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Determination of trace elements of fish from the lower portion of Pomba river by neutron activation

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1. Introduction

River systems have been impacted by human activities due to the use of pesticides and fertilizers for agriculture, changes in vegetation cover, release of *in natura* urban sewage and industrial effluents [1]. Specifically in Brazil, the release of industrial and domestic effluents is among the biggest sources of river degradation. One of the consequences of the strong relationship between the terrestrial and aquatic environment in rivers is the fact that interventions of anthropic origin in the first have strong effects in the second [2]. In Brazil, this process is linked to economic and urban development [3] and, in this context, not only terrestrial biodiversity is affected, but also aquatic ecosystems. However, these environments have been neglected in terms of management and conservation actions [4].

Due to the high industrialization and agricultural activities, rivers have often been contaminated by trace elements (TEs), which are the most dangerous contaminants for aquatic organisms and for man, due to their high potential for bioaccumulation, toxicity and persistence [5]. TEs can occur naturally in river ecosystems [6], however, mining activities, industrial effluents and agricultural activities, the main sources of TEs [7] may affect their concentrations. Certain TEs such as Zn, Co, Fe and Cu are essential for the development of organisms [6]. Elements such as As, Pb, Hg and Cd are non-essential and are toxic to organisms even at low concentrations [6]. Furthermore, high concentrations of essential TEs can be toxic [8]. High levels of TEs in fish can cause serious adverse health effects for people who consume this protein [9]. Therefore, the consumption of fish contaminated with TEs has become an important global concern [8] in the context of food safety.

Food safety is defined, according to the Food and Agriculture Organization (FAO) by all hazards that can make food injurious to the consumer’s health. In food safety, specific concerns about food hazards can be highlighted: microbiological hazards, pesticides residues, misuse of food additives, adulteration and chemical contaminants (including biological toxins) [10].

Contaminants are any substance not intentionally added to food, but present in it, whether by: production, manufacture, processing, preparation, treatment, packing, packaging, transport or as result of environmental contamination [11].

The river basin plays a prominent role in the historical and socioeconomic scenario of the States of Minas Gerais and Rio de Janeiro [12]. The region's commercial dynamics were the extraction of gold in the 18th century, coffee and sugarcane crops in the late 18th century, livestock farming in the mid-19th century and the installation of industries in the early 20th century [13]. Population migrations and commercial activities promoted changes in the landscape, with the existing biome being altered according to the socioeconomic interests of each period [13]. Considering the population growth in the region, with low adherence to the sanitary sewage system and the implantation of industries, the Pomba river basin assumed special importance in the use of water for different purposes. Therefore, this watershed started to receive different types of impacts along its drainage area [14]. The main impacts include (i) degradation of the vegetation cover, implying the relevant transport of sediments to the gutters of water courses and (ii) the absence of treatment of domestic and industrial sewage, which is discharged "*in natura* " and directly in water courses [14].

This work aimed analyzes the level of TEs to assess the food safety of five fish species from the Pomba river: - *Pachyurus adspersus, Satanoperca pappaterra, Prochilodus lineatus, Hypostomus luetkeni and Loricariichthys castaneus*, using the Instrumental Neutron Activation Analysis (INAA) technique.

2. Methodology

The specimens were obtained using the net fishing in the Pomba River potion. A muscle potion from each specimen was weighed, lyophilized, ground, accommodated and sealed in plastic packaging to then be packed in an aluminum envelope to be irradiated in the IEA-R1 Nuclear Reactor at IPEN - CNEN/SP under a thermal neutron flow of 2-5 10^{12} cm^{-2} s^{-1} during a daily operating cycle of this reactor (approximately eight hours). Gamma emission measurements (gamma spectrometry) were performed 7 and 14 days after irradiation using a high purity Germanium Canberra spectrometer (HPGe - GC2018) coupled with a digital spectral analyzer (Canberra DSA 1000).

3. Results and Discussion

The results of the concentrations of elements detected by the INAA technique are shown in table 1. The concentrations are calculated in mg kg^{-1}, except for the elements Ca, Fe, K and Nd, whose concentrations are calculated in percentage by mass in dry base. Table 1 also presents the species of the analyzed samples. Among the elements analyzed, arsenic metalloid is the only one that has a maximum content fixed within the scope of MERCOSUR, whose limit is 1 mg kg^{-1} (ANVISA, 2013). Figure 1 shows the comparison of As values obtained for each specimen with the maximum MERCOSUR value.

In an exploratory analysis, it is possible to verify that As contents obtained in this work are below the maximum value of MERCOSUR, presenting no risk to food safety.

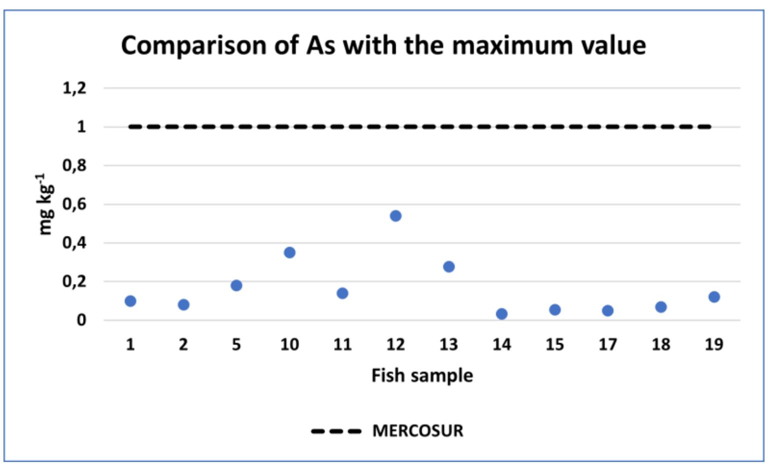

Figure 1: Comparison of As content in fishes species with MERCOSUR maximum limit. For specimens not shown in the figure, values lower than the detection limit were obtained.

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Table 1: Element concentrations, and their errors (E), obtained by Neutron Activation

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Species	*A*	*A*	*B*	*B*	*B*	*B*	*B*	*B*	*C*	*D*	*D*	*D*	*D*	*D*	*D*	*D*	*D*	*D*	*E*
As	0,10	0,08	<LD	<LD	0,18	<LD	<LD	<LD	<LD	0,35	0,140	0,54	0,278	0,034	0,054	<LD	0,05	0,068	0,12
E(As)	0,02	0,02			0,03					0,01	0,005	0,01	0,006	0,005	0,003		0,01	0,005	0,01
Ba	<LD	3,0	41	<LD	<LD	32	14	<LD	6	50	13	21	17	1,5	<LD	<LD	<LD	<LD	53
E(Ba)		0,8	4			2	8		2	5	2	4	4	0,2					10
Br	24,9	30,5	35,9	58,4	55,0	32,5	52,0	21,4	14,27	9,52	32,58	34,7	25,02	8,16	24,07	36,8	46,8	35,6	37,9
E(Br)	0,2	0,2	0,2	0,4	0,3	0,3	0,4	0,1	0,04	0,04	0,08	0,1	0,05	0,05	0,05	0,1	0,2	0,1	0,1
Ca%	1,26	1,28	2,61	2,52	0,92	1,61	1,76	0,69	0,20	3,10	1,56	2,41	2,91	0,03	0,02	0,45	<LD	0,12	3,8
E(Ca)	0,06	0,05	0,16	0,17	0,07	0,09	0,09	0,04	0,01	0,15	0,06	0,10	0,12	0,00	0,00	0,09		0,03	0,1
Co	0,33	0,253	0,24	0,38	0,65	0,271	0,49	0,40	0,206	0,56	0,534	0,68	0,55	0,061	0,072	0,047	0,11	0,107	0,88
E(Co)	0,01	0,004	0,02	0,03	0,02	0,009	0,01	0,01	0,004	0,01	0,007	0,01	0,01	0,002	0,003	0,007	0,01	0,004	0,02
Cr	<LD	1,98	2,2	1,9	1,3	1,3	2,5	2,7	1,9	4,4	2,2	2,8	3,9	0,86	0,6	<LD	5,1	6,6	9,2
E(Cr)		0,07	0,2	0,2	0,3	0,1	0,2	0,2	0,1	0,3	0,1	0,3	0,4	0,06	0,1		0,3	0,3	0,4
Fe(%)	0,0076	0,0097	0,017	0,010	0,0103	0,0083	0,0171	0,0253	0,0082	0,0085	0,0065	0,0117	0,0247	0,0143	0,0064	0,0181	0,0214	0,0161	0,094
E(Fe)	0,0008	0,0001	0,001	0,001	0,0008	0,0004	0,0004	0,0008	0,0001	0,0003	0,0002	0,0004	0,0006	0,0002	0,0003	0,0006	0,0009	0,0003	0,001
K(%)	1,1	1,2	1,1	1,6	1,3	0,52	2,1	1,2	0,43	0,22	0,25	0,22	0,207	0,35	0,27	0,46	0,61	0,47	0,35
E(K)	0,2	0,3	0,2	0,3	0,2	0,09	0,3	0,2	0,06	0,03	0,01	0,01	0,007	0,02	0,01	0,05	0,06	0,05	0,04
Na(%)	0,251	0,289	0,262	0,548	0,378	0,171	0,419	0,312	0,133	0,159	0,244	0,275	0,183	0,057	0,103	0,197	0,223	0,171	0,265
E(Na)	0,005	0,005	0,004	0,008	0,006	0,003	0,006	0,007	0,003	0,003	0,005	0,006	0,004	0,001	0,002	0,004	0,005	0,004	0,006
Rb	28	33	35	41	23	9,9	42	25	21	6,9	7,5	5,6	8,1	7,7	9,5	42	34	23	13,8
E(Rb)	2	2	2	2	1	0,6	2	2	1	0,5	0,5	0,5	0,7	0,5	0,7	2	2	1	0,8
Sc	0,014	0,0080	0,010	0,003	0,007	0,0072	0,0084	0,054	0,0212	0,0070	0,0043	0,012	0,040	0,0313	0,0013	0,008	0,012	0,0085	0,181
E(Sc)	0,002	0,0005	0,004	0,002	0,001	0,0005	0,0007	0,002	0,0003	0,0006	0,0001	0,001	0,001	0,0003	0,0003	0,001	0,001	0,0003	0,002
Zn	23	30	39	67	42	25	76	91	30	155	49	68	74	9	19	25	22	22	59
E(Zn)	1	1	2	3	2	1	3	3	1	4	2	3	4	0	1	1	1	1	3

species: A - Pachyurus adspersus, B - Satanoperca pappaterra, C - Prochilodus lineatus, D - Hypostomus luetkeni and E- Loricariichthys castaneus.
<DL means below detection limit.

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4. Conclusions

All values obtained for As concentrations are below the limit established by MERCOSUR, indicating that the consumption of species captured in the studied portion of the Pomba River is at safe levels for ingesting this element. The other elements detected and quantified by the INAA multi-elementary technique can compose databases for future discussions on adequate intake of micro and macro nutrients.

In the future, other toxic elements present in legislation (Cd, Hg and Pb) will be analyzed even in other fish species, In addition to the necessary comparisons on the consumption limits of Cr.

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