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Pb and Cd assessment in three catfish species from an estuarine ecosystem in São Paulo State, Brazil

Larrisa Y. Miranda[1], Marcos A. Hortellani[2], Jorge Eduardo S. Sarkis[3], Juliana S. Azevedo[4]

[1] larrisa.miranda@unifesp.br
Universidade Federal de São Paulo, Instituto de Ciências Ambientais, Químicas e Farmacêuticas (Unifesp/ICAQF)
Rua São Nicolau 210
09913-030, Diadema, SP
[2] mahortel@ipen.br
Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
[3] jesarkis@ipen.br
Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
[4] juliana.azevedo@unifesp.br
Universidade Federal de São Paulo, Instituto de Ciências Ambientais, Químicas e Farmacêuticas (Unifesp/ICAQF)
Rua São Nicolau 210
09913-030, Diadema, SP

1. Introduction

Coastal aquatic ecosystems such as estuaries are constantly subject to the input of chemical compounds, for instance toxic metals. The Cananéia-Iguape Estuarine-Lagoon Complex (CIELC) is located on the southern coast of the State of São Paulo and is recognized as a UNESCO natural heritage site [1]. Since 2017, it has been established as a priority wetland for conservation in the national and international context, i.e. as a Ramsar site [2]. The southern region of the CIELC receives a major oceanic influence, with more saline conditions and consequently greater chemical purification process and more natural environmental conditions. However, the northern region of this aquatic system is characterized by the freshwater inflow from an artificial channel that links the Ribeira de Iguape River directly to the estuary, representing an important input of different chemical compounds such as metals [3, 4]. Thus, although the region has around 90% of its territory protected by different conservation units [1], the effects of anthropogenic action, especially in the northernmost sector, in the Iguape region, can promote the entry of toxic metals into the system, such as lead (Pb) and cadmium (Cd) [3, 4].

Pb and Cd are non-essential metals, that is, without positive biological function for the organisms and, therefore, are consider toxic for the living organisms [5]. About 90% of Pb is stored in bone and the excessive accumulation of this element can cause changes in the absorption of Ca. Cadmium (Cd) is one the most toxic non-essential element due it high persistent in the environment and organisms, and their high capacity of to accumulate in the food chain [5].

Artisanal fishing is one of the economic activities still present in the region and estuarine species such as catfish from the Ariidae family are among the important representatives of local fishing resources [6, 7]. Furthermore, Ariids are eurihaline species, have benthic feeding habitat, feeding mainly of materials and organisms within the mud (silt and clay), where the bioavailability of contaminants is higher [8]

The goal of this study was to determine the Pb and Cd concentrations in target organs/tissues related to bioaccumulation process, such as muscle, liver, and gills of fish species from the CIELC, that have known ecological and economic importance to the region, namely the Ariidae catfish *Aspistor luniscutis*, *Cathorops spixii* and *Genidens genidens*.

2. Methodology

A total of 45 catfish (Siluriformes, Ariidae) of three species (*Aspistor luniscutis*, *Cathorops spixii* and *Genidens genidens*) were collected in the Cananéia-Iguape Estuarine Lagoon-Complex (CIELC) in November 2021 (rainy season). Fish were collected using a bottom otter trawl (1.6" mesh wall, 1.2" mesh cod end and 11 m length), lasting 10 minutes and trawling at a mean depth of 6 m at 3 mph. The sampling was made in two sites of the CIELC, i.e. southern region and northern region. After collection, fish were identified [9] and dissected for muscled, liver and gill extraction. The obtained samples were washed in ultrapure water and keep at -20°C until metal analysis.

Considering the total number of captured fish (n=45) and the three obtained tissues per animal, 135 samples were prepared for Cd and Pb determinations by Inductively Coupled Plasma Mass Spectrometer (ICP MS). Tissues were weighed, added 5 ml of 65% HNO_3 and 3 ml of 30% H_2O_2 to 1h30 for pre-digestion. After this time, added 2ml of milli-Q water to the individual samples that were taken to total digestion using a microwave (CEM Corporation, Mars 6 model), according to previously established analysis parameters [10]. The samples were diluted again (4 mL or 3 ml depending on sample with up to 10 mL of milli-Q water), 5 µg kg^{-1} of Indium (In) was added to each sample and the most abundant isotopes of each element were measured (Cd^{111} and Pb^{206}).

Results were expressed on wet weight basis as ng g^{-1} (ppb) and the analytical procedure was realized following method described by Azevedo et al. [10]. Limit of detection (LoD) and limits of quantification (LoQ) were 0.143 ng g^{-1} and 0.343 ng g^{-1} to Pb; and 0.016 ng g^{-1} and 0.042 ng g^{-1} to Cd, respectively. The analytical control was checked using certified reference material Dogfish muscle DORM-4, Dogfish liver DOLT-2 and Dogfish liver DOLT-3 (National Research Canada Council NRCC). The obtained results are show in Table 1.

Table I: Pb and Cd contents in the certified reference materials. Data are shown as mean±standard deviation (µg kg^{-1}) and recovery (%).

Element/Reference Mat.	**Certified**	**Found**	**%R**
Cd /Dolt-2	20.8 ± 0.5	16.9 ± 1.6	81
Cd /Dolt-3	19.4 ± 0.6	15.09 ± 0,05	78
Cd /DORM-4	0.306± 0.015	0.250 ± 0.002	83
Pb /Dolt-2	0.22 ± 0.02	0.28 ± 0.13	126
Pb /Dolt-3	0.32 ± 0.05	0.30 ± 0.01	93
Pb /DORM-4	0.416 ± 0.053	0.548 ± 0.366	131

%R: recovery in percentage.

3. Results and Discussion

In general, the liver shown the highest concentrations of Pb and Cd (Figure 1). However, there was a great deal of heterogeneity in the metal values (as evidenced by the high standard deviations). This can be explained by the inherent individual variability of each animal, which metabolizes metals differently depending on life stage (e.g., adult versus juvenile), age, and other bioecological factors [5].

There were no statistically significant differences in Pb and Cd levels between the three catfish species. However, there was greater bioaccumulation in the liver>gills>muscle direction to *G. genidens* and *A. luniscutis*, while to *C. spixii* the bioaccumulation profile was liver>muscle>gill. This pattern suggests a largest Pb and Cd intake of the external environment into the gills to G. genidens and A. luniscutis, both regarding to catfish from the southern and the northern sampling sites (Figure1).

Regarding spatial trends, the values found to Cd in the northern site were: *A. luniscutis* - gill: 1.015±1.143 ng g^{-1}; muscle: 0.089±0.216 ng g^{-1}; and liver: 1,162.165±68.995 ng g^{-1} / *G. genidens* - gill: 1.022±0.969 ng g^{-1}; muscle: 0.121±0.217 ng g^{-1}; liver: 69.518±28.504 ng g^{-1}) / *C. spixii* - gill: 0.275±0.476 ng g^{-1}; muscle: 0.998±0.696 ng g^{-1}; liver: 62.165±68.995 ng g^{-1}). On the other hand, Cd levels in the catfish for the northern region were: *A. luniscutis* - gill: 5.762 ng g^{-1}; muscle: 0.456 ng g^{-1};

liver: 71.039 ng g^{-1} / *G. genidens* - gill: 0.428±0.664 ng g^{-1}; muscle: 0.111±0.144 ng g^{-1}; liver: 59.794±22.157 ng g^{-1} / *C. spixii* - gill: 2.436±3.391 ng g^{-1}; muscle: 0.871±2.037 ng g^{-1}; liver: 70.602±34.305 ng g^{-1}.

With respect to Pb concentrations, in general, the spatial trends have not shown significant differences between the northern and southern regions. The Pb levels in catfish from the northern were: *A. luniscutis* - gill: 252.069±114.896 ng g^{-1}; muscle: 60.774±82.673 ng g^{-1}; liver: 254.606±133.233 ng g^{-1} / *G. genidens* - gill: 171.232±44.815 ng g^{-1}; muscle: 43.525±75.060 ng g^{-1}; liver: 181.835±55.287 ng g^{-1} / *C. spixii* - gill: 272.602±181.254 ng g^{-1}; muscle: 1.806±3.128 ng g^{-1}; liver: 473.141±295.242 ng g^{-1}. However, in the southern areas, the Pb levels were: *A. luniscutis* - gill: 318.960 ng g^{-1}; muscle: <DL; liver: 119.138 ng g^{-1} / *G. genidens* - gill: 238.638±53.288 ng g^{-1}; muscle: 8.032±16.181 ng g^{-1}; liver: 516.601±357.010 ng g^{-1} / *C. spixii* - gill: 105.029±88.347 ng g^{-1}; muscle: 229.181±687.543 ng g^{-1}; liver: 61.638±77.440 ng g^{-1}. These results suggest that some species share similar characteristics, indicating that the sampling sites directly influence the concentrations detected.

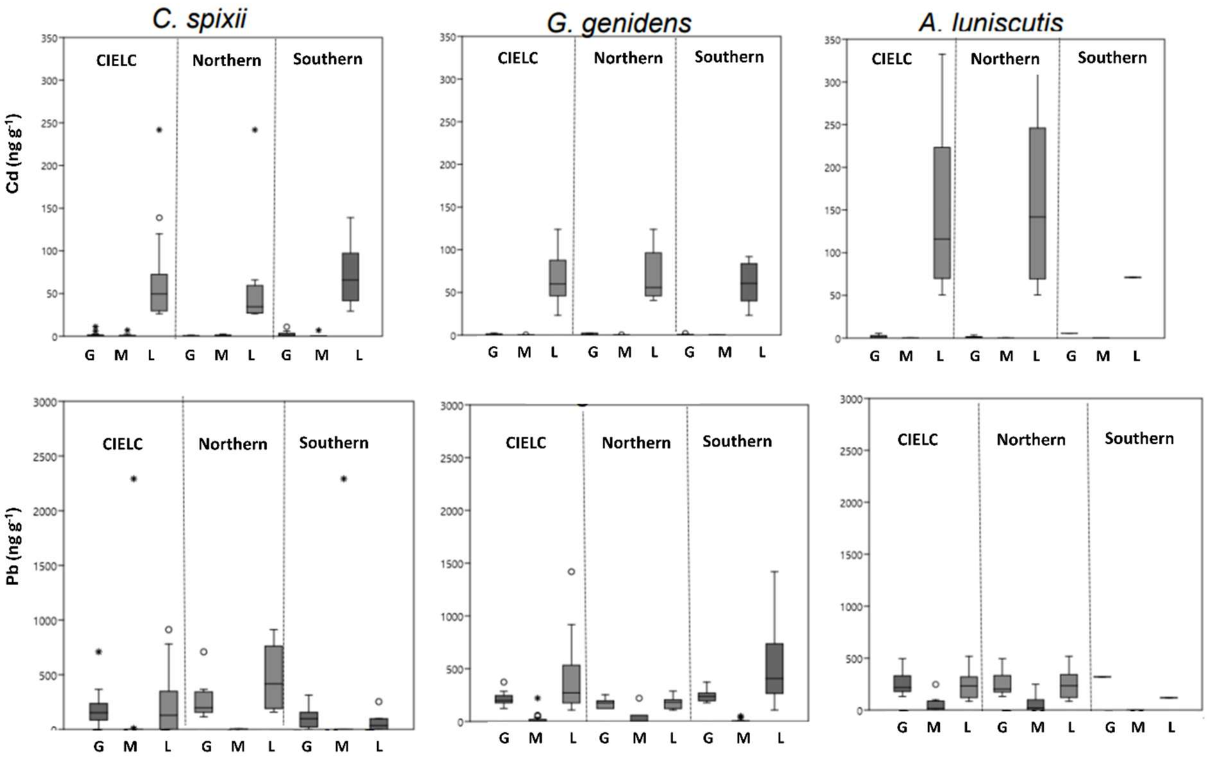

Figure 1: Cd and Pb contents in gill (G), muscle (M) and liver (L) tissues of three catfish species (*C. spixii*, *G. genidens*, *A. luniscutis*) from the Cananeia-Iguape estuarine Lagoon-Complex (CIELC). Data are shown to the estuary (CIELC) and grouped by sampling areas (northern and southern region).

4. Conclusions

The highest levels of concentration of metals observed in the liver confirm their important function in the detoxification process. Changes observed in the levels of metals between the muscle and gill can be associated to differences in the input of Cd and Pb in the CIELC, mainly considering the northern and southern region and their environmental characteristics. Despite the low concentrations of Pb and Cd found in the samples, the bioaccumulation in the different targe tissues is elucidative for advances in the studies of metabolic effects on these toxic metals in the three catfish species studied here.

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