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Vintage analysis on superficial sediments to predict future trends in metal contamination of Santos and São Vicente Estuarine System

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A B S T R A C T

Due to its economic, social, and environmental importance, Santos and São Vicente Estuarine System is largely studied for almost two decades. Although many studies have been conducted, none of them tried to relate past activities to actual ones. This study provides an evaluation of the contamination on vintage superficial sediment samples investigating sediment contamination patterns over the years to help to understand future trends in metal contamination in this area. Thus, this study aims to assess levels of trace elements and rare earth elements (REEs) on samples collected in two seasonal periods of 2005 and 2006 (summer and winter). In each campaign, 16 surface samples were collected onboard R/V Veliger II, and trace elements and REEs were analyzed by neutron activation analysis. Results of metals presented similar levels over the years and it was not related to the port's activities since the levels did now increase following the total movement of containers. In addition, the enrichment of light REEs could indicate anthropogenic activities from steel plants, phosphate fertilizers, and the phosphogypsum piles. The system undergoes through many human pressures and constant monitoring over time it is important to avoid overloading the resilience capacity of the estuarine system because the expansion of port, industry, and urbanization is inevitable. From the results obtained, it was possible to conclude that SSVES undergoes more likely anthropogenic pressures from industrial activities and domestic effluents rather than port activity.

Introduction

Over two decades, many studies have been conducted on Santos - São Vicente Estuarine System (SSVES). In recent years many published articles present new approaches to the assessment of contamination status (e.g., [3, 6, 10, 19, 20, 38]) in the region. Although many studies regarding metal pollution are performed, none of them try to relate past activities to actual ones. In addition, articles published regarding rare earth elements in this region are scarce (e.g., [32]).

SSVES is considered one of the main economically important areas of Brazil. The strategic location between Santos Port, Cubatão city e São Paulo state transforms the Port into the largest port in Latin America, ranking, in 2020, the 43rd position in the world [25], with a total movement of 5.7 million of tons registered in January 2021, represented mainly by the exportation of sugar and soybeans [40]. In addition, the Cubatão Industrial pole represents the largest industrial complex in the country hosting companies from many sectors including petrochemical, steelmaking, chemical, fertilizers, and logistics. Both sectors present economic importance and contribute to the Baixada Santista metropolitan region reaching almost 3% of the state's gross domestic product (GDP) in 2018 [37].

Facing the challenges of the United Nations Decade of Ocean Science and the 14th goal of the 2030 Agenda for sustainable development which aims to conserve and make sustainable use of the oceans it is confirmed the prominence of ocean issues on the global agenda and place ocean health at the heart of sustainable development. Thus, studies regarding heavy metal contamination, in addition to the investigation of potential sources, bring up scientific knowledge to the proper management of potential aquatic resources, considering that these trace elements are well-known contaminants with deleterious effects on human health, once they are persistence, toxic in some forms and concentrations and also can bioaccumulate and biomagnificate through the food chain (e.g., [4, 30])

This study provides an evaluation of the contamination trends on vintage superficial sediment samples investigating sediment contamination patterns over the years. This information could support the understanding of future trends in metal contamination in SSVES. Thus, this study aims to assess levels of trace elements and rare earth elements (REEs) on samples collected in two seasonal periods of 2005 and 2006 (summer and winter) and relate them to a contamination historical deposition

Methodology

Study area and sampling design

SSVES is located on the southeastern Brazilian coast between 23.85°S, 46.50°W and 24°S, 46.10°W. It is composed of two main es-

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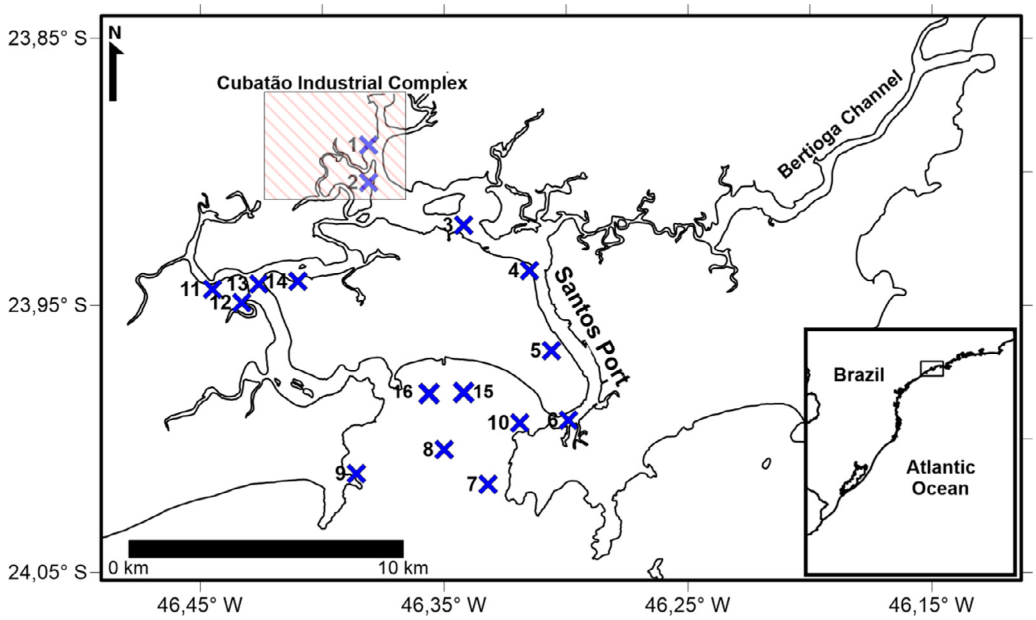


Fig. 1. Location of the surface sediment sampling points in SSVES.

tuarine channels; Santos Channel in the eastern part and São Vicente Channel in the western sector, and a marine component in Santos Bay. The system receives freshwater drainage from many rivers [28] and its sediment deposition is highly influenced by its fluvial transport and tidal currents [2, 35]. In consequence, the sediments represent a mixture mainly a continental source, from weathering and erosion of the rocks, with a small contribution of a marine source [12].

Based on previously published articles (e.g., [19, 22, 29]), SSVES can be divided into 3 main areas: (a) Area 1 covering Santos channel and the upper estuary with high mud content and reported as an area with more anthropic influence from Cubatão Industrial Pole (samples #1 and #2) and Santos Port (samples #3 - #6); (b) Area 2 represented by Santos Bay (samples #7 - #10, #15 and #16) and; (c) Area 3 in Sao Vicente channel reported as influenced by waste disposal (samples #11 - #14). This classification will be further statistically tested and used in the discussion of this article.

Surface sediment samples were collected on board R/V Veliger II from Oceanographic Institute of São Paulo University in 16 different stations along SSVES using stainless steel Van Veen grab and preserved in pre-cleaned polyethylene bags for further analysis, following Csuros and Csuros [9] recommendations. The sampling was carried out in two seasonal periods (winter and summer) in 2005 and 2006. Samples S15 and S16 were not collected in the summer of 2005 (Fig. 1).

Analytical procedures

Sediment samples were dried at 50 °C in a ventilated oven until a constant weight was reached and then sieved through a 2 mm sieve. For the determination of the total content of trace elements (As, Br, Co, Cr, Cs, Fe, Na, Rb, Sb, *Sc*, Th, U, and Zn) and rare earth elements (Ce, Eu, La, Lu, Nd, Sm, Tb, and Yb) in surface sediments, approximately 150 mg of sample (duplicate samples) and reference materials were weighed and sealed in pre-cleaned double polyethylene bags. All samples were irradiated for 8 h under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear research reactor at the Nuclear and Energy Research Institute - IPEN (SP-Brazil). After irradiation, two series of counts were made: the first after one week of decay and the second, after 15–20 days. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively. Data analysis was conducted using in-house gamma ray software, the VISPECT® program, to identify the gamma-ray peaks, and the ESPECTRO program to calculate the concentrations. The uncertainties of the results were calculated by error propagation. The details of the analytical methodology are described by Larizzatti et al. [23]. The methodology was certified by measuring reference materials Buffalo River Sediment (NIST SRM 2704), Soil 7 (IAEA), and BEN (Basalt –IWG-GIT). The Z value criteria was done according to Bode [5]. If $|Z| < 3$, the individual result of the control sample (reference material) lies within the 99% confidence interval of the target value. All Z-score values were in this interval range ($|Z| < 3$), indicating good precision and accuracy of the INAA technique.

Statistical analysis

Statistical analysis, such as Linear discriminant analysis (LDA), Principal Component Analysis (PCA), and regression analysis, were conducted in R Software [34] using "MASS" and "MVar" package [33, 42] to LDA analysis, "FactorMineR" and "factoextra" package [16, 24] to PCA and "ggpubr" [17] for regression analysis. All figures were produced using the "ggplot2" package [43].

Results and discussion

Results of metals in the summer (black columns) and winter (gray columns) of 2005 and 2006 are presented in Figs. 2 and 3, respectively. All obtained values are provided in Table S1 of Supplementary material. The areas were divided by colors where red corresponds to Area 1, green to Area 2, and blue, Area 3. Apart from anomalous values caused by pointed sources, such as anthropogenic or also volcanic input, metals tend to behave following the grain size of the sample, where fine-grained sediments present a reactive surface area higher than a sandy fraction, adsorbing more metals [11, 18, 41]. Area 2 presented the lowest values for all elements suggesting a more hydrodynamic area resulting in sediments composed mainly of sand as Kim et al. [19] reported. It is expected that Areas 1 and 3 would present higher levels of terrigenous elements, such as Cr, Fe, Rb, *Sc*, Th, U, and Zn, once both areas are located in the inner part of the estuarine system.

A linear discriminant analysis was performed to certify the distinction among these groups given by previously published articles. The accuracy was higher than 92% (Table 1, Fig. 4), meaning that almost

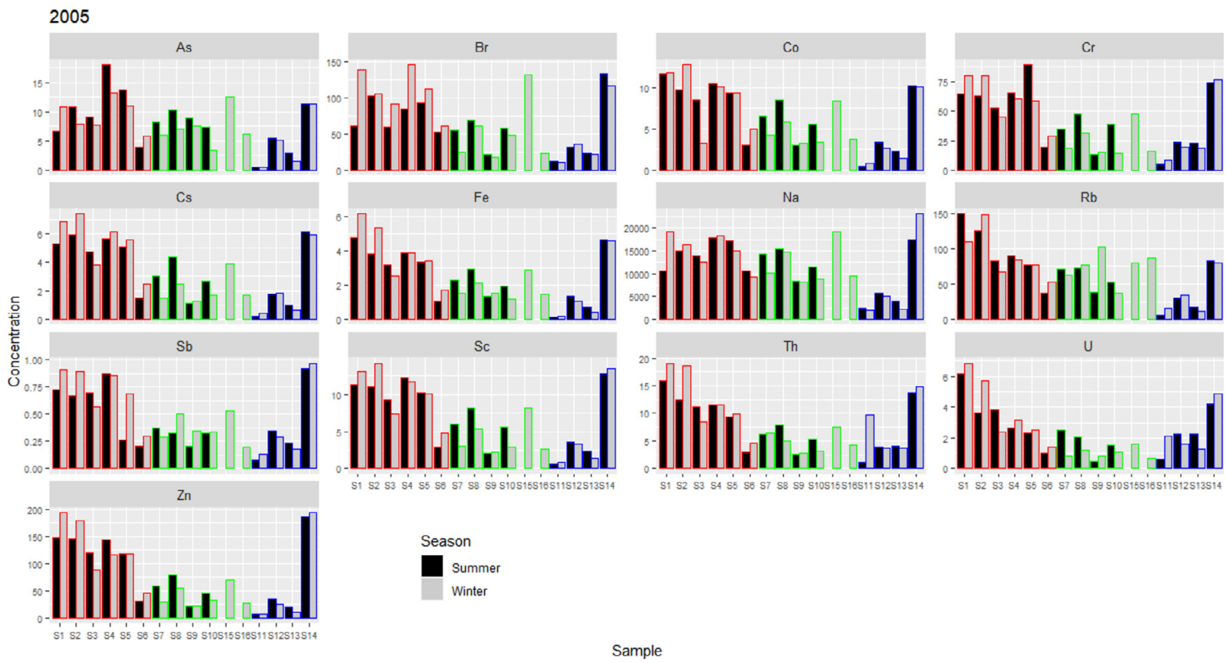


Fig. 2. Concentration (mg kg^{-1} and% for Fe) of trace elements in SSVES during each season of 2005. Colors are represented by the division of the main areas in which: (a) Red: Area 1, (b) Green: Area 2, and (c) Blue: Area 3.

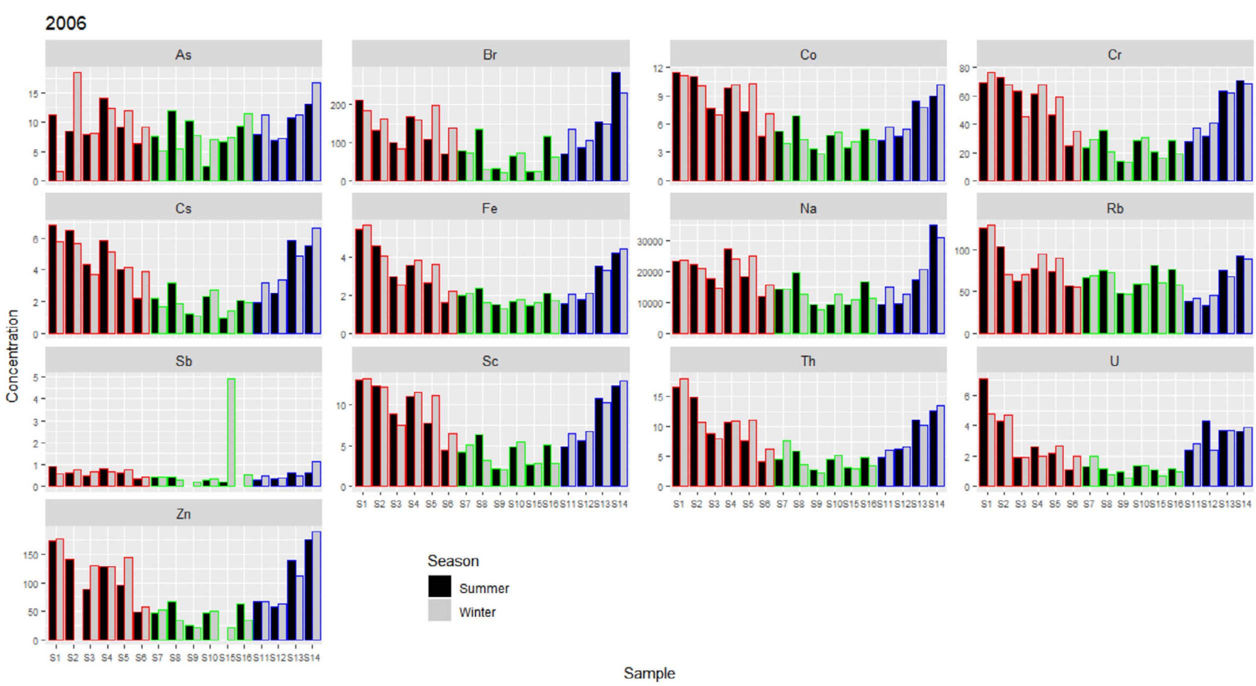


Fig. 3. Concentration (mg kg^{-1} and% for Fe) of trace elements in SSVES during each season of 2006. Colors are represented by the division of the main areas in which: (a) Red: Area 1, (b) Green: Area 2, and (c) Blue: Area 3.

Table 1
Confusion matrix given by the linear discriminant analysis.

	Area 1	Area 2	Area 3
Area 1	23	0	1
Area 2	2	20	0
Area 3	0	0	16
Total	25	20	17
Predicted	23	20	16
Prediction Accuracy	0.92	1.0	0.94

all samples were classified in the groups previously established (error rate = 0.048). Based on these results, it is possible to validate the same distribution found in the recently published articles.

Concerning metal contamination, this study compares the obtained values to the CONAMA 454/2012 [8] regulation which "*establishes general guidelines and reference procedures for the management of dredged material in waters under national jurisdiction*". As other sediment quality guidelines (e.g., [26, 27]), this regulation provides two levels corresponding to the magnitude of observed adverse effects given by empirical integration between chemical data and biological effects [36]. Level

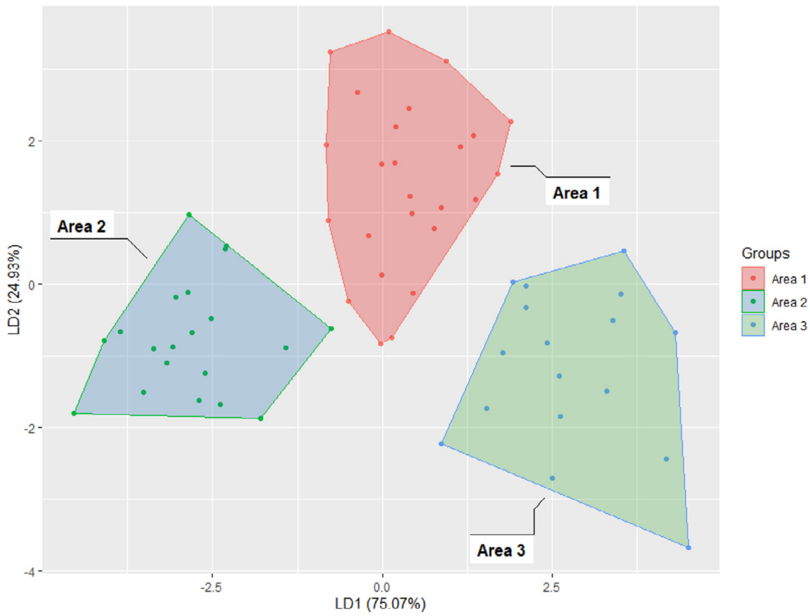


Fig. 4. Distribution of each area into the Linear Discriminant Analysis components (LD1 and LD2).

Table 2
Levels of As, Cr, and Zn established by CONAMA 454/2012, range obtained in this study (mg kg^{-1}) and total movements (in tons) of containers in Santos Port in the respective years.

	Sampling year	As	Cr	Zn	Containers movement*
Level 1	–	19	81	150	–
Level 2	–	70	340	410	–
Abessa et al. [1]	1998, 1999, 2000	–	5.46 – 111.72	42.65 – 83.26	39.940.386 (1998)
This study	2005, 2006	0.4 – 18.5	4.7 – 89.4	6.7 – 194.2	71.902.494 (2005); 76.297.193 (2006)
Silva et al. [38]	2007	1.4 – 22	7 – 113	18 – 343	80.775.867
Gonçalves et al. [14]	2010	5.3 – 18.6	9.4 – 43.24	20.0 – 68.2	96.025.028
Angeli et al. [3]	2012	1.48 – 23.66	5.42 – 50.50	9.52 – 88.19	104.543.783
Kim et al. [19]	2013	0.3 – 14.7	2.5 – 44.8	5.81 – 912.56	114.077.844

* SPA [40].

1 represents the limit in which no adverse effects are observed and Level 2 is the level where adverse effects most likely occur in the biota.

The values of Levels 1 and 2 compared to the range obtained in this study are given in Table 2. Only one sample (S5) slightly exceeds Cr results in Level 1 in the summer of 2005. Zn presented above Level 1 in S14 in all periods and S1 in almost all samples with exception of the summer of 2005. Many articles reported high values of Zn in the same region (Area 1) (e.g., [19, 38]) attributed to anthropogenic actions linked to the proximity to a potential source of this element and also to an area subjected of trapping continental materials from weathering and erosion.

The comparison with other studies in the same region and the total movements of containers (in tons) of Santos' Port in the sampling period of each study are also provided in Table 2. Abessa et al. [1] reported high values of Cr and did not verify a seasonal tendency, the samples surpassed values obtained in this study, but in their study samples were collected in front of the sewage outfall of Santos. Silva et al. [38] and Kim et al. [19] found high values of Zn in Bertioga Channel and the innermost of the SSVES, respectively. Both studies confirm that the sediment samples presented a strong lithogenic influence with an enrichment of this metal attributed to anthropogenic actions. Gonçalves et al. [14] and Angeli et al. [3] studying sediment cores in the upper estuary and Bertioga channel found similar and even lower levels than this study. They reported enrichment associated first, with the 19th century, when Santos Harbor was inaugurated and to the 1960s, the port expansion and the "Great Acceleration" globally happened.

Since the study conducted by Abessa et al. [1] with the sample collection in 1998 and 1999, the levels of metals did not show a significant increase. Many studies conducted in SSVES conclude that the enrichment/contamination of metals is related to anthropogenic actions such as harbor activities, urban development, and discharge of industrial waste (e.g., [14, 22]), however, when comparing those values to total movement of containers, in which increased each year, reaching about 147 millions of tons in 2021 [40], it is possible to conclude that there is not a direct relationship between port expansion to metal levels in sediments for these last years (~20 years). Some anomalous values could be attributed to indirect inter-related activities linked to port expansion or even punctual sources such as an increase in the population, sewage discharge, and industrial production expansion. In their article, Angeli et al. [3] hypothesize that considering all pressure the system undergoes with relatively low enrichment values, the SSVES is likely responding to consequences in the weathering and erosion of adjacent areas, that could be linked to human actions such as land-use, rather than the direct introduction of potentially metals contaminants. Thus, high values in the upper estuary, despite the proximity to Cubatão Industrial Complex, might be derived from natural continental processes that should be occurring with more intensity. This study presents relatively low levels, near the guidelines values, and minimum enrichment in this region (Area 1), not presenting harmful levels, but recent studies are showing reflexes in the diversity of benthic foraminifera [10], and also a large fraction in the exchangeable fraction of sediments [21] that could be easily remobilized and be available to the biological community rising the importance to maintain a temporal and spatial analysis.

Results obtained of REEs on each year; season (black and gray columns) and area (Area 1: red, Area 2: green; Area 3: blue) are pre-

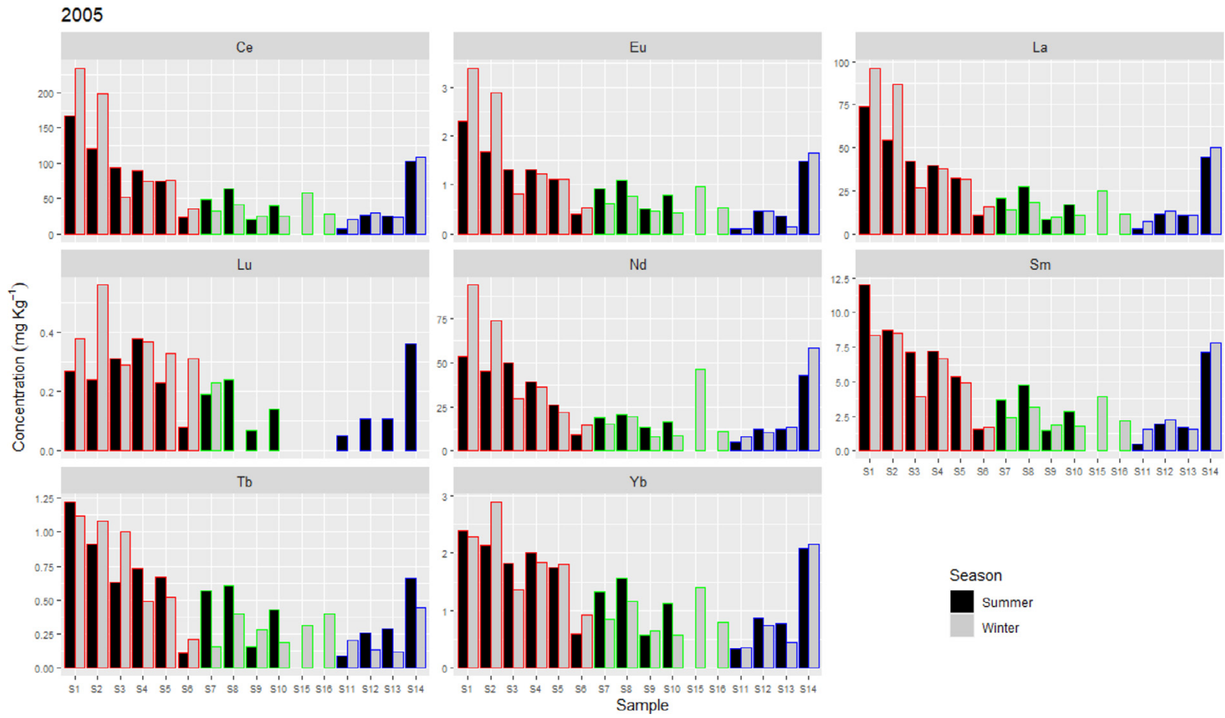


Fig. 5. Concentration (mg kg^{-1}) of REE elements in SSVES during each season of 2005. Colors are represented by the division of the main areas in which: (a) Red: Area 1, (b) Green: Area 2, and (c) Blue: Area 3.

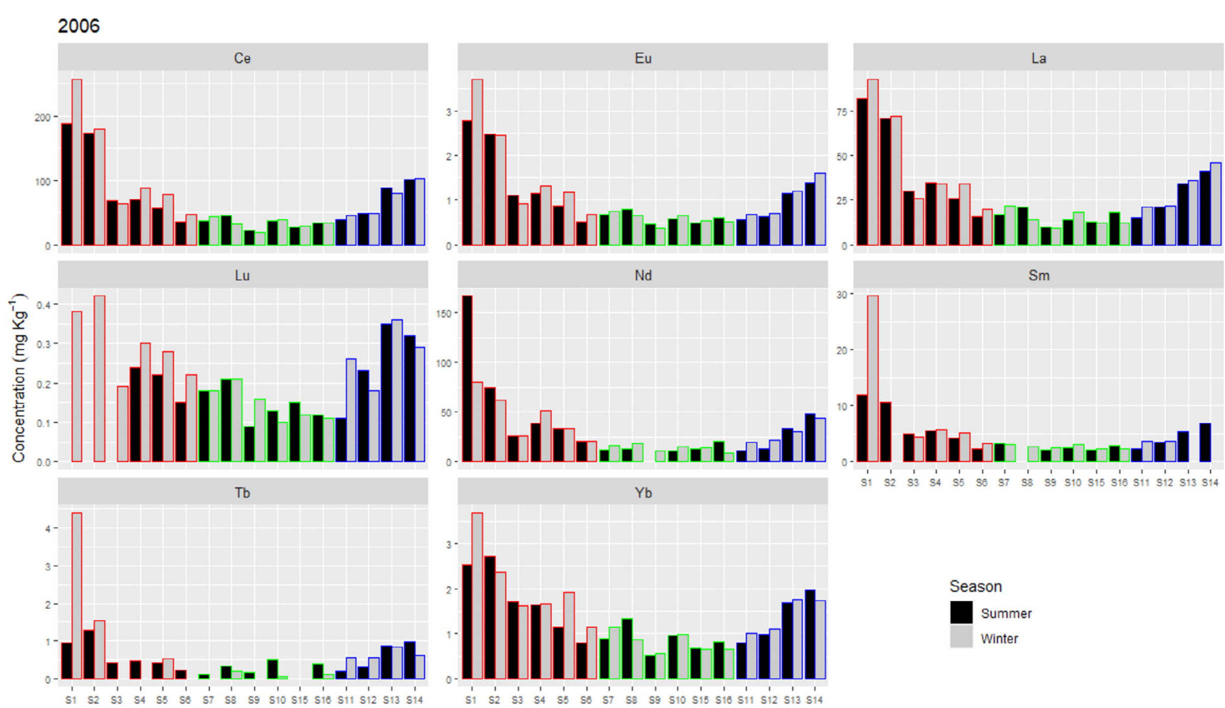


Fig. 6. Concentration (mg kg^{-1}) of REE in SSVES during each season of 2006. Colors are represented by the division of the main areas in which: (a) Red: Area 1, (b) Green: Area 2, and (c) Blue: Area 3.

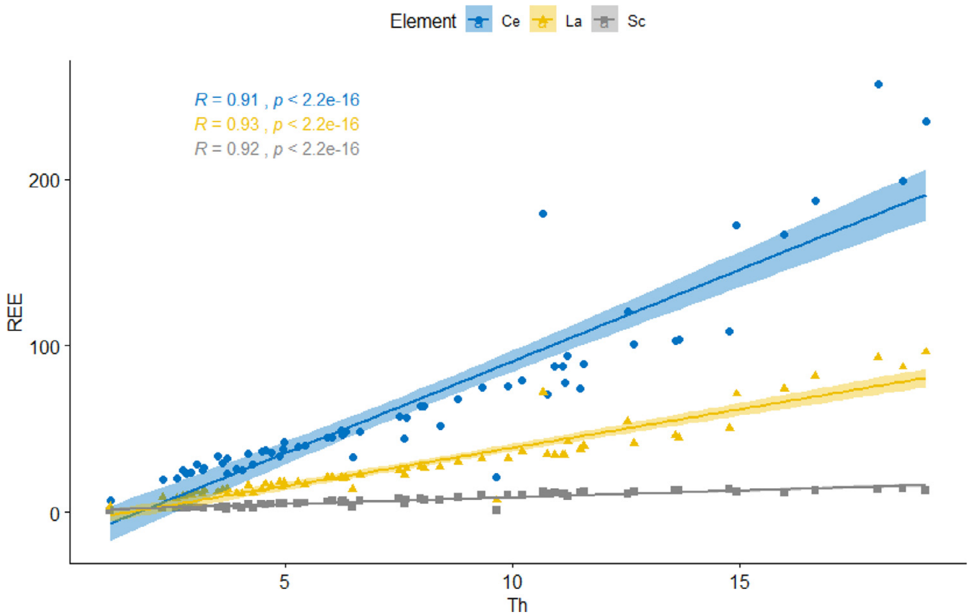


Fig. 7. Concentration of Th vs. Ce (Blue), La (Yellow), and *Sc* (grey). The regression line indicates the evidence of positive and significant ($p < 0.05$) correlation.

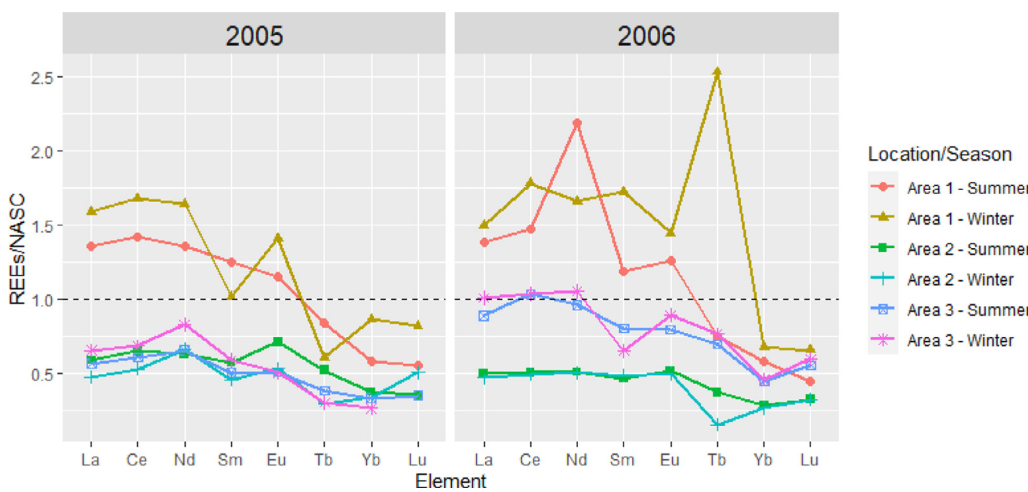


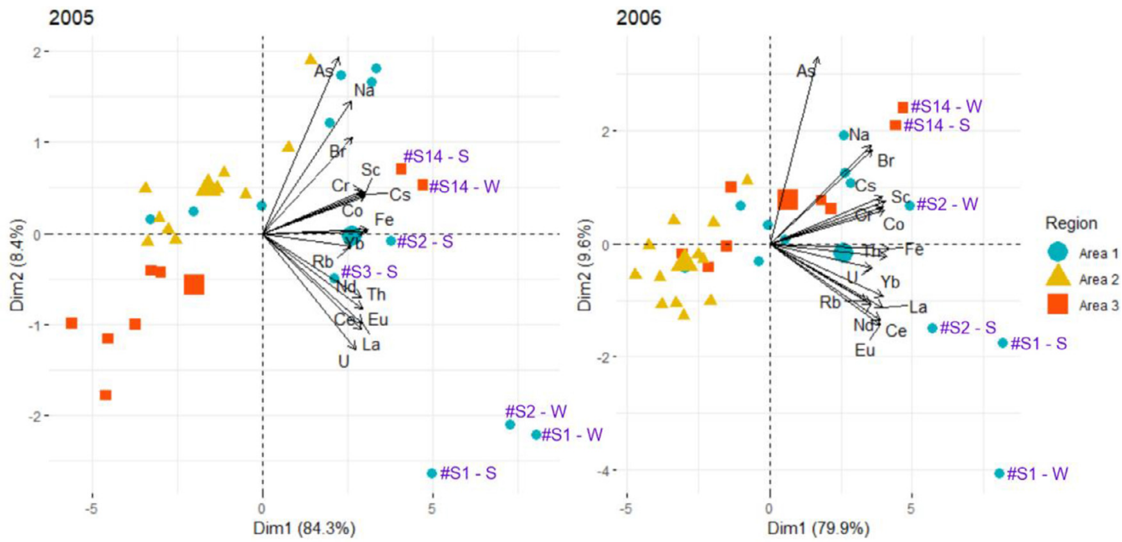
Fig. 8. Normalized rare earth elements (REEs) by NASC values divided by areas, season, and year.

sented in Figs. 5, 6 and Table S2 of Supplementary Material. Similar to metal behavior, Area 2 presented the lowest values of REEs, Area 1 the highest values, and Area 3, intermediate results.

Normally, despite their natural sources, radionuclides belonging to the same group of ^{238}U and ^{232}Th can be released into the aquatic systems through industrial processes like phosphate rocks processing, petrochemicals, and steel [31]. The correlation among Th vs. REEs, such as Ce, La, and *Sc* (Fig. 7 Figure) were positive and significant ($p < 0.05$) and these results might indicate a common source of these elements. Normally, higher concentrations of the REEs and Th and higher degrees of REE fractionation can be evidence for the greater influence of phosphogypsum (e.g., [7, 32])

The REEs results were normalized by the "North American Shale Composition" (NASC; [15]) and the results in each area, season, and year are given in Fig. 8. In both years, Area 1 was remarkable with enrichment of light REEs (La, Ce, Eu, Nd, and Sm). An article published in 2011 [38] also reported enrichment of these light REEs, but in a spatiotemporal analysis along cores, in the same area, in which the concentration of these elements decreased with depth.

This enrichment can be attributed to local industrial activities. Silva et al. [39] found high values of ^{232}Th, compared to the upper continental crust in the Cubatão River attributed to its enrichment-related to U isotopes which could be related to the presence of anthropogenic activities in the region such as steel plants, phosphate fertilizers, and the phosphogypsum piles. Some authors already attributed this enrichment to the influence of fertilizer plants that have been operating in the region producing large volumes of phosphogypsum, a by-product of phosphoric acid production, which is stored on the margins of nearby rivers (e.g., [13, 32, 38, 39]), but with a decrease downstream, indicating a limited area affected by these deposits [32]. Indeed this behavior can be confirmed with Principal Component Analysis (Figure 9). Dimension 1 presented high contributions of these light REEs and the samples with the highest contributions in this dimension are located in the inner part of the system (S1, S2, S3, and S14).



Considering that trace elements results showed similar concentrations over the years, indicating that Santos' Port does not affects directly trace elements enrichment, and the enrichment of light REEs suggested an anthropogenic influence given by fertilized plants, the spatiotemporal analysis showed that SSVES is responding more likely to industrial activities and domestic effluent deposits rather than the port's activities.

In 1984, the Companhia de Tecnologia de Saneamento Ambiental (CETESB) with the Environmental Department of São Paulo State (SEMA SP) initiated an intense government program to control the pollution in SSVES. Concerning metals contamination, the results of this study may suggest the effectiveness of these actions and also, take into account the very resilience of the estuarine environment. Despite the conclusion that seems optimistic, the system undergoes to many human pressures and constant monitoring over time it is important to avoid overloading the resilience capacity of the estuarine system, because the expansion of port, industry and urbanization inevitable.

Conclusions

Trace elements and rare earth elements were quantified in 16 samples collected in two seasonal periods in 2005 and 2006 to understand future trends in metal contamination in SSVES. Trace elements presented similar levels over the years and it was not related to the port's activities since the levels did now follow the total movement growth. The enrichment of light REEs and its association with Th content indicated anthropogenic activities from steel plants, phosphate fertilizers, and the phosphogypsum piles. Thus, it was possible to conclude that SSVES undergoes more likely anthropogenic pressures from industrial activities and domestic effluents rather than port activity.

However results presented more industrial and domestic influence, it seems that the environmental management controlled by governmental sanitary agencies are effective, once the samples, apart from some exception with punctual sources, did not present pollution levels. Nevertheless, it is important to maintain constant monitoring to avoid overload the resilience capacity since human pressure are still going to act through industrial and port development in the region.

Credit author statement

BSMK analyzed and interpreted data and wrote main part of the manuscript. EPA and PSCS were responsible for formal analysis and investigation. RCLF was responsible for supervision and writing, editing and review. ESB and DITF were responsible for funding acquisition, project administration, supervision, and manuscript revision. All authors read and approved the final manuscript.

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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.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtemin.2023.100049.

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