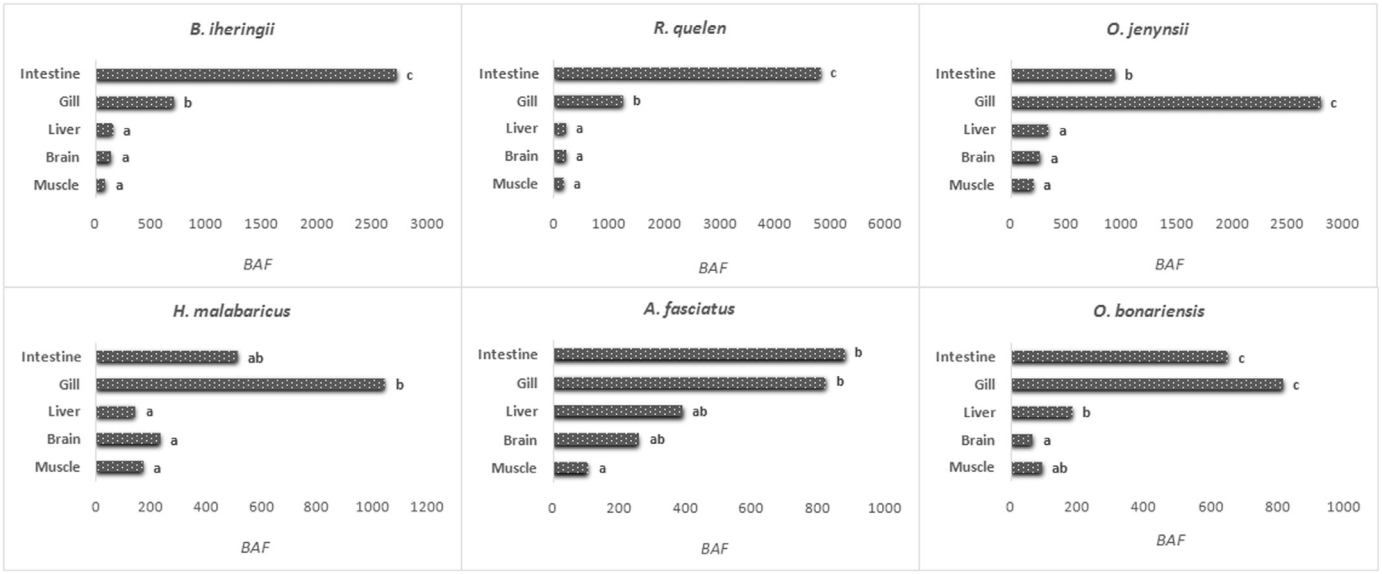

Fig. 3. Total analysis of metals, As and Se (Bioaccumulation Factor: element concentration in organisms ($g\,g^{-1}$)/element concentration in water ($g\,mL^{-1}$)) by organs of the different fish species. Different letters indicate statistically significant differences between the organs of a species ($P < 0.05$).

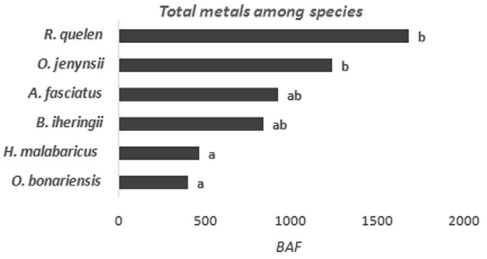

Fig. 4. Total analysis of metals, As and Se (Bioaccumulation Factor: element concentration in organisms ($g\,g^{-1}$)/element concentration in water ($g\,mL^{-1}$)) in different fish species. Different letters indicate statistically significant differences between species ($P < 0.05$).

The results obtained for the accumulation of each metal by organ show no pattern of accumulation in relation to diet or habitat of the species.

Fig. 3 shows the BAF of the sum of all the elements analyzed in each fish organ studied. The intestine and gills were the organs that showed the highest BAF values in all fish species. In *B. iheringii* and *R. quelen*, the BAF values in intestine were significantly higher than in gills, while in *O. jenynsii,* gills had significantly higher values than intestine. In the other species, there were no significant differences in the BAF values between these organs. Gills and intestine have been described as target organs for metal accumulation since they are metabolically active tissues (Yilmaz et al., 2003; Zhang et al., 2007). Gills are more exposed to environmental metals, because they are in direct contact with the environmental matrix (water), which may cause more accumulation and adsorption (Kalay, 2000). In turn, the intestine is considered an active entry point of metals through food (Dhanakumar et al., 2015). Jones et al. (2013) mentioned that fish taking metals from water showed higher concentration in their gills than in other organs, while fish accumulating heavy metals from sediments had higher metal levels in the intestine than in the gills. In the RTR, no greater metal accumulation was found in gills or intestine according to the fish habitat.

The sum of the BAF values registered in all the organs of the fish was used to compare metal accumulation in the whole body of different fish species (Fig. 4). *R. quelen* and *O. jenynsii* presented the highest BAF values and *H. malabaricus* and *O. bonariensis* the lowest, with *A. fasciatus* and *B. iheringii* in an intermediate situation. These results did not confirm the hypothesis that top predator fish accumulate more metals than carnivorous and omnivorous species. Similarly, Yousafzai et al. (2010) showed that omnivorous fish accumulated more metal burden than top predator fish. Moreover, Weber et al. (2013) observed that detritivorous species are those that accumulate the most metals, because, in lower contaminated waters, the metal uptake in fish is mainly through feeding (Farkas et al., 2003). In the RTR, we observed low concentration of metals in water; feeding would thus be the main source of metal intake for fish. The top predator fish should therefore accumulate more metals by biomagnification of these elements along the trophic chain. However, we did not observe greater metal accumulation in the top predator (*H. malabaricus*). Griboff et al. (2018) found no evidence of biomagnification of most elements analyzed in the Los Molinos Lake (Córdoba, Argentina). The concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se and Cd in the food chain studied decreased significantly, showing a trophic dilution behavior.

Some studies have found that trophic level seems to play a major role in controlling Hg concentrations in biota, reaching the highest values (through biomagnification) in top predator fish (Morel et al., 1998; Cabana et al., 1994). However, in Lake Nahuel Huapi (Bariloche, Argentina), a trend towards biodilution of total Hg (THg) along the trophic chain has been reported and THg did not follow the biomagnification trend usually observed in most aquatic systems worldwide (Arcagni et al., 2017, 2018).

We also postulated that the bottom fish would accumulate more metals because they are in direct contact with the sediment. Weber et al. (2013) supported the hypothesis that sediment is the major sink for metal pollution and plays an important role in heavy metal uptake by fish. Confirming this, *R. quelen*, with a habitat near the bottom, showed the highest BAF value. However, the difference in BAF of this species was not significantly different from that of *O. jenynsii*, an open and/or vegetated waters fish. We also expected that *H. malabaricus*, being related to the bottom, would accumulate more metals than a free-water species (e.g., *O. bonariensis*). However, both species accumulated metals in a similar way. Therefore, we observed no direct relation between the habitats of the fish and metal accumulation in this study.

4. Conclusions

In the Río Tercero Reservoir, metal concentrations were higher in sediment than in the water column, indicating sediment as the major sink for metals in the aquatic environment. Among the three studied sites, metal levels in water were the highest at the CN site, but there was no significant difference among them in sediment. However, the potential ecological risk analysis of metal concentrations in sediment indicated low ecological risk in the reservoir in all sampling periods, and the enrichment factor showed that Cu, Pb, Zn and Hg come from anthropogenic sources. The elements were rarely distributed uniformly in body tissues but were accumulated by a particular target organ. The intestine and gills were the organs that showed the highest BAF values in all fish species. In this study, no accumulation of the metals As and Se was observed in relation to the feeding and habitat of the fish. Therefore, the processes by which the metals bioaccumulate in tissues and organs appear to be species-dependent and related to the detoxification and metabolism mechanisms of each organism.

Acknowledgments

The authors thank the National Research Council (CONICET: National Council of Scientific and Technical Research, PIP 112-201101-01084) and the Secretariat of Science and Technology (SECYT, 2014–2015. Res no.: 203/14) of the National University of Córdoba (Argentina) for grants and subsidies. We also thank Joaquín Gastaminza for his help during sample measurement in ICP-MS.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2018.07.023.

References

Agarwal, R., Kumar, R., Behari, J.R., 2007. Mercury and lead content in fish species from the river Gomti, Lucknow, India, as biomarkers of contamination. Bull. Environ. Contam. Toxicol. 78, 118–122. https://doi.org/10.1007/s00128-007-9035-8.

Al-Yousuf, M.H., El-Shahawi, M.S., Al-Ghais, S.M., 2000. Trace metals in liver, skin and muscle of Lethrinus lentjan fish species in relation to body length and sex. Sci. Total Environ. 256, 87–94. https://doi.org/10.1016/S0048-9697(99)00363-0.

Arcagni, M., Juncos, R., Rizzo, A., Pavlin, M., Fajon, V., Arribére, M.A., Horvat, M., Ribeiro, S., 2018. Science of the Total Environment Species- and habitat-speci fi c bioaccumulation of total mercury and methylmercury in the food web of a deep oligotrophic lake. Sci. Total Environ. 612, 1311–1319. https://doi.org/10.1016/j.scitotenv.2017.08.260.

Arcagni, M., Rizzo, A., Juncos, R., Pavlin, M., Horvat, M., Ribeiro, S., Campbell, L.M., Arrib, M.A., 2017. Chemosphere Mercury and selenium in the food web of Lake Nahuel Huapi. Chemosphere 166, 163–173. https://doi.org/10.1016/j.chemosphere.2016.09.085.

Argentinean Environmental Water Quality Guidelines (AEWQG Niveles Guía Nacionales de Calidad de Agua Ambiente), 2003. Subsecretaria de Recursos Hídricos de la Nación, Repuública Argentina. <<www.hidricosargentina.gov.ar/NivelCalidad1.html>>.

Authman, M.M., Abbas, H.H., 2007. Accumulation and distribution of copper and zinc in bothwater and somevital tissues of two fish species (Tilapia zillii andMugil cephalus) of Lake Qarun, Fayoum Province, Egypt. Pak. J. Biol. Sci.: PJBS 10, 2106–2122.

Ballesteros, M.L., Miglioranza, K.S.B., Gonzalez, M., Fillmann, G., Wunderlin, D. a, Bistoni, M. a, 2014. Multimatrix measurement of persistent organic pollutants in Mar

Chiquita, a continental saline shallow lake. Sci. Total Environ. 490C, 73–80. https://doi.org/10.1016/j.scitotenv.2014.04.114.
Bermudez, G.M.A., Jasan, R., Plá, R., Pignata, M.L., 2012. Heavy metals and trace elements in atmospheric fall-out : Their relationship with topsoil and wheat element composition. J. Hazard. Mater. 213–214, 447–456. https://doi.org/10.1016/j.jhazmat.2012.02.023.
Bermudez, G.M.A., Moreno, M., Invernizzi, R., Plá, R., Pignata, M.L., 2010. Evaluating top soil trace element pollution in the vicinity of a cement plant and a former open-cast uranium mine in central Argentina. J Soils Sediments 10, 1308–1323. https://doi.org/10.1007/s11368-010-0243-1.
Bertrand, L., Monferran, M.V., Métais, I., Mouneyrac, C., Amé, M. v, 2015. MTs in Palaemonetes argentinus as potential biomarkers of zinc contamination in freshwaters. Ecol. Indic. 48, 533–541. https://doi.org/10.1016/j.ecolind.2014.09.019.
Boik, R.J., 1987. the normal theory F test when variances are heterogeneous. Briliah J. Math. Slatietical Psychol. 40, 26–42.
Cabana, G., Tremblay, A., Kalff, J., Rasmussen, J.B., 1994. Pelagic food chain structure in Ontario lakes: a determinant of mercury levels in lake trout (*Salvelinus namaycush*). Can. J. Fish. Aquat. Sci. 51, 381e389. https://doi.org/10.1139/f94-039.
Canadian Council of Ministers of the Environment, 2002. Canadian water quality guidelines for the protection of aquatic life. Canadian Environmental Quality 1999 Canadian Council of Ministers of the Environment, Winnipeg, Cananda.
Carreras, H.A., Pignata, M.L., 2002. Biomonitoring of heavy metals and air quality in Cordoba City, Argentina, using transplanted lichens. Environ. Pollut. 117, 77–87. https://doi.org/10.1016/S0269-7491(01)00164-6.
Ciardullo, S., Aureli, F., Coni, E., Guandalini, E., Iosi, F., Raggi, A., Rufo, G., Cubadda, F., 2008. Bioaccumulation Potential of Dietary Arsenic, Cadmium, Lead, Mercury, and Selenium in Organs and Tissues of Rainbow Trout (Oncorhyncus mykiss) as a Function of Fish Growth. J. Agric. Food Chem. 56, 2442–2451.
Dhanakumar, S., Solaraj, G., Mohanraj, R., 2015. Heavy metal partitioning in sediments and bioaccumulation in commercial fish species of three major reservoirs of river Cauvery delta region, India. Ecotoxicol. Environ. Saf. 113, 145–151. https://doi.org/10.1016/j.ecoenv.2014.11.032.
Farkas, A., Salánki, J., Specziár, A., 2003. Age and size-specific patterns of heavy metals in the organs of freshwater fish Abramis brame L. populating a low contaminate site. Water Res. 37, 959–964.
Farkas, A., Salánki, J., Specziár, A., 2002. Relation between growth and the heavy metal concentration in organs of bream Abramis brama L. populating Lake Balaton. Arch. Environ. Contam. Toxicol. 43, 236–243. https://doi.org/10.1007/s00244-002-1123-5.
Giari, L., Manera, M., Dezfuli, B.S., 2008. Histo-cytological responses of Dicentrarchus labrax (L .) following mercury exposure. Ecotoxicol. Environ. Saf. 70, 400–410. https://doi.org/10.1016/j.ecoenv.2007.08.013.
Gioia, S.M.C.L., Babinski, M., Weiss, D.J., Spiro, B., Kerr, A.A.F.S., Veríssimo, T.G., Ruiz, I., Prates, J.C.M., 2017. An isotopic study of atmospheric lead in a megacity after phasing out of leaded gasoline. Atmos. Environ. 149, 70–83. https://doi.org/10.1016/j.atmosenv.2016.10.049.
González del Tánago del Río, M., García de Jalón Lastra, D., 1998. El río y su cuenca vertiente Pp. 19, en Restauración de ríos y riberas. Ed. Fundación conde del valle Salazar (Ediciones mundi-prensa). Madrid. 319.
Graeme, K.A., Pollack, C.V., 1998. Heavy metal toxicity, Part I: arsenic and mercury. J. Emerg. Med. 16, 45–56.
Griboff, J., Horacek, M., Wunderlin, D.A., Monferran, M.V., 2018. Ecotoxicology and Environmental Safety Bioaccumulation and trophic transfer of metals, As and Se through a freshwater food web a ff ected by antrophic pollution in Córdoba, Argentina. Ecotoxicol. Environ. Saf. 148, 275–284. https://doi.org/10.1016/j.ecoenv.2017.10.028.
Griboff, J., Wunderlin, D.A., Monferran, M.V., 2017. Metals, As and Se determination by inductively coupled plasma-mass spectrometry (ICP-MS) in edible fish collected from three eutrophic reservoirs. Their consumption represents a risk for human health? Microchem. J. 130, 236–244.
Jasonsmith, J.F., Maher, W.A., Roach, A.C., Krikowa, F.A., 2008. Selenium bioaccumulation and biomagnification in Lake Wallace, New South Wales, Australia. Mar. Freshw. Res. 59, 1048e1060. https://doi.org/10.1071/MF08197.
Khan, M.A.K., Wang, F., 2009. Mercury - selenium compounds and their toxicological significance: toward a molecular understanding of the mercury - selenium antagonism. Environ. Toxicol. Chem. 28, 1567e1577. https://doi.org/10.1897/08-375.1.
Håkanson, L., 1980. An ecological risk index for aquatic pollution control of sediment ecological approach. Water Res. 14, 975–1000.
Harguinteguy, C.A., Schreiber, R., Pignata, M.L., 2013. Myriophyllum aquaticum as a biomonitor of water heavy metal input related to agricultural activities in the Xanaes River (Córdoba, Argentina). Ecol. Indic. 27, 8–16. https://doi.org/10.1016/j.ecolind.2012.11.018.
Harguinteguy, C., Cofré, N., Fernández-Cirelli, A., Pignata, M.L., 2016. The macrophytes Potamogeton pusillus L. and Myriophyllum aquaticum (Vell.) Verdc. as potential bioindicators of a river contaminated by heavy metals. Microchem. J. 124, 228–234. https://doi.org/10.1016/j.microc.2015.08.014.
Haro, J.G., Bistoni, M.A., 2007. “Peces de Córdoba”. Ed: Universidad Nacional de Córdoba, Córdoba, Argentina, 246.
Has-Schön, E., Bogut, I., Strelec, I., 2006. Heavy metal profile in five fish species included in human diet, domiciled in the end flow of river Neretva (Croatia). Arch. Environ. Contam. Toxicol. 50, 545–551. https://doi.org/10.1007/s00244-005-0047-2.
Henry, F., Amara, R., Courcot, L., Lacouture, D., Bertho, M.-L., 2004. Heavy metals in four fish species from the French coast of the Eastern English Channel and Southern Bight of the North Sea. Environ. Int. 30, 675–683. https://doi.org/10.1016/j.envint.2003.12.007.
Hermann, A.C., Kim, C.H., 2005. Effects of Arsenic on Zebrafish Innate Immune System. Mar. Biotechnol. 7, 494–505. https://doi.org/10.1007/s10126-004-4109-7.
Hilton, J., Davison, W., Ochsenbein, U., 1985. A mathematical model for analysis of sediment coke data. Chem. Geol. 48, 281–291.
Jakimska, A., Konieczka, P., Skóra, K., Namieśnik, J., 2011. Bioaccumulation of metals in tissues of marine animals, part I: The role and impact of heavy metals on organisms. Polish J. Environ. Stud. 20, 1117–1125.
Jones, H.J., Swadling, K.M., Tracey, S.R., Macleod, C.K., 2013. Long term trends of Hg uptake in resident fish from a polluted estuary. Mar. Pollut. Bull. 73, 263–272.
Kalay, M., 2000. Elimination of Essential (Cu, Zn) and Non-Essential (Cd, Pb) Metals from Tissues of a Freshwater Fish Tilapia zilli 24, 429–436.
Kalay, M., Ay, Ö., Canli, M., 1999. Heavy Metal Concentrations in Fish Tissues from the Northeast Mediterranean Sea. Bull. Environ. Contam. Toxicol. 63, 673–681. https://doi.org/10.1007/s001289901033.
Kojadinovic, J., Potier, M., Le Corre, M., Cosson, R.P., Bustamante, P., 2007. Bioaccumulation of trace elements in pelagic fish from the Western Indian Ocean. Environ. Pollut. 146, 548–566. https://doi.org/10.1016/j.envpol.2006.07.015.
Ledesma, C., Bonansea, M., Rodriguez, C.M., 2013. Determinación de indicadores de eutrofización en el embalse Río Determination of trophic indicators in Rio Tercero reservoir, Cordoba (Argentina) 419–425.
Li, J., Zheng, C., 1988. Handbook of Environmental Background Values. China Environmental Science Press, Beijing.
Loska, K., Cebula, J., Pelczar, J., Wiechula, D., Kwapulinski, J., 1997. USE OF ENRICHMENT, AND CONTAMINATION FACTORS TOGETHER WITH GEOACCUMULATION INDEXES TO EVALUATE THE CONTENT OF Cd, Cu, AND Ni IN THE RYBNIK WATER RESERVOIR IN POLAND. Water, Air, Soil Pollut 93, 347–365.
Luoma, S.N., Bryan, G.W., 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. Sci. Total Environ. 17, 165–196. https://doi.org/10.1016/0048-9697(81)90182-0.
Maiz, I., Esnaola, Ma. N., Millfin, E., 1997. Evaluation of heavy metal availability in contaminated soils by a short sequential extraction procedure. The Science of the Total Environment 206, 107–115.
Malik, N., Biswas, A.K., Qureshi, T.A., Borana, K., Virha, R., 2010. Bioaccumulation of heavy metals in fish tissues of a freshwater lake of Bhopal. Environ. Monit. Assess. 160, 267–276. https://doi.org/10.1007/s10661-008-0693-8.
Mancini, M., Grosman, F., 1998. Aspectos poblacionales del Pejerrey Odontesthesis en el Embalse Río Tercero, Córdoba. Nat. Neotrop. 29, 137–143.
Manirakiza, P., Covaci, A., Nizigiymana, L., Ntakimazi, G., Schepens, P., 2002. Persistent chlorinated pesticides and polychlorinated biphenyls in selected fish species from Lake Tanganyika, Burundi, Africa. Environ. Pollut. 117, 447–455. https://doi.org/10.1016/S0269-7491(01)00188-9.
Mariazzi, A.A., Donadelli, J.L., Arenas, P., Di Siervi, M.D., Bonetto, C., 1992. Impact of a nuclear power plant on water quality of Embalse del Rio Tercero Reservoir, (Cordoba, Argentina). Hydrobiologia 246, 129–140.
Mariñelarena, A., Donadelli, J., Hechem, M., 2014. Cambios en las características limnológicas del Embalse Río Tercero por efecto de la invasión de Limnosperma fortunei (Bivalvia: Mytilidae). Biol. Acuática 30, 151–158.
Mason, R.P., Laporte, J.M., Andres, S., 2000. Factors controlling the bioaccumulation of mercury, methylmercury, arsenic, selenium, and cadmium by freshwater invertebrates and fish. Arch. Environ. Contam. Toxicol. 38, 283–297. https://doi.org/10.1007/s002449910038.
Monferran, M.V., Garnero, P.L., Wunderlin, D.A., Bistoni, M., de, L., 2016. Potential human health risks from metals and As via Odontesthes bonariensis consumption and ecological risk assessments in a eutrophic lake. Ecotoxicol. Environ. Saf. 129, 302–310. https://doi.org/10.1016/j.ecoenv.2016.03.030.
Monroy, M., Maceda-Veiga, A., de Sostoa, A., 2014. Metal concentration in water, sediment and four fish species from Lake Titicaca reveals a large-scale environmental concern. Sci. Total Environ. 487, 233–244. https://doi.org/10.1016/j.scitotenv.2014.03.134.
Monteiro, D.A., Rantin, F.T., Kalinin, A.L., 2010. Inorganic mercury exposure: Toxicological effects, oxidative stress biomarkers and bioaccumulation in the tropical freshwater fish matrinxã, Brycon amazonicus (Spix and Agassiz, 1829). Ecotoxicology 19, 105–123. https://doi.org/10.1007/s10646-009-0395-1.
Morel, F.M.M., Kraepiel, A.M.L., Amyot, M., 1998. The chemical cycle and bioaccumulation of mercury. http://dx.doi.org/. Annu. Rev. Ecol. Syst. 29, 543–566. https://doi.org/10.1146/annurev.ecolsys.29.1.543.
Moreno-Sánchez, R., Díaz-Barriga, F., Devars, S., 1999. Mecanismos de toxicidad y tolerancia a los metales pesados. Contaminación ambiental por metales pesados. Impacto en los seres vivos. Editor, A.G.T., S.A. pp. 11–24.
Neuhäuser, M., Manly, B.F.J., 2004. The Fisher-Pitman Permutation Test When Testing for Differences in Mean and Variance. Psychol. Rep. 94, 189–194. https://doi.org/10.2466/pr0.94.1.189-194.
Newman, M., Unger, M., 2002. Environmental contaminants. In: Fundamentals of Ecotoxicology 458. Lewis Publishers, Boca Raton, Florida, pp. 21–50.
Oost, D., Beyer, J., Vermeulen, N.P.E., 2003. Fish bioaccumulation and biomarkers in en v ironmental risk assessment : a re v iew. Enviironmental Toxicol. Pharmacol. 13, 57–149. https://doi.org/10.1016/S1382-6689(02)00126-6.
Orozco Barrenetxea, C., Pérez Serrano, A., González Delgado, M.N., Rodríguez Vidal, F.J., Alfayate Blanco, J.M., 2003. Algunos contaminantes específicos. En: CONTAMINACION AMBIENTAL. Una visión desde la Química. Ed. THOMSOM, 678: 88-97.
Peakall, D., Burger, J., 2003. Methodologies for assessing exposure to metals: speciation, bioavailability of metals, and ecological host factors. Ecotoxicol. Environ. Saf. 56, 110–121. https://doi.org/10.1016/S0147-6513(03)00055-1.
Pignata, M.L., Gudio, G.L., Wannaz, E.D., Plá, R.R., González, C.M., Carreras, H.A., Orellana, L., 2002. Atmospheric quality and distribution of heavy metals in Argentina

employing Tillandsia capillaris as a biomonitor. Environ. Pollut. 120, 59–68. https://doi.org/10.1016/S0269-7491(02)00128-8.
Praveena, S.M., Kwan, O.W., Aris, A.Z., 2012. Effect of data pre-treatment procedures on principal component analysis : a case study for mangrove surface sediment datasets. Env. Monit Assess 184, 6855–6868. https://doi.org/10.1007/s10661-011-2463-2.
R Core Team (2016). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL 〈https://www.R-project.org/〉.
Repetto, R., Repetto, G., 2000. “Metales”. En: Mencías Rodríguez Emilio & Luis Manuel Mayero Franco. “Manual de Toxicología Básica”. Ed Díaz de Santos, S.A, 619-648.
Rundnick, R.L., Gao, S., 2003. Composition of the Continental Crust. Treatise On Geochemistry 3, 1–64.
Shafie, N.A., Aris, A.Z., Haris, H., 2014. Geoaccumulation and distribution of heavy metals in the urban river sediment. Int. J. Sediment Res. 29, 368–377. https://doi.org/10.1016/S1001-6279(14)60051-2.
Swift, M.C., 2002. Stream ecosystem response to, and recovery from, experimetal exposure to selenium. http:// dx.doi.org/. J. Aquat. Ecosyst. Stress Recover 9, 159e184. https://doi.org/10.1023/A:1021299003516.
Tao, Y., Yuan, Z., Xiaona, H., Wei, M., 2012. Distribution and bioaccumulation of heavy metals in aquatic organisms of different trophic levels and potential health risk assessment from Taihu lake, China. Ecotoxicol. Environ. Saf. 81, 55–64. https://doi.org/10.1016/j.ecoenv.2012.04.014.
USEPA (US Environmental Protection Agency), 2009a. . National Recommended Water Quality Criteria. Office of Water. Office of Science and Technology, Washington DC.
Verbovsek, T., 2011. A comparison of parameters below the limit of detection in geochemical analyses by substitution methods. Mater. Geoenvironment 58, 393–404.
Vieira, C., Morais, S., Ramos, S., Delerue-Matos, C., Oliveira, M.B.P.P., 2011. Mercury, cadmium, lead and arsenic levels in three pelagic fish species from the Atlantic Ocean: Intra- and inter-specific variability and human health risks for consumption. Food Chem. Toxicol. 49, 923–932. https://doi.org/10.1016/j.fct.2010.12.016.
Wang, J., Feng, X., Anderson, C.W.N., Xing, Y., Shang, L., 2012. Remediation of mercury contaminated sites – A review. J. Hazard. Mater. 221–222, 1–18. https://doi.org/10.1016/j.jhazmat.2012.04.035.
Weber, P., Behr, E.R., Knorr, C.D.L., Vendruscolo, D.S., Flores, E.M.M., Dressler, V.L., Baldisserotto, B., 2013. Metals in the water, sediment, and tissues of two fish species from different trophic levels in a subtropical Brazilian river. Microchem. J. 106, 61–66. https://doi.org/10.1016/j.microc.2012.05.004.
Ye, C., Li, S., Zhang, Y., Zhang, Q., 2011. Assessing soil heavy metal pollution in the water-level-fluctuation zone of the Three Gorges Reservoir, China. J. Hazard. Mater. 191, 366–372. https://doi.org/10.1016/j.jhazmat.2011.04.090.
Yi, Y., Yang, Z., Zhang, S., 2011. Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. Environ. Pollut. 159, 2575–2585. https://doi.org/10.1016/j.envpol.2011.06.011.
Yilmaz, F., Özdemir, N., Demirak, A., Tuna, L., 2003. Heavy metal levels in two fish species *Leuciscuscephalus* and *Lepomisgibbosus*. Food Chem 487, 233–244.
Yousafzai, A.M., Chivers, D.P., Khan, A.R., Ahmad, I., Siraj, M., 2010. Comparison of heavy metals burden in two freshwater fishes *Wallagoattu* and *Labeodyocheilus* with regard to their feeding habits in natural ecosystem. Pak. J. Zool 42, 537–544.
Zhang, L.P., Ye, X., Feng, H., Jing, Y.H., Tong, O.Y., Yu, X.T., Liang, R.Y., Gao, C.T., Chen, W.Q., 2007. Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. Marine Pollution Bulletin 54, 974–982.
Zhang, J., Liu, C.L., 2002. Riverine Composition and Estuarine Geochemistry of Particulate Metals in China — Weathering Features, Anthropogenic Impact and Chemical Fluxes. Estuarine, Coastal and Shelf Science 54, 1051–1070. https://doi.org/10.1006/ecss.2001.0879.