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A PRELIMINARY TOXICOLOGICAL ASSESSMENT OF METAL CONCENTRATION IN SWIMMING CRAB (*Callinectes danae*) FROM SÃO VICENTE CHANNEL

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ABSTRACT

This preliminary assessment aimed to evaluate the concentrations of Cd, Cu, Hg, Pb and Zn in samples of the swimming crab *Callinectes danae* collected from the São Vicente Channel, in the Santos Estuarine System, comparing these results with limit levels for consumption set by Brazilian and European legislations. Sampling was conducted in December/2010, when ten swimming crabs were collected near to Mariana River, in São Vicente Channel. Swimming crabs muscle, hepatopancreas and gill tissues were removed by dissection. Digestion in high pressure microwaves system was used. Cd and Pb concentrations were determined by HR-ICP-MS, whereas Cu and Zn concentrations were measured using flame mode of a Fast- Sequential Atomic Absorption Spectroscope. Hg concentration was measured by cold vapor generation. Metal concentrations measured in this study corroborates with previous studies in other regions. Most of samples of swimming crabs tissues (including muscle tissue which is appreciated for consumption) presented metal concentrations in agreement to the Brazilian and European legislations, which confirms the quality of *Callinectes danae* collected from São Vicente Channel for consumption.
Keywords: *Callinectes danae*, swimming crab, metal, São Vicente Channel, Brazil

1. INTRODUCTION

The swimming crab *Callinectes danae* Smith, 1869 is found in brackish water environments such as estuaries and also in marine areas until 75 m depth. The species is distributed throughout the Atlantic Ocean from Florida, USA to the southern coast of Brazil [1], including the metropolitan region of Baixada Santista, which is densely urbanized.

Although this region is well known because of its distinct economical significance, it also has noticeable environmental importance since the mangroves of Santos Estuarine System, which surround the whole area, correspond to 43% of total mangrove area of the state of São Paulo [2].

Despite the implementation of control policies, anomalously high levels of multiple contaminants have still been recorded in the Santos Estuarine System [3]. This setting is historically, economically and environmentally important at a regional scale. Human

activities in the estuary started in the beginning of the 16th century, right after the arrival of the first Portuguese explorers in Brazil. The most important petrochemical and metallurgical industrial areas of Brazil (the industrial complex of Cubatão) and the largest commercial harbor of South America (the harbor of Santos) are also located inside this estuarine system.

Due to these circumstances and since *Callinectes danae* survival depends on the environmental quality of this estuary, periodic monitoring of metal concentration in tissues of swimming crabs is necessary, since *Callinectes danae* is an important resource explored by fishermen, mainly from traditional communities [4].

Virga et al. [5] and Virga and Geraldo [6] have already investigated the concentrations of Pb, Cd, Cr, Zn and Cu in individuals of genus Callinectes (including *Callinectes danae*) collected in Cubatão River. Besides these studies, few information was published about this species and its relationship with metals in the Santos Estuarine System, although many studies recorded high concentrations of metals in the local sediment (the species' habitat) [7] [8][9][10].

Thus, this study is a preliminary assessment of metal concentration in tissues of *Callinectes danae* collected in São Vicente Channel, Brazil. In a toxicological perspective, this study aimed to compare the obtained results with limit values set by Brazilian and European legislations, evaluating the quality of the blue crab for consumption.

2. MATERIAL AND METHODS

2.1. Study area and crab samples

Ten individuals of species *Callinectes danae* were collected in December/2010 near to Mariana River (23° 57.521'S, 46° 25.073'O), in the São Vicente Channel (Fig. 1).

Figure 1: Santos Estuarine System. The sampling site is indicated in yellow (Source: Google Earth)

Swimming crabs were identified according to Melo [1]. Total weight, carapace length and width were measured. Muscle, hepatopancreas and gill tissues were removed by dissection. Samples were carried to the laboratory and stored on -20°C until metal analyses.

2.2. Metal analyses

Digestion in high pressure microwaves system (CEM Corporation, model MDS—2000) was carried out. Based on Visnjic-Jeftic et al.[11], the acid extraction solution consisted of a mixture containing 5ml of HNO_3 sub boiling, 3 ml of H_2O_2 and 2ml of H_2O (Milli-Q) with a resistivity 18 MΩ at 25 °C. This mixture was added to 0.5 – 1.0g of each tissue sample or certified reference material in microwave HP-500 vessels (PFA Teflon, fluorocarbon polymer), which were appropriately sealed and heated in the microwave unit. The digestion conducted according the following method: power: 600 W, time of temperature ramp: 10 minutes; temperature: 145 ºC; hold time: 4.5 minutes.

Cd and Pb concentrations were determined by HR-ICP-MS Finnigan MAT, model Element. Cu and Zn concentrations were measured using flame mode of a Fast- Sequential Atomic Absorption Spectroscope Varian, model Spectr-AAS-220-FS. Particularly, Hg concentration was measured by cold vapor generation. Method validation was performed by analyzing certified reference material Lobster Hepatopancreas (TORT-2).

2.3. Descriptive and statistical treatment

The results obtained were compared to Brazilian [12] and European [13] legislations, which establish limit values of some inorganic elements in food.

3. RESULTS AND DISCUSSION

3.1. Method validation

Method validation was accomplished analyzing samples of certified reference material in three replicates. The recovery of samples for most metals during the validation process is presented in table 1.The recoveries of metals support reliable data, since they were above 70%.

Table 1: Recovery of TORT-2 samples submitted to acid digestion.

	Concentration measured±SD (μg g^{-1})	Certified concentration (μg g^{-1})	Recovery (%)
Cd	19.76±3.03	26.7	74.0
Cu	86.68±4.40	106	81.8
Hg	0.28±0.02	0.27	103.7
Pb	0.31±0.08	0.35	88.6
Zn	168.04±4.10	180	93.4

3.2. Biometric data and metal concentration

All individuals collected in this study were females. Total weight ranged from 11.7 to 89.6 g, with a mean value of 35.3±21.2 g. Carapace length and width varied, respectively, from 283 to 494 mm (mean= 379.8±60.9 mm) and from 500 to 852 mm (642.1±92.5 mm).

Concentrations of metals in muscle, gill and hepatopancreas tissues are presented in table 2. Gills presented the highest concentrations for most metals, except for Hg (higher in muscles) and Zn (higher in hepatopancreas).

Table 2. Concentrations of metals in muscles, gills and hepatopancreas of individuals of species *Callinectes danae* (max= maximum value; min= minimum value).

	Metals in muscles (μg g^{-1})					Metals in gills (μg g^{-1})					Metals in hepatopancreas (μg g^{-1})				
Individual	Cd	Cu	Pb	Hg	Zn	Cd	Cu	Pb	Hg	Zn	Cd	Cu	Pb	Hg	Zn
1	0.000	0.010	0.078	0.033	32.483	0.000	0.037	0.293	0.009	20.135	0.000	0.016	0.137	0.004	82.407
2	0.000	0.016	0.134	0.061	32.332	0.000	0.072	0.443	0.013	14.574	0.000	0.018	0.111	0.000	115.630
3	0.000	0.016	0.091	0.066	34.508	0.003	0.043	0.478	0.007	12.508	0.000	0.025	0.178	0.002	96.272
4	0.000	0.013	0.479	0.097	45.512	0.007	0.047	0.366	0.012	9.741	0.000	0.028	0.147	0.014	76.027
5	0.000	0.009	0.144	0.014	19.920	0.000	0.011	0.492	0.000	16.720	0.005	0.023	0.202	0.000	30.877
6	0.000	0.015	0.139	0.033	32.526	0.000	0.042	0.382	0.007	9.383	0.000	0.008	0.140	0.001	96.814
7	0.000	0.019	0.122	0.096	39.986	0.010	0.035	1.015	0.020	11.644	0.000	0.025	0.091	0.012	63.160
8	0.000	0.014	0.148	0.030	39.746	0.003	0.061	0.265	0.006	11.873	0.000	0.031	0.118	0.005	78.066
9	0.000	0.014	0.160	0.142	30.770	0.006	0.051	1.463	0.030	12.772	0.000	0.036	0.284	0.020	70.452
10	0.000	0.009	0.115	0.023	39.281	0.000	0.028	0.199	0.004	13.577	0.000	0.012	0.157	0.000	36.939
mean	0.000	0.014	0.161	0.06	34.706	0.003	0.043	0.540	0.011	13.293	0.001	0.022	0.157	0.006	74.664
min	0.000	0.009	0.078	0.014	19.920	0.000	0.011	0.199	0.000	9.383	0.000	0.008	0.091	0.000	30.877
max	0.000	0.019	0.479	0.142	45.512	0.010	0.072	1.463	0.030	20.135	0.005	0.036	0.284	0.020	115.630

The obtained results for Cd, Cu, Pb and Zn were similar to those observed by Virga et al.[5] and Virga and Geraldo [6] in *Callinectes danae* from Cubatão River. Assessing Hg concentration in *Callinectes danae* from Guanabara Bay (RJ), Wakasa [14] observed an average of 0.024±0.012 μg g^{-1} in muscle tissues, which was lower than that found in this study. Evaluating metal concentrations in *Callinectes danae* (Smith, 1869) from Mundaú-Manguaba Estuarine System (Al), Castelani [15] found Cu averages of 3.3±1.1 a 3.2±0.8 μg g^{-1} in viscera and in muscles, respectively. Rossi [16], in the same estuarine system, observed average concentrations of Cu and Zn of 5.1 ± 1.4 e 28.3 ± 3.5 μg g^{-1} in muscles and 4.6 ± 1.5 e 36.7 ± 6.8 μg g^{-1}, in viscera.

According to Brazilian legislation [12], the limits of Cd, Cu, Hg, Pb and Zn established for fishery products are, respectively, 1 μg g^{-1}, 12 μg g^{-1}, 0.5 μg g^{-1}, 2 μg g^{-1} and 50 μg g^{-1}. Due to European regulation [13], the maximum limit of Cd, Hg and Pb that should be found in crustaceans is 0.5 μg g^{-1}. Thus, although Zn was found in higher concentrations in

hepatopancreas, the concentrations of most metals in tissues samples were below these established limits, including muscle tissues (which are appreciated for human consumption).

3. CONCLUSIONS

In this preliminary study, metal concentrations in most tissues were below the Brazilian and the European legislation. Further studies of metal concentration in swimming crabs collected from other areas of Santos Estuarine System must be done, since it is necessary to confirm if this condition can be extend to the population of *Callinectes danae* present in this estuary.

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