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Tracing Cr, Pb, Fe and Mn occurrence in the Bahía Blanca estuary through commercial fish species

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HIGHLIGHTS

- Accumulation of Cr, Pb, Fe and Mn in six fish species from the Bahía Blanca estuary.
- Concentrations of metals within fish tissues showed a maximum in the gill tissues.
- *Cynoscion guatucupa* accumulated the highest Cr and Fe mean levels in the study period.
- Cr and Mn in the muscle tissues exceeded, at times, the allowable levels for consumption.

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ABSTRACT

Over the last decades the anthropogenic contamination impact has substantially increased in the Bahía Blanca estuarine area, and scarce information exists regarding metals in the biotic compartment of this estuary. Thus, fish tissues were used to evaluate metal accumulation within this aquatic environment. The study focused on the determination of Cr, Pb, Fe and Mn in the gills, liver and muscle tissues of six commercial fish species (*Brevoortia aurea, Odontesthes argentinensis, Micropogonias furnieri, Cynoscion guatucupa, Mustelus schmitti* and *Paralichthys orbignyanus*).

From the results it can be summarized that *C. guatucupa* tends to accumulate higher metal levels in the liver tissues, mostly Cr and Fe, than the other studied species. *O. argentinensis* and *P. orbignyanus*, both permanent inhabitants of the BBE, achieved the highest metal values in the gill tissues, mostly in comparison to *M. schmitti*. The gill tissues were found to be the main organ of Mn and Ni accumulation for most species, whereas in general, minimum concentrations were found for all the analyzed metals in the muscle tissues. Nevertheless, and according to the guidelines, all fish species showed at least one sample with concentrations of Mn and/or Cr above the permissible levels for human consumption.

Finally, it was highlighted the usefulness of selecting these fish species as bioindicators of metal pollution, since they are either permanent inhabitants of the estuary or, according to the sizes under analyses, spend much of their time in this coastal waters.

1. Introduction

Metals occur in the aquatic environment as a result of both natural processes and human being activities (FranÇa et al., 2005). Within anthropogenic activities, metal concentrations could be increased by means of the rapid industrialization and urbanization, massive land use changes and also could be associated to enhance terrestrial runoff, between others (Rahman et al., 2012). Contamination of aquatic ecosystems with metals has seriously increased worldwide attention, and a lot of studies have been published about the accumulation of these elements in the marine biota (Karadede and Ünlü, 2000; Yılmaz et al., 2007).

To assess the environmental condition of coastal zones such as estuaries, the study of metals in aquatic organisms, especially fishes, has been widely promoted (Borja et al., 2004; Breine et al., 2007; Harrison and Whitfield, 2006; Whitfield and Elliott, 2002).

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Fish species inhabiting polluted water bodies are exposed to a wide range of contaminants that eventually accumulate in its tissues. Moreover, metals might not only reach to harmful levels on the fish themselves but also on the top-level organisms that consume contaminated fish (*e.g.* Al-Yousuf et al., 2000; Avigliano et al., 2015). The advantages of using fish species include the ability to accumulate elements in the bioavailable and, potentially, more toxic form (Fernándes et al., 2007). Also, it is important to assess the metal contents in edible fish species in order to study potential risks to final consumers, including the human population.

According to their biochemical properties, many metals are required by living organisms, like fishes, in little but critical concentrations in order to achieve a normal growth (essential metal), but they can produce toxic effects in excessive levels (Merciai et al., 2014). Chromium (Cr), iron (Fe) and manganese (Mn) are essential metals with a significant biological role in aquatic organisms. On the other hand, lead (Pb) has unknown functions in biological systems (non-essential metal), being a toxic element that causes carcinogenic effects in marine biota (Velusamy et al., 2014). Metal accumulation in fishes also depends on other characteristics such as the tissue under analysis, fish sizes, trophic level, feeding habits, between others (Mohammadi et al., 2011).

The estuary of Bahía Blanca (BBE) is a coastal environment located in Argentina, being a mesotidal system characterized by turbid and shallow waters towards the inner zone (Guinder et al., 2009). The BBE is exposed to metals, mainly as a consequence of agricultural activities along with the urban expansion and anthropogenic waste discharges from the surrounding areas. It has a great economic value due to the presence of important industries, cities and port complexes that are in continuous development.

The BBE has one of the biggest petrochemical centers of Argentina, resulting in large amounts of effluent discharges. They mainly consist of heavy hydrocarbon fractions and particulate urea, oil derivatives, particulate polyvinyl, smoke particles, brines, chlorinated organic compounds, metals, between others (Limbozzi and Leitào, 2008). The BBE is also considered to be polluted by untreated sewage discharges (Biancalana et al., 2012; Dutto et al., 2014).

The assessment of the environmental condition of the BBE is essential to consider the association between levels of metals found in the abiotic compartments (Botté et al., 2007, 2010; La Colla et al., 2015) and metal concentrations accumulated in fishes as bioindicators of the biotic compartment. Among the fish communities inhabiting the BBE, six species were selected for metal analyses: the menhaden (*Brevoortia aurea),* the silverside *(Odontesthes argentinensis),* the whitemouth croaker *(Micropogonias furnieri),* the striped weakfish *(Cynoscion guatucupa),* the smooth-hound (*Mustelus schmitti)* and the flounder (*Paralichthys orbignyanus*). These species were selected upon their different feeding characteristics and were believed to be representative of the area of analysis. Metal accumulation was analyzed in three different organs, one being a site of uptake (*i.e.* gills), another of storage and/or excretion (*i.e.* liver) and the third one the tissues used for human consumption (*i.e.* skeletal muscle).

Many studies had been conducted all around the world trying to identify differential metal accumulation processes in fish species (*e.g.* Karadede and Ünlü, 2000; Kwok et al., 2014; Wei et al., 2014). This study is an attempt to report the concentration of metals in commercial fish species from a less studied coastal environment recognized as anthropogenically impacted (Botté et al., 2007). Most literature with reference to metal levels on the coasts of the BBE is related to sediment, seawater or suspended particulate samples (*e.g.* Botté et al., 2007, 2010; Marcovecchio et al., 2010). Meanwhile, available information on metals in fishes is mostly related to data recorded more than 20 years ago (*i.e.* Marcovecchio et al., 1986, 1988a, b) or to technical reports conducted by the local government.

The anthropogenic impact has substantially increased in the BBE over the last decades, not only due the expansion in the amount of industries, factories and port activities, but also due to the increase in their productivity. Thus, the aim of this study is to determine the concentration of Cr, Pb, Fe and Mn in fish, discussing their accumulation as regards the different species and tissues under analysis. Possible bioaccumulation patterns and the usefulness of these fish species as bioindicators of pollution processes in the BBE are also under study. Levels of metals found in the muscle tissues are compared with the certified human consumption safety guidelines recommended by both international as well as national legislations.

2. Materials and methods

2.1. Study area

The BBE (Fig. 1) is a mesotidal system formed by a series of NW-SE tidal channels, separated by flats, marshes and islands (Melo, 2004). It is a coastal environment with two main cities located in the northern margins, Bahía Blanca (300,000 inhab.) and Punta Alta (60,000 inhab.) (INDEC, 2010). Both cities generate waste discharges of about 84,000 m^3/day (CTE, 2003), reaching the estuary with an incomplete pre-treatment. The main freshwater tributaries to the BBE are the Sauce Chico River (drainage area of 1600 km^2) and the Napostá Grande Creak (drainage area of 920 km^2) (Perillo et al., 2001). On the coastlines of these two tributaries there are important areas of cattle breeding and agriculture (Limbozzi and Leitào, 2008) adding different quantities of substances to the water courses without any further treatment.

The wetlands of the BBE are dominated by halophyte vegetation, principally *Spartina alterniflora* and *Sarcocornia perennis (*Negrin et al., 2016). Within estuaries, saltmarshes are widely recognized as important nursery grounds that support valuable coastal fisheries (Valiñas et al., 2012). *C. guatucupa,* together with *M. furnieri,* support the traditional fisheries of the Argentinean, Southern Brazilian and Uruguayan coastal regions (Jaureguizar et al., 2006; Ruarte et al., 2000). They are the most important fishing resources in the area of the BBE, in both social and economic terms (Carozza and Fernández Araoz, 2009; López Cazorla, 2004).

The estuary undergoes intense human-induced disturbances related to urban and industrial developments on its northern boundary, with the most important deep-water port system of Argentina located in the area. The port system contributes to the rapid resuspension of great volumes of cohesive sediment by means of the maintenance and deepening dredging activities. These activities promote the abrupt transfer of immobilized substances into bioavailable compounds that then are disseminated throughout the estuarine environment (Grecco et al., 2011). Several other industries taking part of a petrochemical center are also located in this harbor area (Limbozzi and Leitào, 2008).

2.2. Sample collection and preparation

Fish samples were caught with nets by local fishermen from the middle inner zone of the BBE (Fig. 1), consecutively during the spring season of 2011, 2012 and 2013. In total, 147 individuals were collected, corresponding to six fish species: *Brevoortia aurea*, *Odontesthes argentinensis*, *Micropogonias furnieri*, *Cynoscion guatucupa*, *Mustelus schmitti* and *Paralichthys orbignyanus*.

After being caught, fish samples were transported to the laboratory with ice. Body weight (in kg) and total body length (measured to the nearest cm) were recorded for each fish. Dissection was performed with a stainless steel knife in order to obtain