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Trace elements in *Geophagus brasiliensis* fish from the Billings Reservoir - Riacho Grande, SP/ Brazil

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1. Introduction

Trace elements are essential for human health, but in excess they are considered toxic elements. When they are above what is tolerated by the human body, they cause numerous health problems. Trace element contamination can occur mainly through food, such as the ingestion of contaminated fish. For this study, 5 fish specimens of the *Geophagus brasiliensis* species were collected and analyzed. The collection was carried out in the Billings Reservoir, of the region of Riacho Grande, São Bernardo do Campo, São Paulo State, Brazil. This location was chosen because more than half of its territory belongs to a Watershed Protection Area (APM), being a priority for conservation, but with a lot of contamination with domestic sewage. This aspect of contamination becomes worrying because many fishermen and their families consume fish as the main protein nutrient, and have the possibility of being exposed to toxicity. However, fish is also considered an important protein source and very nutritious food, bringing relevant nutritional aspects to the maintenance of health. Despite the widely recognized nutritional power of fish, there may be health risks associated with its consumption from contaminated water. For this study, it was chosen to carry out the quantification of trace elements K, Mg, Mn, Na and V in fish samples of the species *Geophagus brasiliensis* collected in the Billings Reservoir by the fishermen of the District of Riacho Grande - (São Bernardo do Campo / SP) in the village of Jurubatuba, GPS coordinates (-23.80569597290783, -46.48676904100722). The elements were determined by Instrumental Neutron Activation Analysis (INAA).

In this case study, the quality of food consumed is a very important aspect, since food consumption by the population cannot be subject to any type of contamination risk [1]. Trace elements K, Mg, Mn, Na and V are considered essential for human health. Generally, humans are exposed to these metals by ingestion. Appropriate concentrations of V, for example, can help in the treatment of diabetes, but too high concentrations are involved in the pathogenesis of certain neurological disorders and cardiovascular diseases [2].

Therefore, the objective was to establish an updated spatial-temporal view of the amount of trace elements in the tissue of a fish of interest in the region, aiming to contribute to the guarantee of food safety, especially in relation to the daily recommendation of minerals established by Brazilian legislation.

2. Methodology

2.1. Fish sampling

Geophagus brasiliensis samples used in this analysis were obtained from artisanal fishermen from the Billings Resevoir. This species is knowm as *acará* in Portuguese and measures on average 15 to 40 cm. Samples were collected in the second half of 2019. Prior to performing any step for the quantification of the elements of interest in the fish samples, they were washed with demineralized water and subsequently lyophilized for removal of water from the tissues.

2.2. Instrumental Neutron Activation Analysis (INAA)

The comparative method of Instrumental Neutron Activation Analysis was used for the determination of K, Mg, Mn, Na and V. The analysis by INAA has been widely used because it has many advantages over other analytical methods and has great applicability, as examples, in the analyses of hair, nails, blood, urine and organ tissues. INAA has high sensitivity and accuracy with no risk of sample contamination after irradiation [3, 4, 5]. INAA is a technique that provides simultaneous and non-destructive multielement analysis, being an advantageous method and one of the most important of the techniques of qualitative and quantitative analysis of trace elements.

For the irradiation and measurement of the radioactivity of the elements, approximately 150 mg of the powdered samples were weighted in analytical balance (Shimadzu AEM-5200) in previously decontaminated 1.8 x 1.8 cm polyethylene bag (24 h in 10% v/v Merck HNO_3) and sealed (Selapack). A similar procedure was performed for two certified reference materials (CRM) *Micropogonias furnieri* [6] and NIST SRM 1566b - Oyster Tissue [7].

Elemental standard solutions (Spex CertiPrep) were pipetted into filter papers strips (Whatman 40) using Eppendorf pipettes with previously checked nominal volumes. For some elements, it was necessary to dilute the standard solutions in a 10 mL volumetric flask before pipetting them. The papers strips were dried at room temperature in a laminar flow hood then were folded and placed in polyethylene bags of the same sample size.

Each irradiation batch consisted of a sample or CRM and elemental standards. They were irradiated in the IEA-R1 Nuclear Reactor (IPEN/CNEN) at the pneumatic station for 30 s under thermal neutron flux of approximately 1.9×10^{12} cm^{-2} s^{-1}. After irradiation, the elements were determined by gamma spectrometry of radionuclides of these elements, performed in a CANBERRA HPGe detector (model GC2018) coupled to CANBERRA DSA 1000 digital spectral analyzer.

3. Results and Discussion

Z-scores were used to assess the quality of the INAA results using the reference materials Oyster Tissue 1556b, and *Micropogonias furnieri* TP-1 IPEN. It is considered approval criteria values $|z| < 3$, which means that the CRM results should be in the approximately 99% confidence interval of the certified value. Values of z-score were between ± 2, indicating appropriate accuracy for determination of the mass fraction of K, Mg, Mn, Na and V in the fish tissues under the same analysis conditions. Mg and V are not certified for *Micropogonias furnieri* TP-1 IPEN. Hence, z-scores were not calculated for these elements in this material.

Table I shows the mean mass fractions of Na, K, Mg, Mn and V of the *Geophagus brasiliensis* species. Results are reported with their standard deviations, as the natural variation of the specimens is higher than the uncertainty associated with the respective input quantities for the INAA method in this study.

Mg content varied between 3.08 and 4.82 g kg^{-1} in the musculature. In the Brazilian legislation, it is recommended by ANVISA the daily intake of an adult of 260 mg of magnesium. [8]. Magnesium is an essential and useful element in metabolism, but in cases of food poisoning, it can cause gastroenteritis,

drowsiness, nausea, dehydration and muscular incoordination [9].

Table I: Mass fraction (mean value ± SD) and Range of K, Mg, Mn, Na and V of *Geophagus brasiliensis* specimens (n = 5) obtained by INAA

Geophagus brasiliensis	**Element**				
	K (g kg^{-1})	**Mg (g kg^{-1})**	**Mn (mg kg^{-1})**	**Na (g kg^{-1})**	**V (mg kg^{-1})**
Mass fraction	3.28 ± 0.58	3.62 ± 0.26	0.086 ± 0.035	0.90 ± 0.32	0.60 ± 0.07
Range	3.72 – 4.73	3.08 – 4.82	0.070 – 0.155	0.52 – 1.20	0.48 – 0.72

Daily Mn recommendation is 2.3 mg in Brazilian legislation. The variation in Mn content was 0.070 for 0.155 g kg^{-1} in the musculature. Although Mn is essential for several functions in the body, such as the thyroid, it could also be involved in neurodegenerative diseases besides manganism, such as Parkinson's and Alzheimer's. Excess Mn facilitates changes in protein metabolism and DNA gene expression in brain cells and nerve endings, which can lead to the development of these disorders [9,10,11]. Other elements (K, Na and V) are not regulated by this resolution.

K and Na are related in human cellular metabolism and because they are eliminated by the kidneys, when in large quantities, they are hardly related to toxicity in the human body. There are more reports of imbalances in health due to their lack than due to their excess. Hypo-and hyperkalemia are the most commonly encountered electrolyte abnormalities involving K [12]. Hyponatremia and hypernatremia are common electrolyte disorders of Na and are associated with increased morbidity and mortality [13]. The variation in K content was 3.72 for 4.73 g kg^{-1} in the musculature and the variation Na for 0.52 – 1.20 g kg^{-1} in the musculature.

V content varied from 0.48 to 0.72 mg kg^{-1} in the musculature. V is known to cause toxic effects, but it also has positive health effects, including being essential to the body. As a therapeutic agent, it has actions such as: antidiabetic, anticancer and reversing the resistance of microorganisms to drugs. The insulinomimetic effect is the most studied among all, as diabetes is a common disease throughout the world population, currently about 150 million people in the world and the WHO forecasts a doubling of this number around 2025, which is why it is considered “The disease of the 21st century” [14, 15, 16]. Excess V can be toxic, when inhaled it can cause coughing up mucus, respiratory tract irritation and bronchitis. V ingested in excess causes decreased appetite, diarrhea and worsening of manic-depressive psychosis. It is also neurotoxic and nephrotoxic [17].

4. Conclusions

The procedure for the characterization of edible fish tissues by INAA was adequate, with satisfactory z-scores for the used CRMs under the same irradiation conditions. The musculature of five specimens of the fish *Geophagus brasiliensis* collected in Riacho Grande (SP/ Brazil) was studied, corresponding to the GPS coordinates of (-23.80569597290783, -46.48676904100722). The trace elements K, Mg, Mn, Na and V were determined in the samples. All these elements are essential for human health, but in excess they can bring risks, especially Mn, which is increasing the number of cases of toxicity. The analysis of dam fish is necessary as food safety resource and nutritional aspects of the food. The results obtained in relation to Mg and Mn are within the expected in relation to the allowed of daily ingestion. K, Na and V values are also within the expected values, comparing with results obtained in other studies using fish. Although aspects of food security have been discussed in this article, conclusions in this regard require further analyses.

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