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Metals and arsenic in fish from a Ramsar site under past and present human pressures: Consumption risk factors to the local population

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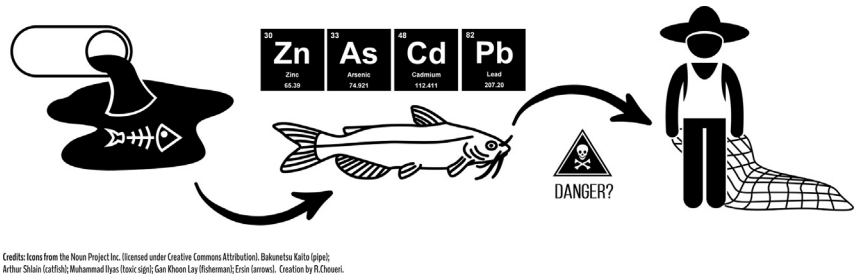
HIGHLIGHTS

- The risk of human health through the ingestion of fish was estimated.
- The study area is a Ramsar site polluted by mining activities and urbanization.
- The consumption of *C. spixii* pose risk to human health due to Cd, Pb and As.
- As in *C. spixii* showed high levels of cancer risk in the surroundings of the city.
- Traditional populations living in Marine Protected Areas may be under risk.

GRAPHICAL ABSTRACT



Credits: Icons from the Noun Project Inc. (licensed under Creative Commons Attribution). Bakunetsu Kaito (pipe); Arthur Shlain (catfish); Muhammad Ilyas (toxic sign); Gan Khoon Lay (fisherman); Ersin (arrows). Creation by R.Choueri.

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ABSTRACT

The risk of metals and As in seafood for traditional populations living in a Marine Protected Areas (MPA) is seldom assessed, although the risk of human exposure to contaminants is one of the indicators associated with the socioeconomic goals of MPAs. The current study aimed to estimate the potential risk of some metals (Cd, Pb, and Zn) and arsenic (As) for human health through the ingestion of fish locally harvested in a Ramsar site, the Cananéia-Iguape-Peruíbe Environmental Protected Area (APA-CIP). Previous studies showed environmental impacts in this area due to former mining activities and urbanization. *Cathorops spixii*, a catfish largely consumed by the local population, was collected along the estuary in three seasons with different rain regimes. Metals and As loads in muscle tissue were quantified and it was estimated (i) the target hazard quotient (THQ) and (ii) the daily intake (EDI) for metals and As, (iii) the cancer risk (CRisk) only for As, and (iv) the number of eligible meals per month. Cd, Pb, and As were found at concentrations above action levels for human consumption. Depending on the level of exposure of the local population, the consumption of *C. spixii* may pose risk to human health. Highest THQs were estimated for fish collected in sites closer to the main contamination sources in the APA-CIP, i.e. the mouth of Ribeira de Iguape River (P1) and the city of Cananéia (P4, P5, and P6). Arsenic showed high levels of cancer risk, although restricted to the area close to the city. The exposure of the local population to metal and As contaminated seafood cannot be disregarded in environmental studies and management of the APA-CIP.

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1. Introduction

Fish is an important protein source to the human population, providing around 37% of the total animal protein consumed by the human population worldwide (FAO, 2000). However, toxic substances released through human activities into aquatic ecosystems have often increased the bioavailability of contaminants to fish and biota in general. Seafood is a natural vehicle of metals to the human population (Copat et al., 2012; Begum et al., 2013).

Mining and smelting activities are serious threats to the aquatic environment in many countries (Kroll et al., 2005; Avellan et al., 2017). Mining contamination can occur mainly through acid drainage, atmospheric deposition, wind-blown particulate matter and mining waste disposal (e.g. Riba et al., 2005a; Taylor et al., 2014; Camizuli et al., 2014; Molina-Villalba et al., 2015). In some instances, such activities can affect more the surrounding areas than the local of the mining operations itself (Fernández-Caliani et al., 2008) since pollutants may be transported by water and air. In the environment, metals can accumulate in different environmental compartments (Riba et al., 2005b; Ruelas-Inzunza et al., 2011; Camizuli et al., 2014) including fish (e.g. Park and Curtis, 1997; Moiseenko and Kudryavtseva, 2001; Riba et al., 2005b; Jordanova et al., 2016). Metals accumulated in edible tissues of fish pose health risks to consumers (Rabitto et al., 2011; Tang et al., 2013; Sow et al., 2013). Indeed, the diet can be an important route of exposure in the case of populations indirectly exposed to mining activities (Fréry et al., 2001; Castro-González and Méndez-Armenta, 2008; Marrugo-Negrete et al., 2008; Zhuang et al., 2014). Therefore, studies focused on the quality of edible fish are relevant for characterizing human health risks in areas under the influence of mining activities (Subotić et al., 2013).

The Environmental Protected Area of Cananéia-Iguape-Peruíbe (hereafter referred as "APA-CIP", an acronym for the *Área de Proteção Ambiental de Cananéia-Iguape-Peruíbe*), Southeastern Brazil, is recognized as a World Natural Heritage Site by UNESCO (2000) and is part of the UNESCO's Biosphere Reserve of the Atlantic Rainforest. The area was recently included in the Ramsar's List of Wetlands of International Importance (https://rsis.ramsar.org/ris/2310). Apart from its ecological relevance, one of the objectives of the APA-CIP is protecting its cultural and historical value for traditional people, such as the traditional fishermen (known as *Caiçaras*), Maroons (known as *Quilombolas*), and native americans.

Small-scale fishery (primarily artisanal fishery) is among the most relevant economic activities in this area (Mendonça and Katsuragawa, 2001). Drag seines, gillnets, vertical longlines, surface drift gillnet, *gerival* (a type of beam trawl for shrimp fishing), dip net, covered pots (for capturing lobsters and prawn), and *iriko* (a small-mesh size net for catching anchovies) are the most common fishing gear in the area of the APA-CIP (Mendonça and Katsuragawa, 2001). More recently, the significance of recreational fishing (especially anglers) has been increasing as well (Barcellini et al., 2013). The madamango sea catfish (*Cathorops spixii*) is abundant in the APA-CIP and is one of the most fished species by both *Caiçaras* and recreational anglers (Mendonça and Katsuragawa, 2001; Motta et al., 2016). Despite not being the target specie neither for artisanal or for recreational fisheries, this catfish is largely consumed by local population (Favaro et al., 2005).

In spite of the legal protection of the APA-CIP (corresponding to category V of IUCN), this estuarine-lagoon environment has experienced increased contamination by metals from former mining activities located in the Ribeira de Iguape River basin (RIR). Additionally, the construction of an artificial navigational channel connecting the river with the lagoon favored the increasing input of metals toward the estuarine lagoon (Guimarães and Sígolo, 2008; Mahiques et al., 2009; Abessa et al., 2014). Recent studies showed that pollution is affecting the biota (Cruz et al., 2014; Gusso-Choueri et al., 2015, 2016).

Previous studies have also provided some evidences that metals and As body burdens in catfish from the APA-CIP could pose a risk to human health (Azevedo et al., 2012a; Gusso-Choueri et al., 2015). Cd, Pb, and Zn were found in the epaxial muscle tissue of *C. spixii* and *Genidens genidens* specimens at levels comparable to the specimens collected at a highly polluted estuary in Southeastern Brazil (Santos Estuarine System) (Azevedo et al., 2012a, 2012b). Hg was studied as well but the measured concentrations showed low levels in catfish tissue, which was an evidence of the low anthropogenic input of this substance in the APA-CIP (Azevedo et al., 2011, 2012b). Moreover, Hg is not related to the mining activities along the Ribeira de Iguape River basin (Guimarães and Sígolo, 2008; Melo et al., 2012; Piedade et al., 2014), thus it does not represent an element of concern for the region. Pb is the main element related to the mining activities in the RIR watershed. Previous studies reported high levels of Pb in the blood of children and adults living nearby the closed Pb refinery (Paoliello et al., 2002), and increased levels of As (compared to the reference area) in the urine of adults and children population (Figueiredo et al., 2007). Sakuma et al. (2010) also conducted studies of arsenic exposure of children from some sites across the RIR watershed and concluded that mining activities contributed to the presence of arsenic in their urine. Gusso-Choueri et al. (2015) made a very preliminary human health risk assessment, focused on *C. spixii* from the APA-CIP, by simply comparing the concentration levels of metals found in the edible part (the axial muscle) of the catfish with consumption limits provided by legal documents such as USEPA (2000), EC (2006), Mercosul (2011), FAO/WHO (2014), and the Brazilian Sanitary Vigilance Authority (ANVISA, 2013). Although this analysis already showed some exceedances, the approach was too simple and may not reveal, for example, the specific risk for sensitive subpopulations or people with increased susceptibility to toxicological effects, such as pregnant women and children (USEPA, 2000). In addition, the legal documents do not establish reference values for some potentially toxic metals (e.g. Zn). The calculation of risk factors to a certain human population is considered a more reliable approach.

The aim of the current study was to assess the potential risk of metals (Cd, Pb, and Zn) and arsenic (As) to human health due to the ingestion of catfish *C. spixii* fished in the APA-CIP. To achieve such a goal, *C. spixii* was sampled along the estuary in three seasons with different rainfall regimes. The human risk assessment was estimated by means of the daily intake (EDI) and the target hazard quotient (THQ) for metals and As, and the cancer risk (CRisk) for As (USEPA, 2000). Lastly, the number of eligible meals per month was estimated in order to subsidize management actions aiming to reduce the risk of chronic systemic effects.

We hypothesize that the consumption of *C. spixii* from some sites of the APA-CIP can pose risk to human health. The quality of human health has been suggested as one of the indicators associated with socioeconomic goals of Marine Protected Areas (MPA) (Pomeroy et al., 2005). However, the risk of dietary metals and As for people living in a MPA is rarely assessed. The current results will provide information that would be useful for the protection of the traditional population living in Marine Protected Areas affected by toxic metals pollution.

2. Material and methods

2.1. Study area

The Cananéia-Iguape-Peruíbe Environmental Protected Area (APA-CIP) (24°40'S and 25°05'S) presents two main climate seasons: a drier winter (mean temperature of 20 °C and mean pluviosity of 95.3 mm month^{-1}) and a rainier summer (mean temperature of 28 °C and mean pluviosity of 266.9 mm month^{-1}). The largest freshwater contributor to the estuarine lagoon is the Ribeira de Iguape River (RIR) (Fig. 1). The river flows into the lagoon through the *Valo Grande* channel, an artificial connection built in 1852 for navigational purposes which significantly altered the natural physicochemical and sediment characteristics of the estuary (Mahiques et al., 2013).