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# Detection of rare-earth elements using fiddler crabs *Leptuca leptodactyla* (Crustacea: Ocypodidae) as bioindicators in mangroves on the coast of São Paulo, Brazil

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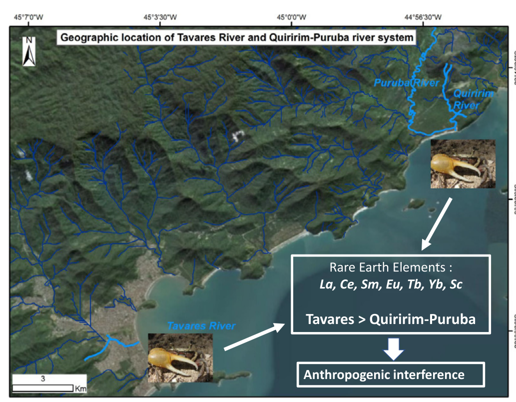
## HIGHLIGHTS

- REE have been detected in crabs *Leptuca leptodactyla* and in sediments by INAA.
- REE concentrations are higher in crabs from Tavares River than Quiririm-Puruba.
- High concentration of REE is linked to anthropic interferences.
- Crabs are good environmental indicators for REE in different locations and seasons.
- Fiddler crabs can be used as indicators of REE in mangroves worldwide.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Rare-earth elements have gained significant attention as they are currently widely used in high tech, chemical, and pharmaceutical industries. Here we used the fiddler crabs *Leptuca leptodactyla* as bioindicators to verify the presence of rare-earth elements in two mangrove areas of the Ubatuba, northern littoral of São Paulo state, Brazil. The specimens were collected in the mangrove areas of the Tavares River and Quiririm-Puruba river system, separated by season (dry and rainy). A total of 243 individuals were collected and analyzed. For determination and quantification of the elements we used the instrumental neutron activation analysis (INAA) technique. In both the dry and rainy season, the elements La, Ce, Sm, Eu, Tb, Yb and Sc were detected in samples of both mangroves, with La and Ce presenting higher concentrations. Samples from Tavares River mangrove had higher concentration levels of rare-earth elements than those of the Quiririm-Puruba river system. That is probably due to the central geographic position of the Tavares River in Ubatuba, which crosses a large portion of the city and receives a great amount of sewage. On the other hand, the Quiririm-Puruba river system has less anthropogenic inputs, thus, it receives much fewer rare-earth elements when compared to the Tavares River.



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## 1. Introduction

The rare-earth elements (REE) refers to a set of 17 elements, 15 of them classified as lanthanides and yttrium (Y) and scandium (Sc), due to their similar chemical properties (Connelly et al., 2005). Although called REE, some elements are relatively abundant in the Earth's crust, with cerium and lanthanum being the most abundant (Tyler, 2004; Zhou et al., 2017). For instance, these elements are found in some minerals, such as allanite, monazite, rhabdophane, and bastnaesite, but also replace some minerals, such as fluorite, sphene, zircon, apatite, xenotime (Clark, 1984). The amount of REE in the sediment can be influenced by the parent materials and organic matter contents, soil texture, pedogenic processes, and anthropogenic activities (Aide, 2018). Because they have low solubility and persistent behavior, these elements have become good tracers of geochemical processes and anthropogenic disturbances in natural environments (Prudêncio et al., 2011, 2015; Bosco-Santos et al., 2017, 2018).

Due to the increasing commercial interest in specific economic sectors of industry and commerce, REE have gained significant attention in the international scenario, as they are used in automobiles and fluid catalysts, metallurgy, medical systems, high technology, clean energy, military defense systems, and several other applications (see Zhou et al., 2017 and references therein). China currently owns 85% of the world's rare-earth oxide production; however, Japan is the main rare earth transformer, with 90% of these elements being imported from China. In Brazil, despite the recent intensification in the exploration, the country still has great potential for the production of REE elements, with reserves estimated at 120 million tons (Ortiz and Viana Júnior, 2014).

In aquatic environments, REE occur in small amounts; however, industrial activities have caused an increase of these elements in natural environments, causing contamination of aquatic ecosystems (Carvalho et al., 2000; Agah et al., 2009). This contamination is especially important in mangroves, which are known to receive large amounts of contaminants (Delgado et al., 2012), acting as a type of natural barrier and removing or immobilizing much of the heavy metals leached by the rivers. This is mostly due to silt and clay particles, abundant organic matter, and low pH enabling the mangroves to easily capture the free metals in the water (Harbison, 1986). Nevertheless, mangroves are very important areas for conservation, playing a huge role in feeding, breeding, predation and refuge, as well as being considered a nursery for countless species (Sheaves, 2005).

In Brazil, the city of Ubatuba, as well as several other coastal cities, has problems with sewage and solid waste discharge transported by river systems, due to ships, disorderly tourism, and a lack of adequate water treatment (Gondolo et al., 2011) affecting mangroves, estuaries, and the ocean shore. Thus, the physical and chemical monitoring of the city residues, and their impact in those areas, is extremely important (Mantelatto and Fransozo, 1999).

Crabs are abundant in mangrove ecosystems and beaches, and are considered good indicators of environmental quality, especially species of the family Ocypodidae (Amaral et al., 2009). Fiddler crabs in particular have a strict relation with the mangrove sediments as they are deposit feeders, ingesting some sediment as part of their diet, and bioturbators, modifying the sediment where they live, making them key organisms in mangrove forests (Smith III et al., 1991; Natálio et al., 2017). *Leptuca leptodactyla* Rathbun, 1898, one of the many species of fiddler crabs, represents the typical invertebrate fauna associated with tropical and subtropical mangroves along the Brazilian coast (Pinheiro et al., 2016). This species has a wide distribution in the Western Atlantic, from Florida (United States), the Gulf of Mexico, the Antilles, and Venezuela to Brazil (Melo, 1996; Pinheiro et al., 2016). Thus, we used L. *leptodactyla* to identify the diversity and quantity of REE through instrumental neutron activation analysis (INAA) in two different locals of Ubatuba in the São Paulo state. In addition, sediments from both locations were also analyzed.

Instrumental neutron activation analysis (INAA) is a multi-element analytical technique used for both qualitative and quantitative analysis of trace and rare elements. Because it is based on the activation of the nuclei present in the sample by a neutral beam and the gamma radiation emitted, the technique allows the analysis of the material very precisely and without additional chemical preparations. INAA is well-known as a reliable analytical technique, that has been used worldwide to analyze different kinds of matrices. This technique is particularly suitable for REE analysis due to their nuclear characteristics, and many studies employed INAA for REE determination at LAN (*e.g.* Figueiredo et al., 2007; Maria et al., 2000; Silva-Filho et al., 2011; Rizo et al., 2012; Lange et al., 2017).

## 2. Materials and methods

### 2.1. Study area

This study was developed in Ubatuba City, located on the northern coast of São Paulo, Brazil (Fig. 1A), with 708.11 $km^2$ area of extension and 78,801 inhabitants (IBGE, 2010). Being a tourist city, it has a floating population of approximately 350,000 people (São Paulo, 2019). The climate in this region is classified as warm and humid tropical, and the area has one the highest precipitation rates in the country (annual averages close to 4000 mm). The high levels of precipitation can be explained by the high humidity brought by winds from the Atlantic Ocean that condenses upon reaching the mountains (Monteiro, 1973).

The predominant geological formation of the region is the Coastal Complex and Charnockitic Ubatuba (IBGE, 2019). The source rock of Ubatuba charnockite magma is an upper crustal rock of high-grade metamorphic facies. The Ubatuba massive charnockite has a chemical composition similar to acidic igneous rocks, such as rhyolites and granites (low-Ca granites) and is characterized by high-K contents. The concentrations of REE in the Charnockitic Ubatuba are comparable to the average upper crust, with some REE being enriched by a factor of 1.5–2.0 (Gasparini and Mantovani, 1979).

The samples were collected in the mangroves of the Quiririm-Puruba river system (−23.350091, −44.926849) (Fig. 1B and D) and the Tavares River (−23.447009, −45.068944) (Fig. 1B and C) in Ubatuba. The two localities have a distance of about 30 km from each other. The Puruba and Quiririm rivers join near the Puruba beach and flow into the Atlantic Ocean (Silva, 2013). The rivers are sourced in the Serra do Mar, one of the few remnants of the Brazilian Atlantic Forest. The Quiririm-Puruba watershed region has part of its area in the Serra do Mar State Park, which is a conservation unit that covers 79.58% of the area of the city of Ubatuba (IF, 2008). Therefore, the Quiririm-Puruba river system still has few anthropogenic disturbances, surrounded by native vegetation and mangroves that still retain their original, preserved features.

The Tavares River, although also sourced in the Serra do Mar State Park, has its main body crossing the central area of the city of Ubatuba. This river is affected by urbanization factors, such as solid waste disposal and irregular emission of domestic and industrial effluents. In Ubatuba, only 39.5% of domestic wastewater is collected, with 99.82% treated resulting in an approximate volume of 4,400,000 m3/year of non-treated wastewater (SNIS, 2018). This means that more than half of the generated domestic effluent is irregularly discharged directly into the city rivers. The industry accounts for a low percentage in the gross domestic product (GDP) at 21.41% (SEADE, 2016), and the industrial effluents mostly come from small industries, such as shipbuilding and canning factories (Avelar et al., 2000).

### 2.2. Identification and preparation of samples

A total of 243 specimens of *Leptuca leptodactyla* was collected by active search, as were two sediment samples for each location and season during the months of August (dry season) and December (rainy season)

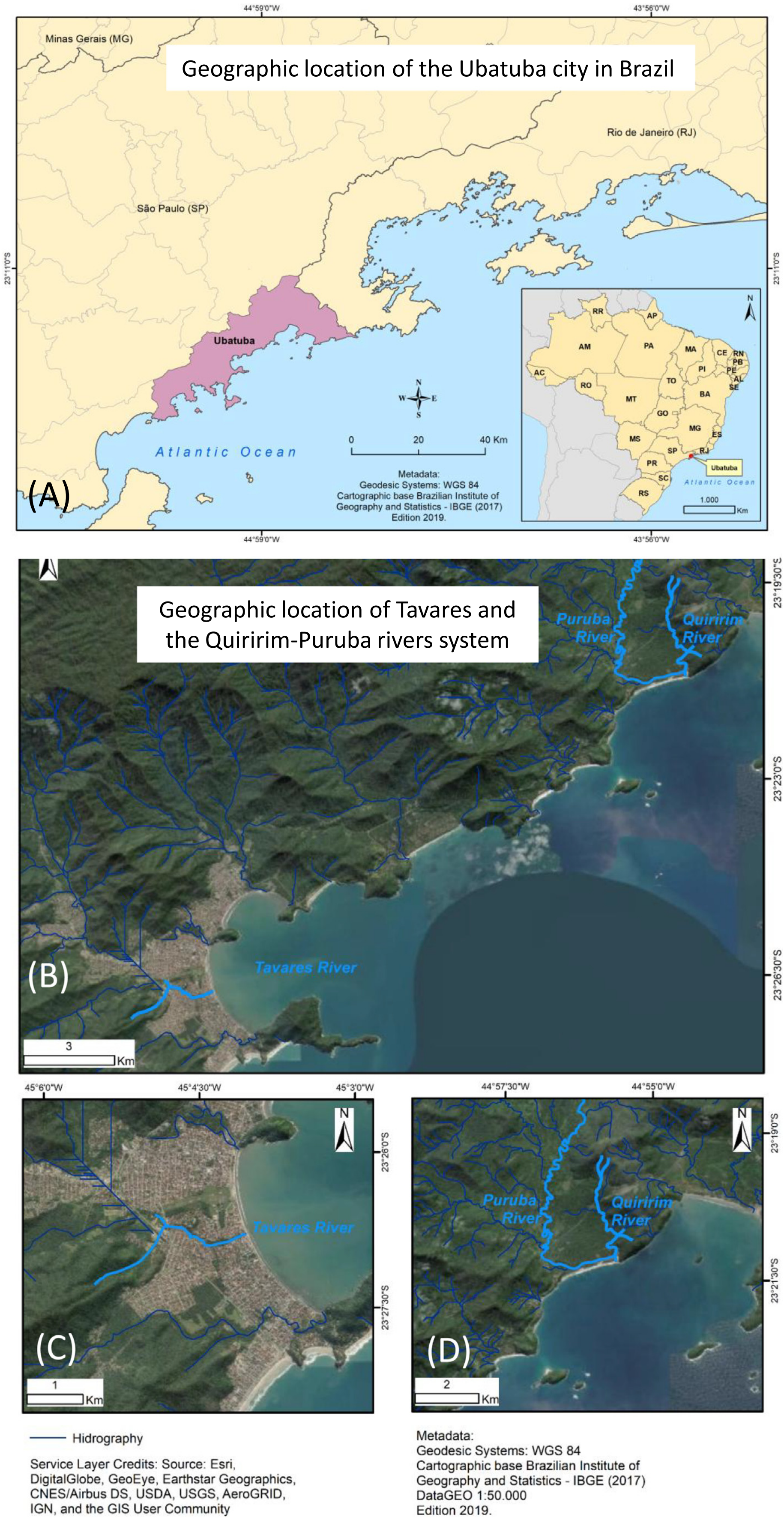


**Fig. 1.** (A) Geographic location of the Ubatuba city in Brazil. (B) Geographic location of the Tavares River and the Quiririm-Puruba river system. (C) Detail of the Tavares River crossing the main area of Ubatuba. (D) Detail of the isolated Quiririm Puruba river system.

2016. Immediately after the capture, the animals were placed in plastic bags, identified according to the collection site and season (dry or rainy) and euthanized in ice at −15 °C. They remained frozen until the beginning of the analysis.

In the laboratory, identification keys were used to determine individuals of L. *leptodactyla* collected (Melo, 1996). After that, the crabs were placed in an ultrasonic washer (Unique Maxiclean 1400) with distilled water for 10 min to remove sediment trapped in the carapace. Each individual was then sexed, measured with a COSA digital caliper 0-01 mm and weighed on a Gehaka AG200 precision scale.

For the neutron activation analysis, the specimens (whole animal) and sediment were dried. For the drying process the samples were separated in glass petri dishes and placed in a drying oven (Esterilifer SX1.3) at 50° for at least 12 h or until reaching constant weight. Then, the crabs from each location and season were grouped into 3 samples to obtain the quantity (in grams) sufficient for INAA analysis. As the analyses were done in triplicate, at the end, 9 concentration values ($n = 9$) were obtained for crabs and 6 ($n = 6$) for the sediment. The dried samples were powdered and sieved in 120 mesh nylon mesh (0.125 mm). The material retained in the mesh was again powdered and sieved until the desired pattern was obtained. The material was then placed in plastic tubes and weighed again using an analytical balance to obtain the dry weight of the samples.

### 2.3. Instrumental neutron activation analysis (INAA)

The INAA was performed in the Neutron Activation Analysis Laboratory (LAN), at IPEN-CNEN/SP (Nuclear and Energy Research Institute - National Nuclear Energy Commission – Brazil). This lab has been applying INAA for decades, and participating regularly in international interlaboratory comparisons testing the accuracy of its analyses (Figueiredo et al., 2006; Moreira et al., 2017). One hundred milligrams of a sample sprayed through a 100–200 mesh were accurately weighed into polyethylene envelopes of about 1 $cm^2$, previously cleaned with a diluted nitric acid solution. After being weighed, the envelopes were heat-sealed (with a soldering iron). The geological reference materials GS-N (GIT-IWG), SL-1 and SL-3 (IAEA) were also weighed. Samples and standards were placed in aluminum containers ("rabbits") specially developed for use in an IPEn-CNEN/ SP IEA-R1 reactor and irradiated for a medium time of 8 h in a thermal neutron flux of $10^{12}$ n $cm^{-2}$ $s^{-1}$. After about five days, the samples and standards were drawn from the aluminum rabbits, transferred to stainless steel containers and brought to the gamma spectrometry system. Counting times were 90 min. A new series of measurements was conducted about 15 days after irradiation. The counting times were 2.5 h. The obtained gamma ray spectra were analyzed by the VISPECT program. This program locates the peaks and calculates their areas and energy. The calculation of the concentration of the elements analyzed was done by the comparative activation analysis method. All materials were analyzed in triplicate.

The quality control of the data was performed by analyzing the reference materials Peach Leaves (NIST SRM 1547) for crabs and granite GS-N (ANRT) for sediment. The results are a mean of 6 replicates and the associated error is the standard deviation (Table 1). The results obtained agree with certified values, with a bias of <10% and variation coefficients of <10%. For the reference material GS-N, which has certified values for the REE, the zeta-score test was applied to the results. All the calculated zeta-score were <|2|, showing that the results were satisfactory within 95% confidence levels. The results obtained for the Peach Leaves reference material agreed with informative values, presenting the bias value of <10%.

### 2.4. Statistical analysis

The software PAST (Hammer et al., 2001) was used for calculations. Graphics were performed using Origin 8.5 (OriginLab Corporation, Northampton, USA). The multivariate technique was done with One-way MANOVA with two statistics: Wilk's lambda and the Pillai trace were performed for both the crabs and sediment. The Hotelling test *post hoc* was applied to verify the variation among groups in pairs, testing the differences between concentrations in crabs and sediments in different locations (Tavares × Quiririm-Puruba) and for the same location different seasons (rainy and dry). The differences were considered statistically significant when $p < 0.05$. Canonical variates analysis (CVA) was applied to calculate the maximum separation among groups. Data were compared with cluster analysis for identification of data belonging to the same group. The dendrogram was made using the unweighted pair-group average (UPGMA) algorithm. Clusters were joined based on the average distance between all members of the two groups. The distance matrix was computed using the Euclidean distance indices.

## 3. Results

During the rainy season, 107 specimens (44%) of *Leptuca leptodactyla* were collected in the mangrove of the Quiririm-Puruba river system and 61 specimens (25%) in the mangrove area of the Tavares River. In the dry season, 48 crabs were captured (20%) in the mangrove of the Tavares River and 27 (11%) in the mangrove of the Quiririm-Puruba river system, totaling 243 individuals.

The REE found in the crabs were Sc, La, Ce, Sm, Eu, Tb, and Yb. Fig. 2(A and B) shows the values found for each element and Table 2 summarizes the values. For all elements observed in the specimens, the concentrations were much higher in specimens from the Tavares River in both dry and rainy seasons. One-way MANOVA test showed significant differences ($p < 0.05$ Wilks Lambda and Pillai trace) in the quantity of REE when compared in different sources (Quiririm-Puruba and Tavares mangroves) and different seasons (dry and rainy). The *post hoc* Hotelling test resulted in $p < 0.05$ for all pairwise comparisons. Table 3 shows the *p*-value according to the comparison. Cerium was the REE with the highest concentration at both study sites and seasons followed by lanthanum (Table 1, Fig. 2A). The concentrations of terbium in the dry season were below the detection level of the INAA in the crabs from the

**Table 1**
Results obtained for the reference materials GS-N (ANRT) and Peach Leaves (NIST SRM 1547) by INAA for 6 replicates in mg kg-1 (dry mass basis).

| GS-N (ANRT) | | | | | Peach Leaves NIST SRM 1547 | | | |
|---|---|---|---|---|---|---|---|---|
| Element | $X_{cert} \pm u_{cert}$ | $X_{Lab}$ | Bias (%) | CV (%) | Informative value | $X_{Lab}$ | Bias (%) | CV (%) |
| La | 75 ± 2.7 | 73.6 ± 0.5 | 1.9 | 0.7 | (9) | 9.0 ± 0.2 | 0 | 2.2 |
| Ce | 135 ± 7 | 136.8 ± 0.9 | 1.3 | 0.7 | (10) | 10.0 ± 0,1 | 0 | 1.0 |
| Nd | 49 ± 1.5 | 54 ± 5 | 10 | 9.3 | (7) | 6.9 ± 0.3 | 1.4 | 4.4 |
| Sm | 7.5 ± 0.22 | 7.7 ± 0.1 | 2.3 | 1.3 | (1) | 1.06 ± 0.03 | 6.0 | 2.8 |
| Tb | 0.6 ± 0.04 | 0.7 ± 0.1 | 17 | 14 | (0.1) | 0.09 ± 0.01 | 10 | 11 |
| Yb | 1.4 ± 0.15 | 1.4 ± 0.1 | 0 | 7.1 | (0.2) | 0.19 ± 0.01 | 5 | 5.3 |
| Lu | 0.22 ± 0.03 | 2.20 ± 0.04 | 9 | 1.8 | – | – | – | – |

CV = variation coefficient.

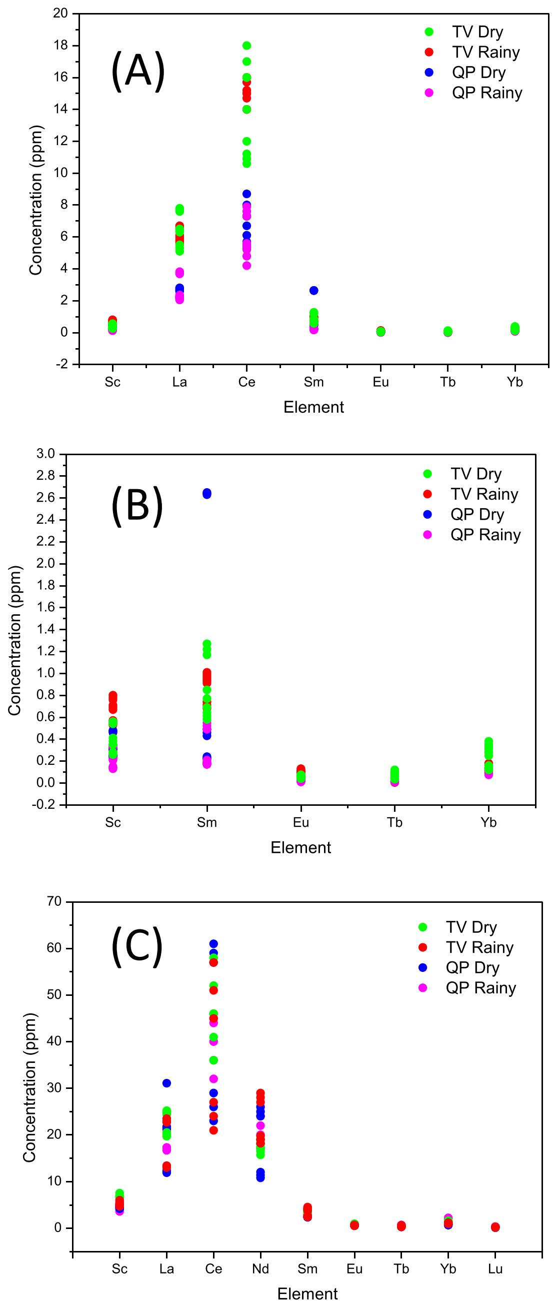


**Fig. 2.** Concentration of REE assessed by instrumental neutron activation analysis. (A) All elements detected in crabs and (B) without lanthanum (La) and cerium (Ce) for better view of other elements. There is an outlier point of samarium (Sm) concentration. (C) All elements detected in sediments.TV: Tavares River; QP: Quiririm Puruba river system.

**Table 3**
*p*-Value obtained by paired Hotelling's test for crab data.

| | QP dry | QP rainy | TV dry | TV rainy |
|---|---|---|---|---|
| QP dry | 0 | 1.57E−02* | 9.19E−07* | |
| QP rainy | 1.57E−02* | 0 | | 9.70E−06* |
| TV dry | 9.19E−07* | | 0 | 1.28E−05* |
| TV rainy | | 9.70E−06* | 1.28E−05* | 0 |

* Difference statistically significant $p < 0.05$.

Quiririm-Puruba river system (Table 1). Fig. 3A shows the CVA scatter plot of data, demonstrating the grouping data from the same region. The Tavares River in both seasons received the highest scores. The season's interference in the concentration of REE (logarithmic scale) in crabs and sediment is shown in the Fig. 4. According to the results for the crabs (Fig. 4A, B and Table 3), it can be concluded that, although the values are all close to $r = 1$ (slopes 0.884 and 1.004 for Tavares and Quiririm-Puruba, respectively), the season influenced the concentration of REE, in both the region of the Tavares River and in the Quiririm Puruba river system region ($p < 0.05$).

Cluster analysis to determine similarity by the Euclidean analyses resulted in the "dendrogram" shown in Fig. 5. The grouping of data belonging to the same region can be clearly seen, reinforcing what was obtained in the analysis by CVA.

For the sediment, the REE found are the same as for L. *leptodactyla* with two additional elements that were not observed in the crabs: Nd and Lu (Fig. 2C and Table 4). All REE concentrations are higher in the sediment than in the crabs. Also similar to the crabs, concentrations of Ce, followed by La, are the highest. The difference is the presence of Nd in high concentrations, similar to La, but below the level of detection of the INAA in the crabs. It can be noted that all values are similar to the average concentrations present in the Earth's crust with the ratio of La/Ce being approximately ½ (Tyler, 2004). The sediments collected in the Tavares and Quiririm-Puruba river system presented significant variations in the concentration of the elements Sc, Ce, Eu, Yb and Lu. The sediment of the Tavares River has higher concentrations for almost all elements than the Quiririm-Puruba river system during the same seasons (Table 4).

The MANOVA test showed significant differences ($p < 0.05$ Wilks Lambda and Pillai trace) in the quantity of REE in sediments when compared in different locations (Quiririm-Puruba and Tavares mangroves) and different seasons (dry and rainy). According to results of the *post hoc* Hotelling test (Table 5), the comparison between locations in the dry season shows a statistically significant difference ($p < 0.05$). Therefore, concentrations in the sediment of the Tavares River region are higher in comparison to the Quiririm-Puruba river system in the dry season. However, in the rainy season, the difference is not significant ($p > 0.05$).

The comparison between seasons of the same location shows that in the region of the Tavares River, the difference is statistically significant ($p < 0.05$). That is, the rain interfered in the concentration of the

**Table 2**
Chemical elements found in *Leptuca leptodactyla* collected in the Quiririm-Puruba and Tavares Rivers in the dry and rainy seasons. Values are given in mean concentration (ppm) with standard deviation and coefficient of variation.

| Locality/season | Concentration (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Sc | La | Ce | Sm | Eu | Tb | Yb |
| Quiririm Puruba (dry) | 0.34 ± 0.10 | 2.53 ± 0.26 | 6.73 ± 1.18 | 1.11 ± 1.15 | 0.03 ± 0.01 | NOB | 0.12 ± 0.02 |
| CV (%) | 29.30 | 10.25 | 17.54 | 103.78 | 29.89 | | 16.7 |
| Tavares (dry) | 0.40 ± 0.12 | 6.47 ± 1.05 | 13.97 ± 2.87 | 0.87 ± 0.28 | 0.06 ± 0.01 | 0.07 ± 0.03 | 0.26 ± 0.10 |
| CV (%) | 30.82 | 16.20 | 20.57 | 32.12 | 22.00 | 39.88 | 37.40 |
| Quiririm Puruba (rainy) | 0.23 ± 0.09 | 2.72 ± 0.78 | 5.93 ± 1.32 | 0.30 ± 0.17 | 0.03 ± 0.02 | 0.03 ± 0.02 | 0.01 ± 0.02 |
| CV (%) | 37.55 | 28.80 | 22.31 | 57.12 | 53.52 | 53.83 | 21.05 |
| Tavares (rainy) | 0.67 ± 0.10 | 6.10 ± 0.41 | 15.07 ± 0.76 | 0.89 ± 0.14 | 0.11 ± 0.01 | 0.06 ± 0.04 | 0.13 ± 0.03 |
| CV (%) | 15.13 | 6.66 | 5.02 | 14.75 | 11.61 | 64.99 | 22.17 |

NOB, element not observed in the samples. Sc, scandium; La, lanthanum; Ce, cerium; Sm, samarium; Eu, europium; Tb, terbium; Yb, ytterbium.

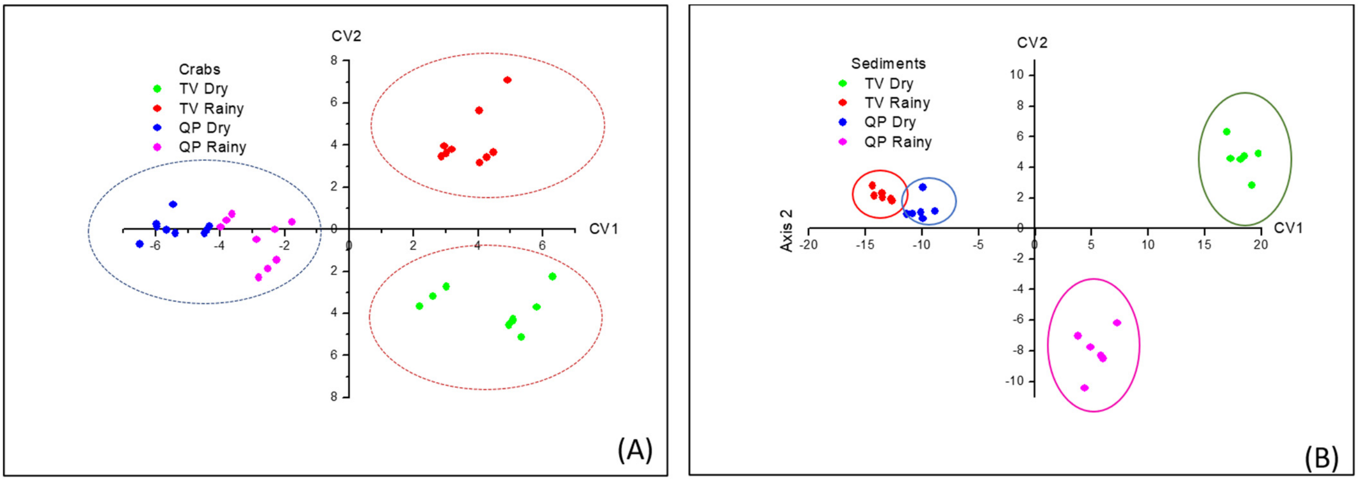


**Fig. 3.** CVA (canonical variates analysis) scatter plot of REE data. (A) Crabs and (B) sediment. Note the grouping data from the same region.

elements in the sediment, reducing them (Fig. 4C). On the other hand, in the region of the Quiririm-Puruba river system, the values do not differ ($p > 0.05$). Thus, there was no interference from the amount of rainfall (Fig. 4D). CVA scatter plot (Fig. 3C) also shows the data grouped according to the region but, different from what we observe in the crabs, Tavares sediment is distant according to axis 1. The cluster analysis (Fig. 3B) does not show clusters associated with the location of samples.

## 4. Discussion

In the last decades, rare earth elements (REE) have been widely used for industrial purposes, fuel production, high-tech products, and agricultural additives. These activities, simultaneously with population growth and inadequate sewage disposal, are contributing to a substantial increase in the amount of REE released into the environment (Bartolini et al., 2011; Romero-Freire et al., 2019). Although surrounded

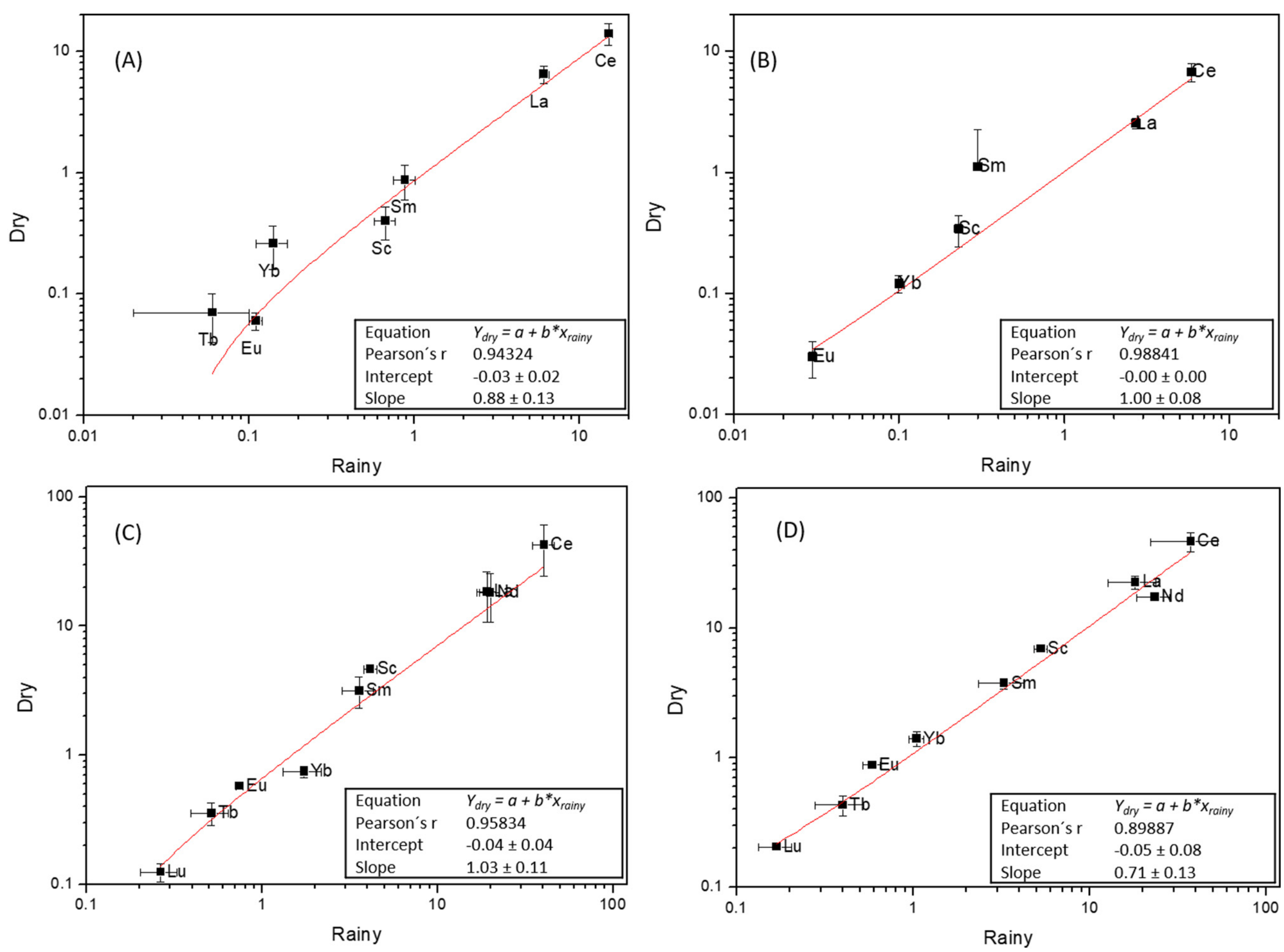


**Fig. 4.** REE concentration in crabs and sediment in the rainy and dry seasons, for each location. (A) Crabs from Tavares River (TV); (B) crabs from Quiririm-Puruba (QP); (C) sediment from TV and (D) sediment from QP. Linear fitting of data points was performed: $Y_{dry} = a + b * x_{rainy}$ and the parameters are shown in each figure.

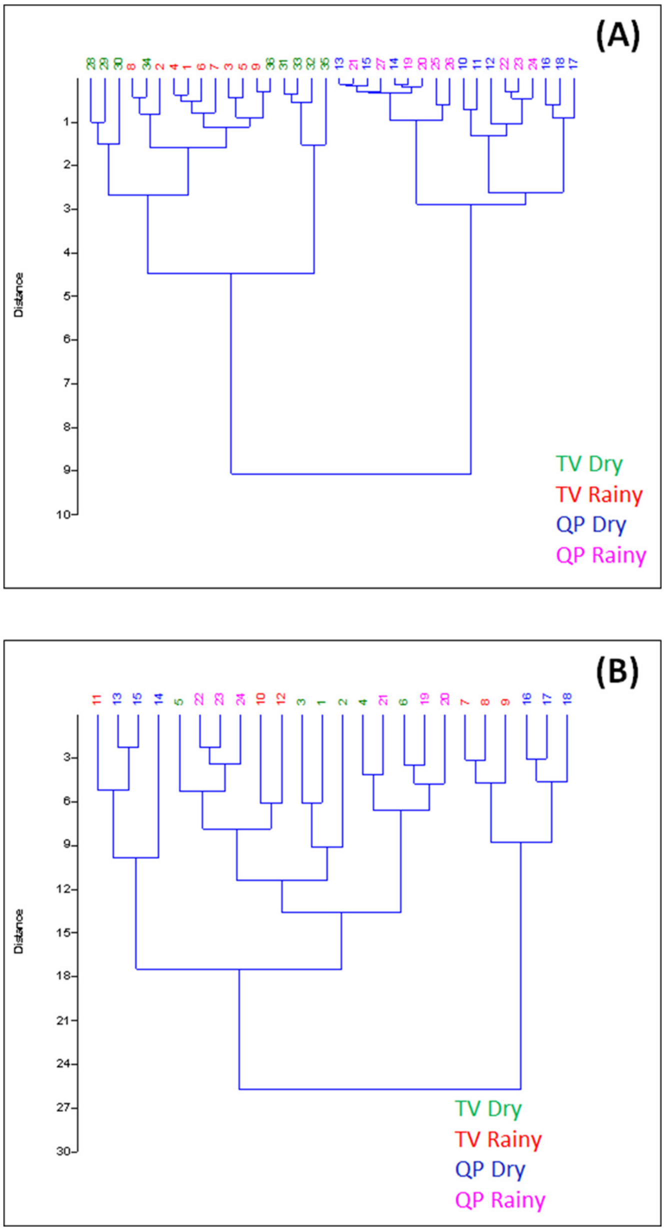


**Fig. 5.** Dendrogram obtained by cluster analysis using Euclidian distance. The color of number indicates the region: Tavares (TV) or Quiririm Puruba (QP) in dry or rainy seasons. (A) Data from crabs, Tavares and Quiririm Puruba clearly grouped and (B) data from sediment, where there are no clusters associated with the location. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 5**
*p*-Value obtained by paired Hotelling's test for sediment data.

| | QP dry | QP rainy | TV dry | TV rainy |
|---|---|---|---|---|
| QP dry | 0 | 4.66E−01 | 7.52E−03* | |
| QP rainy | 4.66E−01 | 0 | | 4.87E−01 |
| TV dry | 7.52E−03* | | 0 | 3.41E−02* |
| TV rainy | | 4.87E−01 | 3.41E−02* | 0 |

* Difference statistically significant $p < 0.05$.

by the Serra do Mar State Park, Ubatuba is a city compromised by solid residue discharge transported by river systems, mining activities, household waste, and possible oil spills (Alonso et al., 2010; Gondolo et al., 2011). Ubatuba has an extensive exploration of sandy clay mining from soil originated by granitic-gneiss rocks (Ferreira et al., 2008).

The two mangrove areas studied here are very close, but also very different (Fig. 1). Tavares is a river that crosses the city and receives large amounts of non-treated domestic sewage and several sources of waste leading to a huge impact on the mangrove region. The region of the Tavares River has a very high degradation index from mining activities (Ferreira et al., 2008). Also, there is a fishing port near the river mouth with dozens of boats that may eventually leak oil into the sea. Rare earth elements are known to be components of catalysts and petrol-producing industries. Therefore, during high tides, these components can be carried to the Tavares mangrove area. The other area, the mangrove of the Quiririm-Puruba river system is nearly free of human activity and maintains most of its original characteristics. The mining of sandy clay material has a medium degradation index in this region (Ferreira et al., 2008). Thus, all these factors are directly linked to higher concentrations of REE found the Tavares River in comparison with the Quiririm-Puruba river system.

Among the elements traced, cerium, lanthanum and ytterbium had the highest concentrations compared to other elements in both locations and seasons. Cerium is widely used in metallurgical processes and petroleum refining, and it is present in catalytic converter for cars, lamps, cigarette lighter flints, and others objects (Haque et al., 2014). In high concentrations, Ce may damage cell membranes, which has several negative influences on reproduction and the functions of the nervous system of organisms (Dahle and Arai, 2015). Lanthanum can be accumulated within organisms and can interfere with cellular functions, and crustaceans are especially sensitive to this REE, leading to the death and/or a delay in the age of maturity, affecting reproduction (Herrmann et al., 2016). On the other hand, Ytterbium is highly toxic to humans (Rim et al., 2013) and is known to cause delay of embryo and larval development, decreased survival and hatching rates, and causes malformation in zebra fish (Hongyan et al., 2002).

In fact, in the crabs, we found that Sc, La, Ce, Sm, Tb, and Yb had higher concentrations with statistically significant differences in the mangrove area of the Tavares River in the dry and the rainy seasons in comparison to the Quiririm-Puruba river system (Tables 2, 3 and

**Table 4**
Chemical elements found in the sediment collected in the Quiririm-Puruba and Tavares mangrove areas in the dry and rainy season. Values are given in mean concentration (ppm) with standard deviation and coefficient of variation.

| Locality/season | Concentration (ppm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sc | La | Ce | Nd | Sm | Eu | Tb | Yb | Lu |
| Quiririm Puruba (dry) | 4.65 ± 0.31 | 18.4 ± 7.74 | 42.50 ± 18.22 | 18.20 ± 7.49 | 3.16 ± 0.85 | 0.58 ± 0.03 | 0.36 ± 0.07 | 0.75 ± 0.07 | 0.12 ± 0.02 |
| CV (%) | 6.77 | 42.08 | 42.87 | 41.13 | 26.96 | 5.47 | 19.74 | 9.74 | 15.57 |
| Tavares dry | 6.90 ± 0.36 | 22.43 ± 2.61 | 46.50 ± 7.79 | 17.30 ± 1.13 | 3.74 ± 0.35 | 0.88 ± 0.05 | 0.43 ± 0.08 | 1.40 ± 0.18 | 0.21 ± 0.01 |
| CV (%) | 5.19 | 11.58 | 16.75 | 6.54 | 9.29 | 5.59 | 16.96 | 12.97 | 5.12 |
| Quiririm Puruba (rainy) | 4.15 ± 0.34 | 19.20 ± 2.43 | 40.5 ± 5.57 | 20.00 ± 2.61 | 3.58 ± 0.71 | 0.75 ± 0.04 | 0.52 ± 0.12 | 1.74 ± 0.43 | 0.27 ± 0.06 |
| CV (%) | 8.17 | 12.66 | 13.77 | 13.04 | 19.96 | 4.86 | 23.96 | 24.88 | 23.72 |
| Tavares (rainy) | 5.30 ± 0.46 | 18.15 ± 5.43 | 37.5 ± 15.40 | 23.50 ± 5.99 | 3.28 ± 0.93 | 0.59 ± 0.07 | 0.40 ± 0.12 | 1.05 ± 0.10 | 0.17 ± 0.03 |
| CV (%) | 8.61 | 29.92 | 41.03 | 21.26 | 28.47 | 11.27 | 30.54 | 9.58 | 21.47 |

Sc, scandium; La, lanthanum; Ce, cerium; Nd, neodymium; Sm, samarium; Eu, europium; Tb, terbium; Yb, ytterbium; Lu, lutetium.

Fig. 3A). This distinction is not so clear in the sediment (Tables 4, 5 and Fig. 3B), in which there were no statistically significant differences between the sediment data from Quiririm-Puruba and the Tavares River during the rainy season, for instance. Additionally, the crabs were more responsive to differences between seasons in the same region (Table 3). From the results of Figs. 3A, 4A and B it is possible to observe that the REEs in crabs sampled at Tavares River are strongly affected by the weather conditions; rainy and dry season ($r = 0.884$ Fig. 4A). In the crabs sampled at Quiririm-Puruba, the concentrations are more similar during dry and rainy periods ($r = 1.00$ Fig. 4B). These results are probably derived from different pollution inputs into Tavares River, crossing the central area of the city of Ubatuba. The Quiririm-Puruba, positioned at the protected area of Serra do Mar State Park, receives much less pollution. All of these factors make the crabs excellent bioindicators of REE accumulation.

Mangroves are areas of great importance to coastal communities, providing not only a source of food and resources but also protecting coastlines, preventing erosion and regulating our climate in tropical areas of 123 countries worldwide (UNEP, 2014). The excess of REE in mangroves can be harmful to this fragile ecosystem. According to the Brazilian legislation, mangroves, and their extension areas, are considered areas of permanent preservation and should be respected throughout the national territory. However, as we have shown here, some elements continue to be improperly discarded and reach the mangroves through the rivers.

The presence of REE elements in aquatic environments can affect the entire food chain, from the smallest living things to human beings themselves. Fiddler crabs can be found in all continents except Antarctica, including tropical, subtropical, and temperate regions of the world (Crane, 1975; Pinheiro et al., 2016). These small crabs are part of the food chain of several mangrove and estuarine species, such as blue crabs and fish, products largely sold in the fish markets and consumed by people and exported by many countries to different parts of world.

## CrediT authorship contribution statement

**Bruna Lavezzo:** Investigation, Formal analysis, Writing - original draft. **Angela Kinoshita:** Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing, Visualization. **Ana Maria G. Figueiredo:** Methodology, Investigation, Formal analysis, Writing - review & editing. **Mayara Maezano Faita Pinheiro:** Formal analysis, Visualization. **William Santana:** Conceptualization, Methodology, Investigation, Resources, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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