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Full Length Research Papers

Study of metal and trace metals in shrimps *Macrobrachium rosenbergii* in creating captivity, aimed at domestic consumption and export.

Danilo C. Vasconcelos^a, Cláudia Pereira^a, Arno H. Oliveira^a, Mário R. S. Silva^a, Fernando R. Carvalho^a, Thiago C. de Oliveira^a, Maria A. C. Borges^b, Maria I. G. Severo^c and Linda Ayouni-Derouiche^d

^aDepartamento de Engenharia Nuclear, Universidade Federal de Minas Gerais – Bloco 4 – Escola de Engenharia, Av. Antônio Carlos, 6627- Campus Pampulha, CEP 31.270-901, Belo Horizonte, MG, Brazil.

^bEntrepósito de Pescados São Pedro Ltda. Prata, MG, Brazil

^cDepartamento de Biologia, Universidade Estadual de Santa Cruz, Km 22 rodovia Ilhéus–Itabuna, CEP 45650-000, Ilhéus, Bahia, Brazil.

^dService Central d'Analyse-Institut des Sciences Analytiques, 5 rue de la Doua - 69100 Villeurbanne, France.

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With the increase of global imports and exports, diversification of the food chain, changes of habits and consumer demands become necessary to use new strategies in the food industry, especially in terms of quality management and product safety. The world market currently requires knowledge of the concentrations of toxic contaminants at levels of trace and ultra-trace as well as the establishment of mechanisms that enable food traceability, ensuring the provision of safe and proven quality. To ensure the reliability of these data, since 1994, several international organizations have defined the concept of traceability, which was modified, and subsequently the European Parliament and the Council of the European Union adopted Regulation (EC) 178/2002, which became mandatory from January 2005. This study aims to determine the content of metals and trace metals in samples of shrimp, *Macrobrachium rosenbergii*, collected in the Prata City, region of the state of Minas Gerais, Brazil, for the domestic consumption and export. Ten samples of three different sizes (as traceability regulation) were collected at four different sites (breeding ponds available) over two seasons (considered representative of the climate in the region). The elements detected above $30 \mu\text{g g}^{-1}$, using Mass Spectrometry Inductively Coupled Plasma (ICP-MS), in different samples analyzed, were the Cu, Zn, Mg and Fe. Already the Cr, Cd, Pb, As and Hg were detected in trace levels. The values of all metals are below acceptable value, for daily consumption per unit, by the Food and Agriculture Organization - United Nations (FAO) and World Health Organization (WHO), with the exception of copper.

Keywords: traceability process; biomonitoring; shrimp; metals-trace

INTRODUCTION

Studies of the presence of organic and inorganic contaminants are methods used to obtain the concept of

traceability and bio-monitoring, which arose from the need to know the position of a product in the logistics chain. This

concept gained prominence in the 1990s, after a series of incidents involving the consumption of meat from animals affected by Bovine Spongiform Encephalopathy, BSE, mad cow disease, which in humans can cause Creutzfeldt-Jakob syndrome, degenerative neurological disease, with fatal consequences, initially in the UK and later in other European Union countries.

Traceability is the ability to trace, follow and identify uniquely a product unit or batch through all stages of production, processing and distribution (Derick and Dillon, 2004). That allows the control of risks during all production process steps. Thus, it is possible to react quickly in any event to protect consumer health. It is an important factor for quality and safety assurance of the products of animal origin. The main consumer markets of the world require products with quality certification (Hilbrands 2001). The International Standards Organization (ISO) defines traceability as:

"The ability to trace the history, application or location of that which is under consideration. When considering products this can relate to the origin of material and parts, and the processing history".

In Brazil, production of shrimp farms are growing and as so; the need to establish quality credibility for the consumer market. The production of freshwater shrimps of the type *Macrobrachium* is expanding. This production is based on two species: *Macrobrachium rosenbergii* (60%) and *Macrobrachium nipponense* (38%). The presence of heavy metals in the environment could hazard to food security and public health. They can be accumulated in aquatic animals such as shrimp, and be consumed by people.

Although traceability is not necessarily specifically mentioned all matters that relate quality, our research group of the Departamento de Engenharia Nuclear (DEN)/Universidade Federal de Minas Gerais (UFMG) began a research to quantify the levels of toxic metals in shrimp's fillet and to compare with values established by World Health Organization (WHO) and subsequently allowing to determine your quality and safety.

The first part of this research was quantify the concentration of toxic metals using ICP-MS in freshwater shrimps of specie *Macrobrachium rosenbergii* from a shrimp farm localized in Prata City, Minas Gerais State from Brazil.

METHODOLOGY

Site selection

All shrimp samples were collected from a shrimp farm São Pedro localized in Prata City, Minas Gerais State from

Brazil in dry and rainy seasons. That farm sells all production for Asian food restaurants in São Paulo. Figure 1 shows the location of the Prata city.

Sampling

240 samples were collected in four shrimp ponds and selected by size (post-larval, juvenile and adult) and immediately preserved in an ice box, and then they were taken to the laboratory.

Sample preparation

Total shrimp length and weight were measured. The muscles (edible parts) have been selected for lyophilization. After approximately 40 to 60 mg of each sample were digested in microwave using nitric acids.

Sample analysis

The samples were analyzed using Mass Spectrometry Inductively Coupled Plasma (ICP-MS), in the Institut des Sciences Analytiques, CNRS, Lyon, France, to determine the concentration of the metals: Cr, Cu, Zn, Mg, Fe, Cd, Pb, As, and Hg. Certified reference material of mussel tissue (ERM-CE278k) was used for quality control and assessment of method performance.

Statistical analysis

One way analysis of variance (ANOVA) was used to verify the difference between the length of the sample and the concentration of metals, with measures of association and correlation coefficient of Pearson $P < 0.05$.

RESULTS AND DISCUSSIONS

Measured concentrations of the *Macrobrachium rosenbergii* are shown in Table 1. The Cu, Zn, Mg and Fe were the most abundant elements in the different samples analyzed. There were detected traces of Cr, Cd, Pb, As and Hg.

Chromium

Traces of Chromium in muscle of the *Macrobrachium rosenbergii* were lower (0.68 ± 0.2 - $1.27 \pm 0.2 \mu\text{g.g}^{-1}$) than values limits of FAO/WHO $< 12 \mu\text{g.g}^{-1}$.

Copper

High levels of Cu were found in muscle material of the *Macrobrachium rosenbergii* (53 ± 5 - $86 \pm 6 \mu\text{g.g}^{-1}$). The according to FAO/WHO high levels of Cu ($60 \mu\text{g.g}^{-1}$) is toxic for humans, although it is essential for all living

*Corresponding Author's Email: danilochagasvas@gmail.com;
Tel: + 55 31 3499 6686; Fax: + 55 31 3499 6660.



Figure 1. Location of Prata city in Minas Gerais state from Brazil.

Table 1. Metal Concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ dry mass) in muscles of *Macrobrachium rosenbergii* and acceptable value for daily consumption

Length (mm)	Cr	Cu	Zn	Mg	Fe	Cd	Pb	As	Hg
50-85	0.72±0.2	53±5	38±3	1600±120	68±6	0.08±0.05	0.07±0.03	0.4±0.1	0.2±0.1
86-90	0.76±0.2	58±4	39±2	1713±125	117±11	0.11±0.06	0.07±0.01	0.3±0.1	0.03±0.03
91-99	0.76±0.2	86±6	43±4	1643±130	123±13	0.25±0.06	0.04±0.02	0.3±0.1	0.4±0.2
100-110	0.68±0.2	57±4	42±4	1661±140	54±6	0.13±0.08	0.04±0.04	0.2±0.2	0.2±0.1
111-180	1.27±0.2	60±5	44±3	1500±135	52±6	0.10±0.05	0.07±0.03	0.5±0.1	0.3±0.2
181-250	0.86±0.1	58±5	56±7	1710±130	52±4	0.03±0.01	0.07±0.04	0.4±0.1	0.2±0.1
FAO/WHO[4,5]	12	30	50	4000	60g[6]	1.0	2.0	*	1,0[7]

* None (except if indicated by manufacturing method or source)

organisms (Yilmaz and Yilmaz 2007). In crustaceans, copper is a constituent of the blood pigment hemocyanin.

Zinc

Zinc (38 ± 3 - $56\pm7\mu\text{g}\cdot\text{g}^{-1}$) has a much lower toxicity to crustaceans than copper (Canli and Furness 1993). The maximum zinc level permitted for food is $50\mu\text{g}\cdot\text{g}^{-1}$ according to FAO/WHO.

Magnesium

Magnesium is an essential mineral used in protein synthesis and the transport of energy. It is an essential mineral for the human body used for over 300 very important biological processes, including the production of

adenosine triphosphate (ATP) and muscle contraction. This metal in *Macrobrachium rosenbergii* was lower (1500 ± 135 - $1713\pm125\mu\text{g}\cdot\text{g}^{-1}$), than values limits of FAO/WHO ($<4000\mu\text{g}\cdot\text{g}^{-1}$) (FAO/WHO-JECFA 2002); (Stoltzfus and Dreyfuss 1997).

Iron

Iron deficiency causes anemia in the body, in excess this mineral can also be harmful to health and cause a disease called hemochromatosis. The iron in *Macrobrachium rosenbergii* was lower (52 ± 4 - $123\pm13\mu\text{g}\cdot\text{g}^{-1}$) than the value limits of International Nutritional Anemia Consultative Group (INACG), 60 g for daily consumption (Stoltzfus and Dreyfuss 1997).

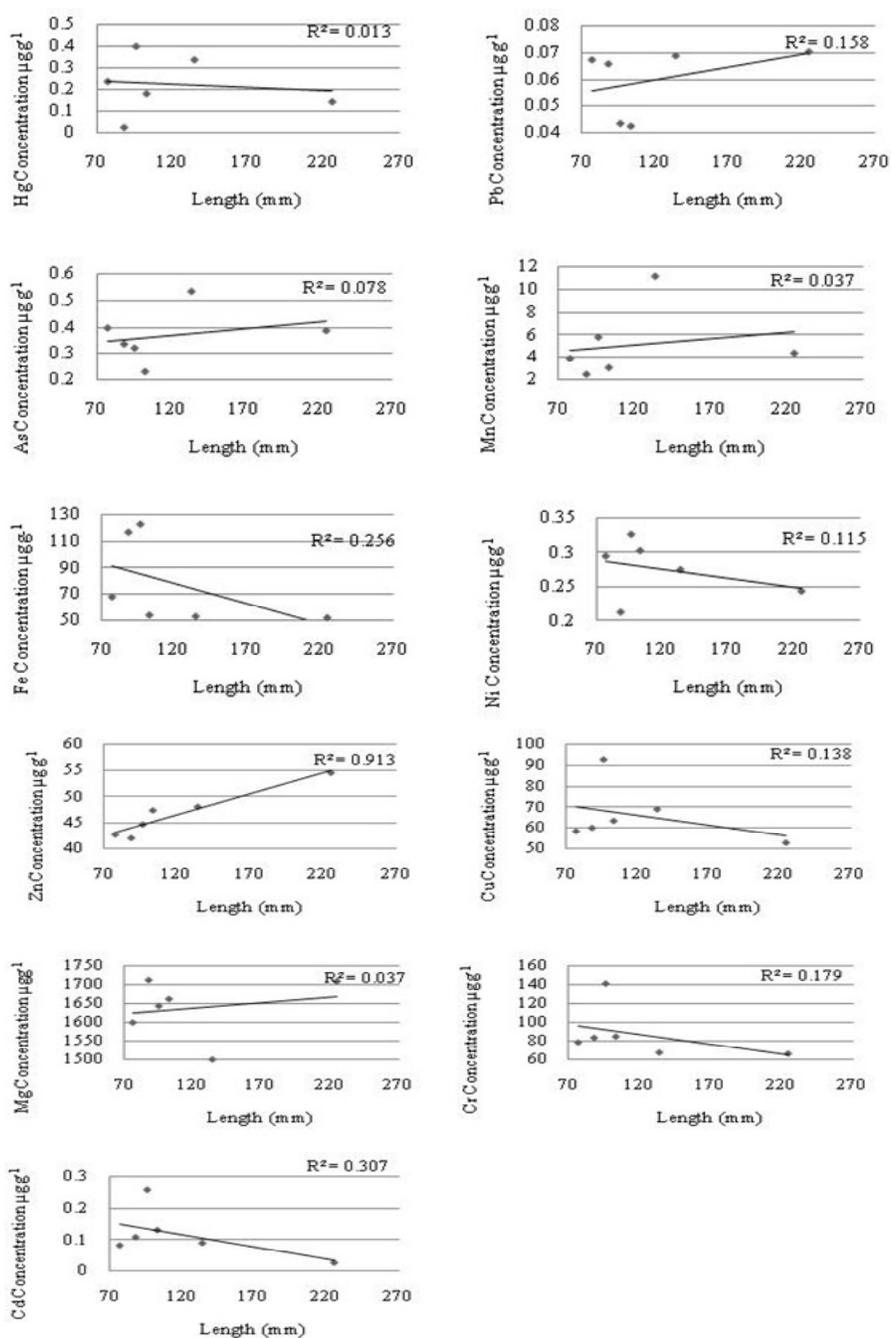


Figure 2. Pearson correlation between 6 set of length of shrimps and metal concentrations in the muscles.

Cadmium

Cadmium is a highly toxic metal causing long-term risks in humans. It means values of Cd in samples studies were not elevated ($<0.25 \pm 0.06 \mu\text{g}\cdot\text{g}^{-1}$).

Lead

Lead is a common contaminant of the environment due to its natural occurrence. Lead poisoning or compounds containing this metal can cause serious harm to health and

in some cases can lead to death. Lead occurs primarily in the inorganic form in the environment. Human exposure is mainly via food and water, with some via air, dust and soil (CONTAM 2013). Traces of lead in *Macrobrachium rosenbergii* were lower ($0.04 \pm 0.02 - 0.07 \pm 0.01 \mu\text{g.g}^{-1}$), than value limits of FAO/WHO ($<2.0 \mu\text{g.g}^{-1}$).

Arsenic

The element arsenic exists in nature in a variety of chemical forms, including organic and inorganic species, as a result of their participation in complex biological processes. High levels of toxicity from arsenic are very well known due to the arsenic compounds readily absorbed. Any consideration of the impact of arsenic to human health must take into account the various common chemical forms of arsenic to which man is normally exposed. This aspect of arsenic in relation to human health is given special emphasis. Traces of arsenic in *Macrobrachium rosenbergii* were lower than $0.4 \pm 0.2 \mu\text{g.g}^{-1}$, despite being a null value for acceptable daily intake, unless indicated by the method of manufacture or source.

Mercury

The provisional values for a tolerable weekly intake (TWI), established by the Joint Expert Committee of FAO / WHO Food Additives (JECFA) for methyl mercury, $1.6 \mu\text{g.kg}^{-1}$ body weight (b.w.) and $4 \mu\text{g.kg}^{-1}$ b.w. for inorganic mercury were still considered adequate by the European Food Safety Authority (EFSA). Agreed, the JECFA and the EFSA Panel on Contaminants in the Food Chain (CONTAM Panel) established to inorganic mercury $4 \mu\text{g.kg}^{-1}$ b.w., expressed as mercury. Values of Hg in studied samples no were elevated ($<0.4 \pm 0.2 \mu\text{g.g}^{-1}$) (CONTAM 2012). Figure 2 shows positive correlation between 6 sets of length of the shrimps and concentrations of metal in the muscles. There was no linear relationship between the variables concentrations of Cd, Cr, Cu, Mg, Fe, Pb, As, Hg and the length of the shrimps. However, there was positive Pearson's correlation between the Zn concentrations and length of the shrimps. Thus, the larger shrimp have higher concentrations of Zn than the smaller ones.

The intensive activities of the livestock and mining industries in the region known as Triângulo Mineiro, generate tons of waste left in the open that accumulate in considerable concentrations of heavy metals and toxic elements. These pollutants in the soil can be transported to surface waters and groundwater, causing changes in environmental quality.

CONCLUSION

This research evaluated the concentrations of essential and non-essential elements and analysis of variance

(ANOVA) used to investigate indices, with Pearson correlation $P < 0.05$, between the length of the samples and the concentration of metals and trace metals in shrimp *Macrobrachium rosenbergii*. The results shown that there was positive Pearson's correlation between the variables Zn concentrations and 6 set of length of the shrimps. Values of Cu in the muscles were greater than recommended levels ($30 \mu\text{g.g}^{-1}$). Information of the mean value of essential and non-essential elements in traceability process is an important contribution to ensuring the quality of the product for the consumer. The analysis of the elements mentioned above, using ICP-MS determined the toxicity and eco-toxicity of these organisms (sentinel) collected *in situ*, at different times, enabling the bio-monitoring for assessment of environmental quality within a spatial and temporal scale allowing and determining different gradients of contamination or pollution. Certificate seal should be studied to products as proof of quality and traceability.

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