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Determination of K, Mg, Mn, Na and V in tissues of bivalve mollusks native to Caraguatatuba, SP, Brazil by Instrumental Neutron Activation (INAA)

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1. Introduction

Caraguatatuba, on the northern coast of the State of São Paulo, Brazil, coordinates -23,64773, -45,42481, is exposed to significant sources of marine pollution such as domestic effluents, oil and its derivatives. This is due to its hydrodynamic characteristics and its proximity to the São Sebastião Channel, where the discharge of submarine outfalls takes place and where the largest oil transport terminal in Brazil is located. Its coastline is partially sheltered by the presence of São Sebastião Island, which reduces the action of ocean waves, reflecting in low hydrodynamics and high input of materials and pollutants. The transport of surface water from the Channel to Caraguatatuba depends on the direction of the wind, depending on weather conditions, with NE (northeast) or SW (southwest) winds, but the transport and deposit of sediments is predominantly to the NE, occurring from the plains of the bay of Caraguatatuba and reaching the beaches further north of the municipality where Praia da Cocanha is located [1, 2, 3, 4].

As for sanitary quality, Caraguatatuba deserves to be highlighted, with treatment of 100% of the 64% of collected sewage. However, this positive condition can be affected by the proximity to the municipalities of Ilhabela, which has treatment of only 11% of the 16% of the collected sewage and São Sebastião, which treats 71% of the sewage, but collects only 46%, and in both municipalities, this sewage is released through an underwater outfall directly into the São Sebastião Channel [5, 6]. Furthermore, there are risks of accidents with oil spills and there were 232 accidents recorded between 1978 and 2000 [7]. In the last oil spill, in 2013, around 3,500 L of oil were released, reaching the bay of Caraguatatuba and the mussel cultures at Praia da Cocanha [8]. Anyway, Caraguatatuba continues to be an important stronghold of artisanal fishermen, mariculture farms and mollusk gatherers, which raises concerns regarding the consumption of these organisms by the local population and tourists [9, 10].

Trace and toxic elements from seawater and marine sediments can be accumulated by many species of marine invertebrates, especially filter-feeding mollusks such as oysters, scallops and mussels. The use of these species as biomonitors provides an estimate of the availability of trace elements to the biomass of different areas and locations. These mollusks, generally benthic, are able to accumulate pollutants without dying [11].

In a study in 2004, instrumental neutron activation analysis (INAA) was used to evaluated the pollution of coastal areas of the Peninsula of Malaysia, analyzing the levels of trace and toxic elements in bivalve mollusks. The authors concluded that bivalves have great potential to be used as biomonitors [11]. INAA has been widely used, as it has many advantages over other analytical methods and has great applicability, having high sensitivity and accuracy, providing multi-elemental analyses, being an advantageous method and one of the most important qualitative and quantitative analytical techniques for trace elements [12].

The intention of this study was to determine the concentration of the elements K, Mg, Mn, Na and V in three species of native bivalves: *Tivela mactroides* and *Anomalocardia brasiliana* cockles and *Perna perna* mussels, using INAA to assess the potential of using these species as biomonitors.

2. Methodology

To determine the elements K, Mg, Mn, Na and V, mollusks of the species *Tivela mactroides*, *Anomalocardia brasiliana* and *Perna perna* were used. Cockles were collected at the beaches of Porto Novo (PN-1), Palmeiras (PA-2), Indaiá (IN-3), Centro (CE-4) and Camaroeiro (CA-5) in the bay of Caraguatatuba and the mussels were acquired in the cultivation of Praia da Cocanha (CO-6), in the winter of 2019.
After removing the organisms from the shells, the samples from each site were crushed, homogenized, lyophilized and ground. After this preparation, triplicates were made of the sample from each site, being weighed on an analytical balance with about 0.150g, packaged in previously decontaminated polyethylene vials and sealed. The same procedure was used for two certified reference materials (CRM) NIST SRM 1566b - Oyster Tissue [13] and IPEN TM-1 - Mussel Tissue [14]. Multi-element standards were produced using filter paper strips with nominal masses for each element of interest previously verified, being packaged in polyethylene vials and sealed in the same sample size of the samples.
Each batch of irradiation consisted of a sample or CRM and multi-element standards. They were irradiated in the IEA-R1 Nuclear Reactor at the Research Reactor Center (CERPq) at the Nuclear Energy Research Institute (IPEN/CNEN) by the pneumatic station for 30 s under a thermal neutron flux of approximately 1.9 x 10^{12} cm^{-2} s^{-1}. After irradiation, the elements were determined by gamma spectrometry of the radionuclides of these elements, performed in a CANBERRA HPGe detector (model GC2018) coupled to a CANBERRA DSA 1000 digital spectral analyzer.

3. Results

Z-scores for each element of interest in this work were calculated for the used CRMs. The results are only considered satisfactory when z-scores are in the range of $-3 < z < 3$. Our results were < 2 for all elements and CRMs analyzed under the same conditions as the samples, indicating that the used INAA method is satisfactory, guaranteeing the reliability of the results obtained in the analysis of the samples.
The mass fractions of Na. K, Mg, Mn and V in the analyzed bivalve species are shown in Table I.

Table I: Mass fraction (mean ± standard deviation) of K. Mg. Mn. Na and V in bivalves mollusks from Caraguatatuba (n = 3)

site	species	g/kg			mg/kg	
		K	Mg	Na	Mn	V
PN - 1	*T. mactroides*	11.95 ± 0.92	3.85 ± 0.63	26.40 ± 2.30	28.70 ± 1,60	0.46 ± 0.07
PA - 2	*T. mactroides*	10.17 ± 0.78	5.33 ± 0.79	20.86 ± 2.21	18,60 ± 6.62	0.24 ± 0.23
IN - 3	*T. mactroides*	10.44 ± 1.37	7.88 ± 2.00	22.01 ± 0.15	29.24 ± 1.58	0.58 ± 0.12
CE - 4	*T. mactroides*	13.33 ± 0.70	9.97 ± 2.89	27.10 ± 1.28	37.82 ± 1.84	0.34 ± 0.29
CA - 5	*A. brasiliana*	12.94 ± 1.53	3.44 ± 0.64	19.86 ± 0.77	13.78 ± 1.13	0.33 ± 0.30
CO - 6	*P. perna*	13.47 ± 0.93	6.41 ± 0.13	46.00 ± 1.35	7.06 ± 0.65	0.68 ± 0.32

In the results, it was observed that the K mass fractions were similar among the tissues of the analyzed bivalve species. The largest Mg mass fractions were found in the tissues of the species *T. mactroides* and the smallest in the tissue of the species *A. brasiliana*.
The Na mass fractions in the analyzed samples followed the influence of salinity, characteristic of its habitat. The *P. perna* mussel is from a marine environment, being the one with the highest concentration of this element. The cockle *A. brasiliana* had the lowest Na mass fraction, being a typical species from an estuarine environment. The *T. mactroides* cockle had an intermediate Na mass fraction.
The largest Mn mass fractions were found in the *T. mactroides* cockle tissues and the smallest fraction in the *P. perna* mussel tissue. However, mussels had the highest mass fraction of V.

Regarding the *T. mactroides* cockle collection sites, the mass fractions of K, Mg and Mn were relatively close, with the exception of Praia do Centro (CE-4), with mass fractions higher than those of the other sites.

4. Conclusions

In this study, the mass fractions of K, Mg, Mn, Na and V were determined in 3 species of bivalve mollusks from Caraguatatuba, São Paulo State, Brazil by Instrumental Neutron Activation Analysis. The largest mass fraction variation was observed for *Perna perna* mussels, from the mariculture farms at Praia da Cocanha, particularly for the Mn and V trace elements. Slight mass fractions differences were observed for the 2 cockle species (*T. mactroides and A. brasiliana*) from the different sites of the bay of Caraguatatuba. The observed differences may be due to differences in the biological roles of the studied elements for each species but may also reflect different element availability in the different sampling sites. These preliminary results are still under evaluation and will be better understood with the analysis of other elements in the tissues of these animals and surrounding sediments, and with the correlation of ecotoxicological analyzes of the points that were collected.

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