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

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ABSTRACT

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



## 1. Introduction

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

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

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

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

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

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

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

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

## 2. Materials and methods

### 2.1. Study site

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

### 2.2. Sample collection and analysis

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

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