Original Article

Chemical elements in sediments and in bivalve mollusks from estuarine regions in the south of Bahia State, northeast Brazil

Elementos químicos em sedimentos e em moluscos bivalves de regiões estuarinas do sul do Estado da Bahia, Nordeste do Brasil

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Abstract

Estuaries receive daily inputs of chemical elements which can impact the quality of water and sediment, as well as the health of biota. In addition to the sediment, bivalve mollusks have been used in the chemical monitoring of these systems. This study investigated the presence and contents of **As**, **Ba**, **Cd**, **Co**, **Cr**, **Cu**, **Fe**, **Mn**, **Ni**, **Pb** and **Zn** in superficial sediment and in bivalves (*Crassostrea gasar*, *C. rhizophorae* and *Mytella guyanensis*) from estuaries in the south / extreme south of Bahia State, northeast Brazil. The samples were evaluated with inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 710). Except for **Cd**, all other elements were found in the samples, being that **Co** was exclusive in the sediment. The estuaries equivalent to sampling stations #1 - Valença, #2 - Taperoá, #3 - Ilhéus and #4 - Belmonte showed levels of metals compatibles with those established by the Brazilian legislation, however, the #5 - Santa Cruz Cabrália, in addition to the presence of **As**, presented a high level of **Pb** and **Cu** in *C. gasar*, which was attributed to the impacts of nautical activities in that locality.

Keywords: arsenic, heavy metals, lead, mangroves, pollution, preservation.

Resumo

Estuários recebem entradas diárias de elementos químicos, que podem impactar a qualidade de água e do sedimento, assim como a saúde da biota. Além do sedimento, moluscos bivalves têm sido utilizados no monitoramento químico desses sistemas. Neste estudo investigou-se a presença e os teores de **As**, **Ba**, **Cd**, **Co**, **Cr**, **Cu**, **Fe**, **Mn**, **Ni**, **Pb** e **Zn** no sedimento superficial e em bivalves (*Crassostrea gasar*, *C. rhizophorae* e *Mytella guyanensis*) de estuários do sul / extremo sul do estado da Bahia, Nordeste do Brasil. As amostras foram avaliadas por espectrometria de emissão óptica de plasma indutivamente acoplado (ICP-OES, Varian 710). Exceto **Cd**, todos os demais elementos foram encontrados nas amostras, sendo que **Co** foi exclusivo no sedimento. Os estuários equivalentes às estações amostrais #1 - Valença, #2 - Taperoá, #3 - Ilhéus e #4 - Belmonte mostraram níveis de metais compatíveis com os estabelecidos pela legislação brasileira, porém, a #5 - Santa Cruz Cabrália, além da presença de **As**, apresentou alto nível de **Pb** e de **Cu** em *C. gasar*, o que foi atribuído aos impactos por atividades náuticas nesse local.

Palavras-chave: arsênio, metais pesados, chumbo, manguezais, poluição, preservação.

1. Introduction

Estuaries and mangroves receive daily discharges of chemical elements, like heavy metals. This input being the partial result of natural processes, whose substances are usually leached from their place of origin and transported by river waters to their final destination, represented almost always by estuarine sediments (Liu et al., 2020). However, human activities, such as the discharge of industrial and domestic effluents into water bodies, are the most accountable for the increase in chemical levels in these systems (Bakshi et al., 2017; Charry et al., 2018). When a chemical element is released into the aquatic

environment, it usually associates with particulate matter in suspension, being subsequently deposited in the sediment and, through remobilization, the particles of the element return to the water column, then becoming bioavailable (Hatje et al., 2009).

All aquatic invertebrates accumulate, to a lesser or greater degree, chemical elements in their tissues, whether they are essential or not to their metabolism (Rainbow, 2002). When the rate of elimination (by detoxification or excretion) is less than the rate of entry of the chemical agent into the organism, bioaccumulation occurs (DeForest et al.,

2007; Gomes and Sato, 2011). For this reason, in chemical studies and monitoring of estuarine areas, in addition to sediment, biological matrices have also been used. Bivalve mollusks are especially interesting in this context because they have a filtering habit, are generally sessile and usually have a wide geographical distribution (Kimbrough et al., 2008; Melwani et al., 2014). Metals are transferred to bivalve tissues through phytoplankton, which is at the base of the marine food chains (Bragigand et al., 2004).

On the Brazilian coast, sediments have often been used in the analysis of metallic contaminants in aquatic systems (e.g., Onofre et al., 2007; Hatje et al., 2008; Barros and Barbieri, 2012; Mirlean et al., 2012; Kim et al., 2016; Cagnin et al., 2017; Silva et al., 2018). Bivalve mollusks have also been gaining prominence as metal analysis matrices, citing the studies done by: Barros and Barbieri (2012) in Cananeia Estuary (São Paulo, SE-Brazil), using *Crassostrea brasiliana* (= *C. gasar*) (Adanson, 1757) (Ostreidae), Lino et al. (2016) in Guanabara Bay and in Ilha Grande (Rio de Janeiro, SE-Brazil), with respective use of *Perna perna* (Linnaeus, 1758) (Mytilidae) and *Nodipecten nodosus* (Linnaeus, 1758) (Pectinidae), Campolim et al. (2018) in Santos Bay (São Paulo, SE-Brazil), using *P. perna*, Barbosa et al. (2019) in Todos os Santos Bay (Bahia, NE-Brazil), using *Anomalocardia brasiliana* (Gmelin, 1791) (Veneridae), *Iphigenia brasiliana* (Lamarck, 1818) (Donacidae), *Lucina pectinata* (Gmelin, 1791) (= *Phacoides pectinata*) (Lucinidae) and *Trachycardium muricatum* (Linnaeus, 1758) (Cardiidae), Moreira et al. (2019) in Mucuripe bay (Ceará, NE-Brazil) with *Anomalocardia flexuosa* (Linnaeus, 1767) (Veneridae) and *Crassostrea rhizophorae* (Guilding, 1828) (Ostreidae), and Vilhena et al. (2021) in estuaries of the Mocajuba, Tijoca and Pará Rivers (Pará, N-Brazil), using *C. gasar* and *Paxyodon ponderosus* Schumacher, 1817 (Hyriidae).

In the present study, we used sediment samples and also the bivalves: oysters *C. rhizophorae* and *C. gasar*, and the mangrove mussel ("sururu") *Mytella guyanensis* (Lamarck, 1819) (Mytilidae) as metal analysis matrices. *Crassostrea rhizophorae*, the mangrove oyster, lives generally on aerial roots (rhizomes) and stems of red mangle *Rhizophora mangle* L., while *C. gasar*, the bottom oyster, is often attached to rock outcrops, clearly at a lower intertidal level than *C. rhizophorae* (Boehs et al., 2019). In turn, *M. guyanensis* lives superficially buried in mangroves, adhering by byssus to underground roots of mangrove plants (Boehs et al., 2010). The three species are economically important throughout the Brazilian coast, mainly as extractive resources for coastal populations.

The estuaries in the south of the state of Bahia, comprising a coastal region of approximately 500 km of extension, are poorly contemplated in relation to studies on chemical elements, citing the study made by Hatje et al. (2008) in sediments from Camamu Bay, as well as by Cagnin et al. (2017) in mangroves and in the continental shelf region of Abrolhos and by Angeli et al. (2019) in Caravelas estuary, both in the extreme south of the State. In Todos os Santos Bay, central region of the State, there are the works done by Onofre et al. (2007) and Barbosa et al. (2019), analysis of metals in sediment and bivalves, respectively. In the present study we aimed to investigate the presence and content of the elements As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in estuaries in

the south / extreme south of the state of Bahia, between the municipalities of Valença and Santa Cruz Cabrália. The hypothesis of the study is that the mangroves/estuaries in the region are little impacted by chemical elements, given the low industrial activity and other potentially polluting sources in this region.

2. Material and Methods

2.1. Study area

The study was conducted in estuarine areas between latitudes 13°26' S and 15°87' S, along a coastal stretch of about 450 km in length (Figure 1). This region, which comprises the south/extreme south coast of the Bahia State, northeastern Brazil, is characterized by the presence of numerous estuaries and extensive mangroves, whose forests are predominantly constituted by the red mangrove *Rhizophora mangle* (Brasil, 2018). The region has an *Af* type climate in the Köppen classification (humid tropical climate, without a dry season, with an average temperature of the warmest month exceeding 18 °C and total rainfall in the driest month exceeding 60 mm). This coast is also defined by the cocoa culture (mainly in Ilhéus and Belmonte counties) and by the extraction of fishing resources, as well as for beach tourism. Several stretches are protected by Environmental Protection Areas (EPAs), such as the Guaibim and *Caminhos da Boa Esperança* in municipalities of Valença and Taperoá, the *Lagoa Encantada/Rio Almada*, in Ilhéus and the *Coroa Vermelha*, which covers part of the coast of Santa Cruz Cabrália. According to Brasil (2018), these conservation units are primarily responsible for protecting biological diversity and ensuring the sustainability of natural resources in coastal areas, including estuaries and mangroves.

2.2. Field methodology

Sampling was carried out in December 2018 in five estuaries (#1- Valença, #2 - Taperoá, #3 - Ilhéus, #4 - Belmonte and #5 - Santa Cruz Cabrália) (Figure 1). The collects of sediment and of biological material was previously authorized by the Chico Mendes Institute for Biodiversity and Conservation - ICMBio, Brazil, License number 20912-6. Manual samples of surface sediment were obtained at each estuary, with three repetitions. With regard to bivalves, were captured 15 to 30 specimens / species / estuary, being that *C. rhizophorae* was collected from the aerial roots and trunks of the red mangrove *R. mangle*, *M. guyanensis* in the sediment among the mangrove trees (where sediment samples were also obtained) and *C. gasar* in artificial substrate in an area of pier, close to the ground. This last bivalve was collected only at #5, as the only analysis matrix at that place. Sediment and bivalves were packed in properly labeled plastic bags and transported in polystyrene boxes with ice to the laboratory.

2.3. Laboratory processing

Sub-samples of sediment were separated, in triplicate, which were dried in an oven at 65 °C until constant weight, after which the sediment was macerated, sieved and stored in plastic tubes, at room temperature. Nitric acid (HNO_3)
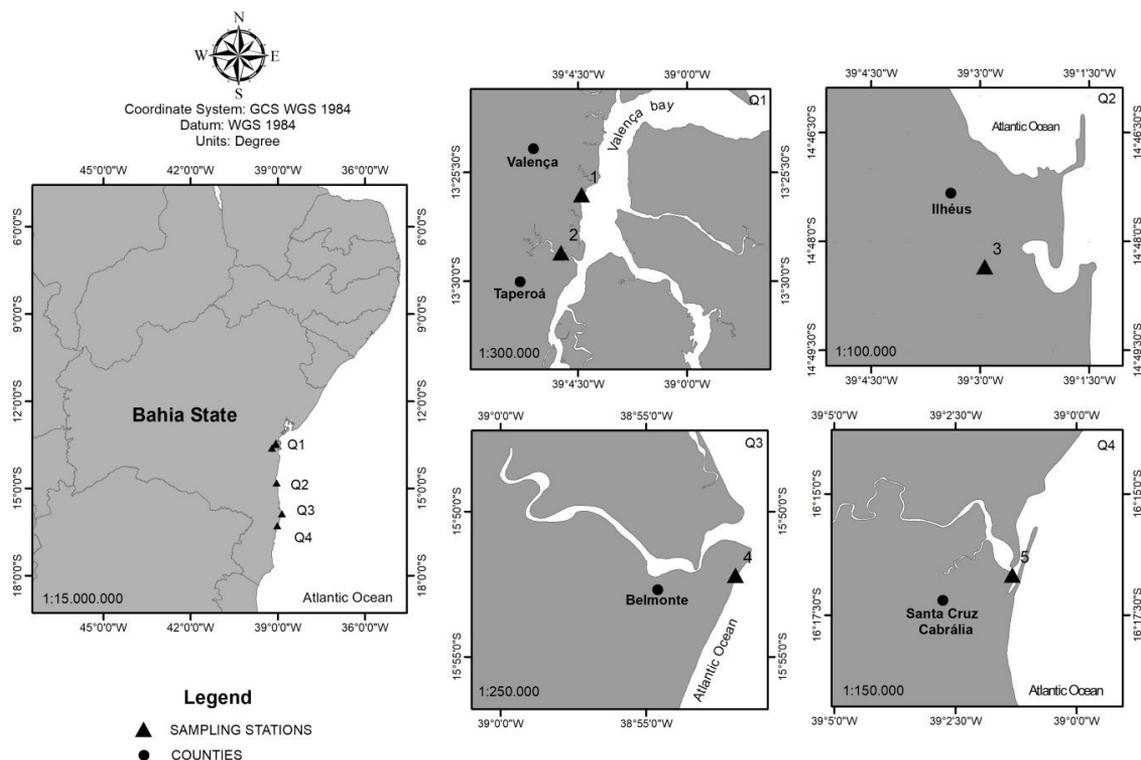
Figure 1. Map of the region indicating the sampling stations and counties, where Q1-Q4 define details of each sampling station.

10% was used for 24 hours for the previous decontamination of the tubes. Procedures for processing bivalves included: measurement of animals (shell height = distance between the umbo and the ventral region; Galtsoff, 1964), removal of the shell, washing the edible part (meat) with Milli-Q water (to remove possible impurities), freezing the samples in a freezer at -80 °C, lyophilization (FreeZone 4.5 L Labconco) until constant weight, manual crushing with the help of mortar and pistil, screening, and storage in plastic bags at -20 °C.

The digestion process was based on the protocols of the Environmental Protection Agency (EPA, 1996) and Costa et al. (2009), for sediment and bivalves, respectively. For the determination of the chemical elements in all matrices, an Inductively Coupled Plasma Optical Emission Spectrometer - ICP-OES (Varian 710 - ES) was used. For the validation of the chemical analysis of the elements, was used standard reference material certified by the Environmental Protection Agency (EPA, 1996).

2.4. Data processing and parameters of Brazilian legislation

The values of the chemical elements were compared among matrices and among localities through one-way analysis of variance (followed, when convenient, by Tukey's test) or by Kruskal-Wallis test, according to the normality of the data, with use of BioEstat 5.0 software. The data were also analyzed through a Principal Component Analysis - PCA, in the MVSP-Multi-Variate Statistical Package, version 3.22. For this analysis, the

data (variables = matrices / localities and cases = chemical elements) were standardized and transformed into log (2). For all analyzes, a 95% confidence level (α = 0.05) was used.

As legal parameters for maximum values contained in the matrices for each element, was used the Resolution nr. 420 of the National Environment Council - CONAMA (Brasil, 2009) for soils, as the Decree number 55.871 (Brasil, 1965) and Ordinance number 685 (Brasil, 1999), both from the National Health Surveillance Agency of the Ministry of Health - ANVISA, for food.

3. Results

Except for **Cd**, all the elements investigated (**As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb** and **Zn**) were detected in the samples. **Co** was exclusive in the sediment and this matrix was still characterized by high **Fe** contents, as well as by expressive values of **Ba, Cr, Mn** and **Zn**, the latter, however, in lower levels than those found in bivalves (Tables 1 and 2).

As was found only in #5 - Santa Cruz Cabrália, whose sampling station was also characterized by high levels of **Pb** and **Cu** (Table 1; Figure 2) in *C. gasar*. Regarding **Pb**, #5 was the only place where this metal was found in a biological sample, since in other localities (#1-4) it was found exclusively in the sediment (Tables 1 and 2). With regard to **Cu**, in addition to the high concentration of this metal in *C. gasar* in #5 (significantly higher than in other localities), a high content of this metal was also

Table 1. Means and standard deviation of shell height (between parenthesis, in cm), and of chemical element contents (in mg kg^{-1}, dry weight) of bivalves from estuaries on the south/extreme south coast of the State of Bahia (NE-Brazil).

	Sampling stations, species and shell height values								
	#1		#2		#3		#4		#5
	Cr	**Mg**	**Cr**	**Mg**	**Cr**	**Mg**	**Cr**	**Mg**	**Cg**
	(5.63±0.75)	(4.60±0.48)	(6.53 ±1.05)	(4.95±0.33)	(5.42 ±0.74)	(4.97±0.45)	(9.28 ±1.78)	(5.37±0.93)	(3.77±0.51)
As	-	-	-	-	-	-	-	-	3.22±0.22
Ba	4.40±0.00	7.96±0.01	5.35±0.29	7.22 ±0.57	4.46±0.26	7.72±0.48	5.38±0.07	6.40±0.03	5.64±0.68
Cr	3.20±0.02	4.55±0.03	3.46±0.45	4.55±0.04	3.05±0.17	5.08±0.10	3.37±0.06	4.32±0.04	3.33±0.02
Cu	17.39±0.44	9.93±0.41	14.7±0.40	11.14±2.42	23.6±1.04	14.6±1.11	**37.2***±0.47	18.19±0.68	**160.2***±2.25
Fe	337±2.83	**1,057**±77.39	403±2.69	**1,085**±15.02	299±8.37	**1,690**±70.84	382±5.98	**1,133**±61.33	522±29.08
Mn	20.46±0.53	**64.24**±1.22	15.32±0.36	**71.56**±0.68	26.08±0.67	**78.02**±6.34	15.91±0.44	**102.54**±4.77	22.77±0.49
Ni	-	1.92±0.14	-	3.86±0.20	-	3.83±0.55	-	2.71±0.12	-
Pb	-	-	-	-	-	-	-	-	596.73±391.52
Zn	**1,202.1**±13.49	61.6±1.49	**1,528.6**±21.04	69.9±0.33	**1,212.2**±39.69	76.4±5.68	**1,801.7**±9.73	74.4±0.73	**2,631.2***±291.35

Cg: *Crassostrea gasar*; Cr: *Crassostrea rhizophorae*; Mg: *Mytella guyanensis*; #1: Valença; #2: Taperoá; #3: Ilhéus; #4: Belmonte; #5: Santa Cruz Cabrália; - not detected; in bold: higher values (p<0.05) in relation to other (s) bivalve (s); *higher values in relation to other sampling stations.

Table 2. Means and standard deviation (in mg kg^{-1}, dry weight) of chemical element contents found in sediments in estuaries on the south/extreme south coast of the State of Bahia (NE-Brazil) and maximum values allowed by CONAMA Resolution number 420 (Brasil, 2009).

Chemical Elements/ Stations	#1	#2	#3	#4	CONAMA reference*
Ba	43.4 ±2.02	44.27 ±1.45	47.3 ±3.83	59.43 ±9.82	150
Co	7.12 ±0.49	9.47 ±0.12	7.15 ±0.17	9.59 ±0.14	25
Cr	56.41 ±1.95	63.54 ±2.49	37.22 ±3.00	40.80 ±0.55	75
Cu	4.68 ±0.34	5.88 ±0.38	9.91 ±1.00	11.36 ±0.27	60
Fe	18,851 ±1,55	21,992 ±517.3	20,628 ±1,318	22,604 ±2,000	**
Mn	115.01 ±3.69	135.06 ±4.89	195.3 ±15.51	187.82 ±4.02	**
Ni	14.76 ±0.64	16.6 ±0.65	12.06 ±0.58	16.2 ±0.29	30
Pb	6.97 ±1.24	7.53 ±2.19	7.90 ±4.52	9.42 ±3.62	72
Zn	53.3 ±3.27	68.1 ±6.29	74.9 ±9.95	68.9 ±7.26	300

#1: Valença; #2: Taperoá; #3: Ilhéus; #4: Belmonte; *maximum allowed values;**not established.
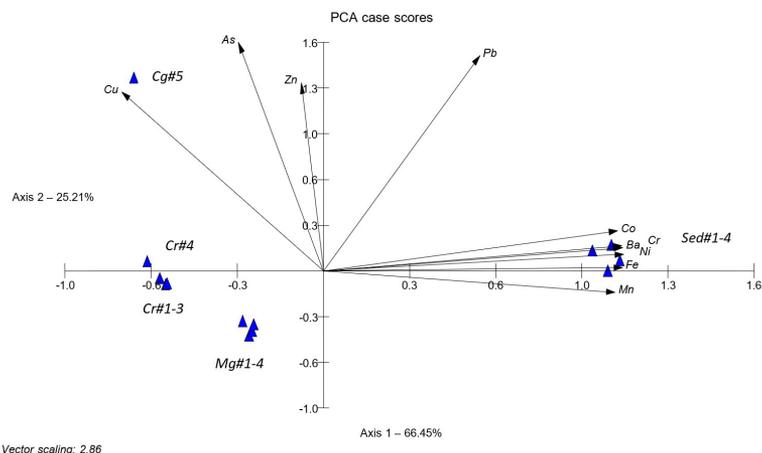
Figure 2. Graphic result of Principal Component Analysis (PCA), showing variables (chemical elements) and observations (analysis matrices and localities) on axes 1 and 2, which together explained 91.66% of the data variability, with axis 1 being defined mostly by sediment (and associated elements) and also by Cr and Mg matrices, while axis 2 was basically defined by matrix Cg and associated elements. Cr: *Crassostrea rhizophorae*; Cg: *Crassostrea gasar*; Mg: *Mytella guyanensis*; Sed: Sediment; #1-5: Sample stations.

found in *C. rhizophorae* at #4 - Belmonte, whose the value differed significantly (p<0.05) from the values found in this species and also in relation to *M. guyanensis* of the estuaries corresponding to sample stations #1-3 (Valença, Taperoá and Ilhéus, respectively) (Table 1).

The two species of oysters (*C. gasar* and *C. rhizophorae*) were characterized, together, by the high content of **Zn** (Table 1). The levels of this metal in *M. guyanensis* were also lower in relation to the sediment, in all places where this species was investigated (#1-4). In turn, this species was more expressive (p <0.05) when compared with the oysters, both in the content of **Fe** and **Mn**. Although there was no statistical difference at the level of α = 0.05 in relation to the two species of oysters, in *M. guyanensis* there was also greater expression of the **Ba** and **Cr**. Furthermore, *M. guyanensis* was exclusive in relation to oysters regarding the occurrence of **Ni** (Table 1).

In general, especially considering sample stations #1-4, all matrices were consistent with regard to the content of each chemical element, that is, the values of each element were close to each other. This was also evidenced by the graphic result of the principal component analysis (PCA), in which there was a separation among the matrices, with the formation of specific groups of matrices involving the sampling stations #1-4, being separated only to #5. The PCA, whose axes 1 and 2 defined more than 90% of the total variability of the data, also corroborated that the elements **Cu**, **As**, **Pb** and **Zn** were mainly correlated to the oyster *C. gasar*, at the sampling station #5 (Santa Cruz Cabrália). In turn, the elements **Co**, **Ba**, **Cr**, **Ni**, **Fe** and **Mn** were strongly associated with sediment in the other sampling stations (# 1-4), in a negative correlation with biological matrices (Figure 2).

4. Discussion

The results of the present study showed that the chemical element levels in the superficial sediment of the mangroves corresponding to the sampling stations #1-Valença, #2-Taperoá, #3-Ilhéus and #4-Belmonte were compatible with the maximum limits recommended by Resolution CONAMA nr. 420 (Brasil, 2009) with regard to the elements **Ba**, **Co**, **Cr**, **Cu**, **Ni**, **Pb** and **Zn**. In this context, comparing all values in dry weight, the levels of **Pb** (6.97-9.42 mg kg^{-1}) in sediment were something similar to the results found in Camamu Bay (Bahia), where Hatje et al. (2008) observed an average of 4.48 mg kg^{-1}. Our values of **Pb** were also similar to the levels obtained by Onofre et al. (2007) in Todos os Santos Bay (BTS) (Bahia) (6.27 mg kg^{-1}), but above those verified by Barros and Barbieri (2012) in Cananeia estuary (São Paulo), which observed mean values below 1 mg kg^{-1}. Additionally, Vilhena et al. (2021) observed levels of 4 and 12 mg kg^{-1} in two estuaries of Pará State, northern Brazil and Kim et al. (2016) found an average of 11.41 mg kg^{-1} in the SãoVicente estuary, Baixada Santista (São Paulo). The CONAMA legislation (BRASIL, 2009) indicates a maximum of 72 mg kg^{-1} of **Pb** for soils to be classified as no contaminated. The levels of **Cu** (4.68-11.36 mg kg^{-1}) were in alignment with other results found on the Brazilian coast, such as in BTS

(5.55 mg kg^{-1}) (Onofre et al., 2007), Amazon estuary (6.5 mg kg^{-1}) (Silva et al., 2018), Pará State estuaries (4.2 and 7.6 mg kg^{-1}) (Vilhena et al., 2021) and in Baixada Santista (8.87 mg kg^{-1}) (Kim et al., 2016). The CONAMA legislation establishes a maximum limit of 60 mg kg^{-1} for **Cu** in soils (Brasil, 2009). As for **Ba**, the aforementioned legislation provides for a maximum of 150 mg kg^{-1}. In our study, the mean values of this element ranged from 43.4 to 59.43 mg kg^{-1}, Hatje et al. (2008) observed an average of 42.4 mg kg^{-1} in Camamu Bay (Bahia) and Vilhena et al. (2021) found 133 and 210 mg kg^{-1} in two estuaries in Pará State. Therefore, these last authors found higher values of **Ba** than those found in the state of Bahia and in extrapolation to that recommended by the Brazilian legislation. The maximum **Co** limit stipulated by CONAMA is 25 mg kg^{-1}. The average value of this element observed in the Camamu Bay (Hatje et al., 2008) was 1.63 mg kg^{-1}, in the Amazon estuary was 13.3 mg kg^{-1} (Silva et al., 2018) and in the present study the variation was from 7.12 to 9.59 mg kg^{-1}. The **Cr** values obtained in this study (37.22-63.54 mg kg^{-1}) were below the limit proposed by CONAMA, which is 75 mg kg^{-1}. Even so, our levels were higher than those found in Baixada Santista (18.21 mg kg^{-1}) (Kim et al., 2016) and in Camamu Bay (4.42 mg kg^{-1}) (Hatje et al., 2008) but were lower than those observed in the Amazon estuary (91.5 mg kg^{-1}) (Silva et al., 2018), whose values went beyond the limits of Brazilian legislation. The last authors related the fact to the dynamics of this element in the environment, with a positive correlation to rainfall and an increase in organic matter in the estuary. **Ni** is established in the CONAMA resolution with a maximum limit of 30 mg kg^{-1}. In the present study, **Ni** averages ranging from 12.06 to 16.6 mg kg^{-1} were obtained, whose values were close to the found by Silva et al. (2018) in an Amazonian estuary (22.3 mg kg^{-1}), but lower values of **Ni** were found for BTS (6.07 mg kg^{-1}) (Onofre et al., 2007), Camamu Bay (1.9 mg kg^{-1}) (Hatje et al., 2008) and in Baixada Santista (7.41 mg kg^{-1}) (Kim et al., 2016). As for **Zn**, CONAMA establishes the maximum limit of 300 mg kg^{-1}. In the present study, the average values of **Zn** in sediment were 53.3 to 74.9 mg kg^{-1}. These values were, however, at least three times higher than those found by Onofre et al. (2007) at BTS (18.27 mg kg^{-1}) and at least four times higher than those observed in Camamu Bay (13.7 mg kg^{-1}) (Hatje et al., 2008), but only slightly above those obtained by Kim et al. (2016) in Baixada Santista (47.68 mg kg^{-1}). The levels of **Fe**, which varied in this study from 18,851 to 22,604 mg kg^{-1}, were similar to the **Fe** values in the sediment of the São Vicente estuary (SP), which was 18,893 mg kg^{-1} (Kim et al., 2016). There is no maximum limit established in Brazilian legislation for this metal. Equally not having a maximum limit established by CONAMA, **Mn** was at slightly lower levels (115.01 to 195.3 mg kg^{-1}) in the present study at the average obtained by Kim et al. (2016) (258.9 mg kg^{-1}) on São Vicente estuary (SP).

As for the bivalves, in # 5-Santa Cruz Cabrália, **As** was detected in the tissues of *C. gasar*, an element that was not found in the sediment or in the bivalves of the other estuaries. In #5 there was also a high level of **Pb** and, although compatible with current Brazilian legislation, a conspicuous **Cu** content in this oyster. Both *C. gasar* (#5)

and *C. rhizophorae* (#1-4) were characterized by high levels of **Zn**. *Mytella guyanensis* was a protagonist in terms of **Fe** and **Mn** contents in relation to the oysters and was also exclusive in terms of the presence of **Ni**. The three species were also characterized by excess levels of **Cr** to those recommended by the Brazilian food legislation (ANVISA). Bivalves were also protagonists in levels of **Zn** and **Cu** in relation to the sediment.

The level of **As** in *C. gasar* (0.33 mg kg^{-1}, in wet weight - ww) at #5 was below the maximum value established by ANVISA (Brasil, 1965, 1999), which is 1 mg kg^{-1} in ww and this element was found exclusively in Santa Cruz Cabrália. With multiple uses (e.g., in herbicides and insecticides), one of the main uses of **As** is as a wood preservative (ATSDR, 2007a; Reimann et al., 2009). In addition, there is also the use of **As** in anti-fouling paints on vessels (Almeida et al., 2007). Samples of oysters from #5 were collected on a dock for crossing ferries and small fishing and tourism vessels, which may have been the immediate cause of contamination of that oyster by this metalloid. Barbosa et al. (2019) found **As** levels above those allowed by ANVISA (Table 3) for food in the bivalves: *Anomalocardia brasiliana* (3.07 mg kg^{-1}), *Iphigenia brasiliana* (4.23 mg kg^{-1}), *Lucina (Phacoides) pectinata* (3.5 mg kg^{-1}) and in *Trachycardium muricatum* (3.05 mg kg^{-1}) (all values in ww), in different localities in the Todos os Santos Bay (BTS) (Bahia), therefore higher than those found in Santa Cruz Cabrália and also not compatible with the level allowed by ANVISA, remembering that all the aforementioned bivalves are used in human food. The most expressive values of **As** observed by Barbosa et al. (2019) were those from bivalves (mainly in *L. pectinata*) collected in areas close to industrial and port activities, which reinforces that the presence of this pollutant is directly related to anthropic impacts. **As** is a persistent chemical element and it generally reaches the estuarine aquatic environments by fluvial flow, with the major part being deposited in the sediment (Kimbrough et al., 2008). When comparing values in dry weight (dw), other studies carried out on the Brazilian coast confirm levels exceeding 15 mg kg^{-1} (BRASIL, 2009) of this contaminant in sediments. This is the case of the study carried out by Mirlean et al. (2012) on the continental shelf of Espírito Santo State, however, these authors observed lower levels in the mangrove sediments (average of 9.2 mg kg^{-1}, dw). The authors attributed the conspicuous levels of this element in platform sediments to natural phenomena related to the composition and dynamics of the soils of this region. Cagnin et al. (2017), who investigated the **As** in the continental shelf of Abrolhos region, southern Bahia, verified values of up to 232.32 mg kg^{-1} in the surface sediments. In addition to analyzing natural causes as the primary source of this element, these authors considered the influence of gold and iron mining in adjacent areas as a cause of the high values in the region.

Regarding **Pb** in bivalve tissues, this metal was not detected in #1-4, however, the high level of this element in the tissues of *C. gasar* in #5 was evident: 61.82 mg kg^{-1} in wet weight (ww), whereas the ANVISA legislation (Brasil, 1965, 1999) provides for a maximum of 2 mg kg^{-1} in ww, therefore, this limit has been exceeded by at least 30 times

in the tissues of this oyster in this estuary. The **Pb** values in *C. gasar* in #5 were also at least 20 times higher than the averages found by Barbosa et al. (2019) in other bivalves of economic interest in BTS (Bahia): 0.11 mg kg^{-1} in *A. brasiliana*, 0.13 mg kg^{-1} in *I. brasiliana*, 0.18 mg kg^{-1} in *T. muricatum* and 3.17 mg kg^{-1} in *L. pectinata*, all values in wet weight. The value of **Pb** obtained in *L. pectinata* by these authors also exceeded the maximum allowed by ANVISA (Table 3). In its turn, Campolim et al. (2018) found an average value of 0.38 mg kg^{-1} (ww) in *Perna perna* from Santos Bay (São Paulo), compatible with ANVISA legislation, while Lino et al. (2016), curiously, they did not detect this element in *P. perna* in Guanabara Bay (Rio de Janeiro), which is known to be polluted, nor in *Nodipecten nodosus* collected in Ilha Grande, also in the state of Rio de Janeiro (Table 3). When comparing dry weight (dw) values in bivalve tissues (for which there are no parameters in Brazilian food legislation), Vilhena et al. (2021) reported **Pb** averages of 1.85 mg kg^{-1} in *C. gasar* from the Mocajuba river in the Pará State, in contrast to the alarming value of 596.73 mg kg^{-1} found in the present study in *C. gasar* of Santa Cruz Cabrália (Table 3). According to ATSDR (2007b), **Pb** is a naturally low-abundant element in the earth's crust, but certain industrial activities and its addition to gasoline have generated increases in this pollutant worldwide in recent decades. In #5 of the current study, nautical activities may have been the cause of the high levels of **Pb**, since it is used in paints and pigments and in the burning of fossil fuels (e.g., painting boats and supply of gasoline and diesel oil vessels near or in the body of water, with possible leaks and washing of boats). These results in #5 converge with that observed by Barbosa et al. (2019) in BTS (Bahia), which registered an expressive level of **Pb** in *L. pectinata* collected near the port and industries. **Pb** is known to be neurotoxic and carcinogenic for humans (ATSDR, 2007b; Kimbrough et al., 2008).

As for the **Cu** levels found in the current study, the highest values were also those of #5-Santa Cruz Cabrália, in *C. gasar* (16.59 mg kg^{-1}, in wet weight and 160.2 mg kg^{-1}, in dry weight). In the oyster *C. rhizophorae* of the other localities, the values ranged from 14.7 to 37.2 mg kg^{-1} (dw) (Table 1) and the average, in wet weight, was 2.09 mg kg^{-1} (Table 3), that is, below that established by ANVISA. The average values of **Cu** in *M. guyanensis* were also low (9.93 to 18.19 mg kg^{-1}, in dry weight and 2.31 mg kg^{-1}, in wet weight: Tables 1 and 3, respectively). In the intraspecific comparison, *C. rhizophorae* from #4 had higher averages (p <0.05) of **Cu** in relation to specimens from #1-3, but the exact cause of this fact could not be verified. One detail that could be considered is that the samples from this first locality were constituted of animals slightly larger than those from the other locations (see Table 1), however, this aspect would have to be further investigated. Although at high levels, **Cu** levels in #5 were below that established by ANVISA legislation, which is 30 mg kg^{-1}. When verifying the values of this metal in bivalves from other places on the Brazilian coast, we find some values that went far beyond the limits of the legislation. For example, Barbosa et al. (2019) found an average of 121.3 mg kg^{-1} (ww) in *L. pectinata*, from a region close to the port and industries in BTS (Bahia) and

Table 3. Comparison of results obtained in the present study with some other studies carried out on the Brazilian coast and values established by ANVISA-Brazil (Decree nr. 55.871 and Ordinance nr. 685; Brasil, 1965, 1999, respectively).

Chemical Elements	Localities/Matrices										ANVISA reference values
	BTS				GB	IG	BS	Present Study			
	Ab	Ib	Lp	Tm	Pp	Nn	Pp	Cr	Cg	Mg	
As	3.07	4.23	3.5	3.05	*	*	*	-	0.33	-	1
Cr	0.13	0.46	0.29	0.82	2.8	2.6	0.37	0.29	0.35	0.79	0.1
Cu	2.63	2.48	121.3	0.43	698	3.3	1.63	2.09	16.59	2.31	30
Fe	*	*	*	*	197	40	179.97	32.03	54.06	213.36	**
Mn	*	*	*	*	22	76	2.33	1.75	2.36	13.61	**
Ni	*	*	*	*	2.3	-	2.31	-	-	0.53	5.0
Pb	0.11	0.13	3.17	0.18	-	-	0.38	-	61.82	-	2.0
Zn	11.15	30.2	28.97	11.15	62	52	27.11	129.54	272.59	12.26	50

Average values, in mg kg⁻¹, wet weight. BTS: Baía de Todos os Santos (Barbosa et al., 2019); GB: Guanabara Bay (Lino et al., 2016); IG: Ilha Grande (Lino et al., 2016); BS: Baía de Santos (Campolim et al., 2018); Ab: *Anomalocardia brasiliana*; Cg: *Crassostrea gasar*; Cr: *Crassostrea rhizophorae*; Ib: *Iphigenia brasiliana*; Lp: *Lucina pectinata*; Mg: *Mytella guyanensis*; Nn: *Nodipecten nodosus*; Pp: *Perna perna*; Tm: *Trachycardium muricatum*. -: not detected; *not investigated; **not established.

Lino et al. (2016), found a value of 698 mg kg⁻¹ (ww) in *P. perna* in Guanabara Bay (Rio de Janeiro). When comparing dry weight values of **Cu** in *C. gasar*, Vilhena et al. (2021) observed an average of 75 mg kg⁻¹ in an estuary in the state of Pará, while in #5 this oyster showed 160.2 mg kg⁻¹. Among the anthropic activities that generate the presence of **Cu** in the environment, are nautical activities related to the use of this metal as a wood preservative and also in anti-fouling paints (ATSDR, 2004). The high content of **Cu** in oysters of #5 is probably related to activity of boats of this locality, mainly used in artisanal fishing in the region. This metal has been used for thousands of years in anti-fouling paints and after the ban of inks containing tributyltin (TBT) worldwide in 2003, manufacturers replaced TBT with **Cu** (and Zn) as biocides (Almeida et al., 2007). **Cu** can be toxic to aquatic animals and humans when present at levels above those supported by them, but at trace levels it is essential for the functioning of organisms (ATSDR, 2004). Studies made by Pan and Wang (2009) and by Cai and Wang (2019) showed a correlation of **Cu** with metallothioneins in bivalves, proteins related to the control and elimination (detoxification) of this metal by these organisms, causing large concentrations to be supported and metabolized by these mollusks.

As for the presence and contents of **Zn**, *M. guyanensis* presented about ¼ of this metal at the maximum value stipulated by ANVISA, which is 50 mg kg⁻¹ (ww). On the other hand, the two species of oysters were prominent as to the occurrence of **Zn**. In *C. rhizophorae*, considering the estuaries corresponding to sampling stations #1-4, an average of 129.54 mg kg⁻¹ (ww) was obtained and consistent (similar) values were found among localities. In *C. gasar* at #5, mean **Zn** values was 272.59 mg kg⁻¹ (ww), slightly more than the double found in *C. rhizophorae*, which was probably determined by the characteristics of the place and not by the species of oyster. Despite its low toxicity, nautical activities related to the use of anti-fouling paints potentially introduce artificially **Zn** into the

environment (Almeida et al., 2007), which may be one of the reasons for the high concentration of this element in #5. In other bivalves of economic interest from BTS (Bahia), Barbosa et al. (2019) recorded **Zn** levels below 30 mg kg⁻¹ (ww), the same having been recorded for *P. perna* in the Santos Bay (São Paulo) (Campolim et al., 2018). Lino et al. (2016) obtained mean values of 62 mg kg⁻¹ (ww) for this same species in Guanabara Bay (Rio de Janeiro), while these same authors found 52 mg kg⁻¹ of **Zn** in *N. nodosus* from Ilha Grande (RJ) (Table 3). These comparisons allow us to suppose that the levels of **Zn** are greatly influenced by the levels of this metal in the environment (water and soil), but that, in addition, some species (such as oysters) have a natural propensity to bioaccumulate this element. Góngora-Gómez et al. (2017) found mean **Zn** values of 267.42 mg kg⁻¹ (dw) in *C. gigas* cultivated in the La Pitahaya estuary, Gulf of California (Mexico). Likewise, Vilhena et al. (2021) found an average of 8.017 mg kg⁻¹ in *C. gasar* from Mocajuba river (Pará, Brazil), while in *Paxyodon ponderosus*, an untrue oyster (belonging to the family Hyriidae and not Ostreidae), the average content was 184 mg kg⁻¹ (dw) on the Pará river, therefore, at a much lower level than that of *C. gasar*. The physiological reason why oysters accumulate **Zn** in high proportion remains to be investigated, but it is possible that it is related to the detoxification proteins mentioned above.

As for **Cr**, all bivalve samples in this study exceeded the limits established by ANVISA, which is 0.1 mg kg⁻¹ in wet weight. Studies carried out in BTS (Barbosa et al., 2019), as well as in Santos Bay (São Paulo) (Campolim et al., 2018) showed values in order of magnitude similar to ours in other species of bivalves, but Lino et al.. (2016) obtained higher values of **Cr** in bivalves in the state of Rio de Janeiro (Table 3). In the analysis of the dry weight averages of our study (Table 1), there is a similarity among places and species, with a variation between 3.05 and 5.08 mg kg⁻¹. Góngora-Gómez et al. (2017) observed an average value of 24.97 mg kg⁻¹ (dw) in *C. gigas* from the Gulf of California

(Mexico), but did not explain the possible cause of this high value. These authors drew attention to the importance of **Cr** in glucose tolerance by the human body and that its excess can cause diabetes. Although not exceeding the maximum value of Resolution CONAMA nr. 420 (Brasil, 2009) for **Cr** in the sediment (75 mg kg⁻¹, dw), the values obtained in the soil for this study are conspicuous (averages between 37.22 and 63.54 mg kg⁻¹) when, for example, compared to estuarine sediments obtained in the Baixada Santista (18.21 mg kg⁻¹) (dw) (Kim et al., 2016). As anthropogenic activities that potentially introduce **Cr** into the environment (e.g., tanneries and metallurgies) are scarce on the southern coast of the state of Bahia, it is assumed that the presence of this element is related to particularities of the region's soil composition, since the state has the greater reserves of this metal among all Brazilian states (33.53%) (Lima and Neves, 2016), however, specific and detailed studies regarding the presence of **Cr** in the state's estuaries are necessary to obtain more precise conclusions.

Ni is included in the observance of ANVISA with maximum levels of 5 mg kg⁻¹ (ww), a limit not reached for *P. perna* in Guanabara Bay (Lino et al., 2016) and also not for *M. guyanensis* in present study, the only species in which this metal was recorded, at low levels (0.53 mg kg⁻¹) (ww) (Table 3). Lino et al. (2016) and Campolim et al. (2018) recorded 2.3 and 2.31 mg kg⁻¹ (ww), respectively, in *P. perna* in other Brazilian states. Although it is an essential element in small quantities, exposure to high doses can cause problems with bronchitis and for long-term exposure, cancer (Kimbrough et al., 2008).

The maximum values of **Ba**, **Fe** and **Mn** in food are not established in Brazilian legislation. In the case of **Ba,** in the present study this element was present at low levels in the species investigated. In dry weight, in *C. rhizophorae* the averages were from 4.4 to 5.38 mg kg⁻¹, in *M. guyanensis* from 6.40 to 7.96 mg kg⁻¹ and in *C. gasar* 5.64 mg kg⁻¹. Comparing these results to those obtained by Vilhena et al. (2021), these obtained averages of 1.70 mg kg⁻¹ (dw) in *C. gasar* and 1.286 mg kg⁻¹ (dw) in *P. ponderosus*, therefore, the greatest accumulation of **Ba** occurred in this last bivalve, a species of fresh water. As for **Fe** and **Mn**, the high level of these metals in *M. guyanensis*, when compared to the levels observed in the oysters, drew attention in the current study. Thus, *M. guyanensis* collected in the same localities where *C. rhizophorae* samples were obtained showed six times higher **Fe** and eight times higher **Mn** values in relation to this oyster. In the dry weight comparison, the **Fe** values obtained for *C. gasar* by Vilhena et al. (2021) were 374 mg kg⁻¹, for 522 mg kg⁻¹ in the same species in our study, as well as for averages from 299 to 403 mg kg⁻¹ in *C. rhizophorae*, also in the present study. For *M. guyanensis*, the values of **Fe** in our study were from 1.057 to 1.690 mg kg⁻¹. Although it does not live in the sediment, but rather adheres to consolidated substrates (mainly in rocky shores), it is observed that high values of **Fe** were also found in *P. perna*, both in Guanabara Bay (Lino et al., 2016) and in Santos Bay (Campolim et al., 2018) (Table 3). For **Mn**, Vilhena et al. (2021) observed an average of 14 mg kg⁻¹ (dw) in *C. gasar* and in the present study we obtained 22.77 mg kg⁻¹ (dw) in this species, values between 15.32 and 26.08 mg kg⁻¹ (dw) in *C. rhizophorae* and 64.24 and

102.54 mg kg⁻¹ (dw) in *M. guyanensis*, therefore, the latter species showed much higher values than those found in oysters. It is possible that the habit of living buried in the sediment (Boehs et al., 2010) provides *M. guyanensis* with a greater advantage of acquiring **Mn** from the substrate. Vilhena et al. (2021), observed an average **Mn** content of 2.020 mg kg⁻¹ (dw) in *P. ponderosus* in the Pará river (Pará), a species that lives in the sediment. According to Cheng et al. (2013), the sediment is the main source of metals for organisms, which accumulates levels of metals that are higher than those in the water. Oysters such as *C. rhizophorae*, generally live attached to the aerial parts of mangrove plants (Boehs et al., 2019), having less contact with the soil, which could partly explain these differences in the levels of these elements.

We conclude that the levels of chemical elements investigated indicated, in general, low anthropic impact of estuarine areas of the south/extreme south coast of the state of Bahia, confirming the hypothesis of the present study. The exception was #5, regarding the presence of **As** and the high levels of **Pb** and **Cu**, attributed to the nautical activities in that locality.

Acknowledgements

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