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Trace element fluxes during the "Anthropocene" in a large South American industrial and port area (Santos and São Vicente estuarine system, SE, Brazil)

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Abstract The worldwide evidence of human activities on the environment led the scientific community to recognize a new geologic time unit known as the "Anthropocene." Since the twentieth century, urbanization and industrialization needs driven by population and economic growth have impacted several ecosystems including the estuaries. To assess the contamination, provenance, and fluxes of trace elements (As, Cr, Cu, Ni, Pb, Sc, V, and Zn) over the last century, a geochemical and chemometric technique was employed in sediment cores of an industrial and port region of international importance, the Santos and São Vicente Estuarine System (SSVES). The results indicated low contamination, with the highest enrichment factors (EFs) for Cu (EF = 3.1), Pb (EF = 2.7), Zn (EF = 2.4), and As (EF = 2.3) found next to the harbor area. The Pre-industrial records confirm the relatively high concentrations of As and its naturally enriched occurrence on the Brazilian shelf. Sediment accumulation rates and trace element fluxes showed a general increase over the years, since the early 1960s, associated with the "Great Acceleration" of the mid-twentieth century. These alterations are human-induced and include urbanization and industrialization. Nonetheless, as the contents and enrichment of trace elements indicate that the region is not severely polluted, we hypothesize that the contamination in the SSVES is likely related to the drainage and erosion of the urbanized adjacent area, rather than direct disposal of inorganic contaminants from the industrial activity.

Keywords Preindustrial levels · Anthropogenic pressure · Trace element fluxes · Sediment records · Santos and São Vicente estuarine system

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Introduction

The extensive impact of anthropogenic activities and their unique mark on geological records led the scientific community to debate the definition of a new geologic epoch, the Anthropocene (Crutzen & Stoermer, 2000; Waters et al., 2016). The Anthropocene Working Group (AWG) of the Subcommission on Quaternary Stratigraphy (SQS) of the International Commission of Stratigraphy (ICS) established that the Anthropocene is stratigraphically distinct from the Holocene and decided to its formalization as a new geochronologic unit; however, the topic is currently under evaluation (Waters et al., 2016).

Although the human influence on the environment is undeniable, the exact period in which the Anthropocene began is still debatable. Initially, it was proposed that James Watt's invention of the steam engine catalyzed the beginning of the

Anthropocene, thus linking it directly to the Industrial Revolution (Crutzen & Stoermer, 2000). These technological advances marked a shift from a long period of slow population growth, landscape modification by agricultural activities, and energy use mainly from wood burning, to an interval of accelerated population growth, urbanization, and industrialization driven by increased use of fossil fuels (Zalasiewicz et al., 2015).

Precisely, the period following the end of World War II associated with rapid demographic expansion, paralleled by an increase in the global economy and associated environmental changes, is termed by many as the Period of the Great Acceleration. Zalasiewicz et al. (2015) proposed the year of 1945 (Trinity explosion; the first nuclear test) as the GSSA (Global Standard Stratigraphic Age, i.e., the starting point) of the Anthropocene, due to the clear presence of artificial radionuclides from nuclear tests. However, the radioactive record in sediment cores in the South American coast of the South Atlantic Ocean suggests 1963 as a chronostratigraphic marker, in which the maximum fallout from the nuclear test is observed (Ferreira et al., 2016). Given that Zalasiewicz et al. (2015) and Ferreira et al. (2016) are based on precisely dated stratigraphic records, this study will follow this methodological approach.

During the "Great Acceleration," the population doubled in just 50 years, and the global economy increased by more than 15-fold. Since 1960, petroleum demand has increased by a factor of 3.5. Additionally, the number of vehicles rose significantly from approximately 40 million at the end of WWII to almost 700 million in 1996. Between 1950 and 2000, the world's population living in cities increased from 30 to 50%, and this increasing trend continues (Steffen et al., 2007).

In this situation of worldwide environmental change, the coastal zone is significantly susceptible. Specific reasons include a high demographic and industrialized index, and the characteristic sustained growth and development of these regions over the past 150 years (Ontiveros-Cuadras et al., 2019; Ramesh et al., 2015). Moreover, estuarine and coastal systems receive significant fluvial inputs, as well as dissolved and particulate matter. As a result, anthropogenic fluxes of trace elements to estuaries and coastal zones have risen significantly, disrupting biogeochemical cycles (Andrade et al., 2017).

Metal contamination has been a worldwide focus of study due to its harmful impact on different ecosystems and, ultimately, human health (Birch, 2018). In recent years, several studies have focused on metal concentrations and their distribution, historical trends, sources, and environmental fate (e.g., Rubio et al., 2010; Chabukdhara & Nema, 2012; Gonçalves et al., 2013; Kim et al., 2016; Angeli et al., 2019; Ontiveros-Cuadras et al., 2019. Varol et al., 2020; Manju et al., 2020; Álvarez-Vázquez et al., 2020; Álvarez-Iglesias et al., 2020). Studying the role of sediment in trapping different pollutants is essential to assess the ecological state of water environments.

The mid-twentieth century marked a rapid urbanization and solid industrial developmental process in Brazil, resulting in substantial ecological impacts (Bregunce et al., 2011). These environmental impacts were more pronounced in estuaries and are linked to port operations and urban and industrial waste dumps (Chakraborty et al., 2014). The Santos and São Vicente estuarine system (SSVES) is an example of this situation (Braga et al., 2000; Luiz-Silva et al., 2002). The estuarine system houses the largest port of Latin America, deemed the 39th largest in terms of loading and unloading worldwide (CODESP, 2011). For the maintenance of port operations, it is essential to drag the contaminated sediments of the Santos and Piaçaguera channels, resulting in the resuspension of pollutants and ultimately impacting the water quality and the biota. Previous studies showed a metal pollution problem (e.g., Cu, Pb, Zn), especially at the upper estuary, where the main industrial complex (Cubatão Industrial Complex) of this region is located (Bordon et al., 2011; Buruaem et al., 2013; Gonçalves et al., 2013; Hortellani et al., 2008; Kim et al., 2016, 2019).

To understand the impact of increasing human influence, we studied two main aspects in this region: (i) the possible sources of trace elements in the SSVES and (ii) the fluxes of trace elements during the Anthropocene. To address these questions, dated sediment cores were analyzed combining a geochemical and chemometric approach. Therefore, this study can provide new data to confirm or discard the new proposed geological epoch and give insights into human influence as a significant geological agent in the Southeastern coast of Brazil.

Material and methods

Study area and sampling

The SSVES is located on the central coast of the State of São Paulo. Brazil (23° 90′ S–24° 00′ S, 46° 30′ W–46° 50′W), with the rainy season from October to April and the dry season extending from May to September. The climate is characterized as hot tropical humid. Three morphological sectors can be distinguished within the estuarine area: the Bertioga channel, Santos Bay, and the upper estuary (Kim et al., 2019). In the upper estuary, several rivers transport the sediments from the Serra do Mar into the SSVES. Precambrian metamorphic rocks of granitic composition are the source of the sediments of this system (Perrota et al., 2005). Relatively complex hydrodynamics characterizes the estuarine environment, which receives sediments from the region's watershed, becoming particularly vulnerable to sedimentation and contaminant accumulation from nearby industrial areas (Abessa et al., 2008).

The study area has been characterized by high anthropogenic activity over the last 120 years, with the construction of the Port of Santos in 1896 and its expansion after the opening in the 1920s of the Henry Borden hydroelectrical plant (Jesus et al., 2020; Martins et al., 2007). Nonetheless, urbanization and industrialization along the estuarine system started around the 1950s with the beginning of the activities of the Cubatão Industrial Complex and the expansion of the Port of Santos (Luiz-Silva et al., 2008). The operation of a steelplant, with extensive use of caustic soda (employing the mercury cell technique), marked the 1960s. Fertilizer industries (phosphate and nitrogen-based products) appeared by the 1970s and have already produced, as waste, about 69 million tons of phosphogypsum (Hortellani et al., 2008). Large quantities of solid waste discharges from domestic activities of the cities of Santos and São Vicente coincided with the fertilizer industries implantation (Martins et al., 2007). Moreover, both harbors of the steelplant and the fertilizer industry are located in the estuary, where iron and phosphate ores are handled (Luiz-Silva et al., 2008). The degradation of the estuarine system and the harmful effects of pollution would be reversed only from 1984, when an intensive environmental program was conducted to improve the environmental quality and control the air, water, and soil pollution (CETESB, 2001). Despite the efforts to improve environmental quality in the 1980s, population, urbanization, and industrialization continued to rise in the following years.

Several studies have found that inorganic contaminants still impact the estuarine system (Bordon et al., 2011; Hortellani et al., 2008; Kim et al., 2016, 2019; Luiz-Silva et al., 2008; Torres et al., 2009). Moreover, according to CETESB (2001), the industrial activities in the region can be grouped based on its products and trace metal potential emission. This grouping resulted in one steel plant with potential emission of Cu, Mn, Ni, and Zn; two oil refineries with potential emission of Cu, Cr, Ni, Hg, and Zn; eleven chemical and petrochemical industries with potential emission of Cd, Cu, Cr, Mn, Ni, Pb, Zn, and Hg; and seen fertilizer industries with possible emission of Pb, Ni, and Zn.

In April 2012, four sediment cores were collected along the SSVES with a gravity core sampler. The position of the sampling stations is shown in Fig. 1, and their coordinates and core information are given in Table S1 in Supplementary Material. The cores were fractionated into 2-cm-thick slices and freeze-dried.

General analyses

In order to quantify the mud fraction (clay + silt; < 0.063 mm), grain size analysis was conducted by subjecting the samples to wet sieving in a 0.063-mm mesh sieve. This technique was chosen because most contaminants are adsorbed on the fine-grained fraction, where the contact surface is larger (Förstner & Salomons, 1980). Variation in element concentrations as a function of sediment grain size is attributed to differences in their adsorption potential on clay minerals, metal oxides, and organic matter, which tend to be concentrated in smaller aggregates (Kersten & Förstner, 1995).

Bulk samples were subjected to a partial acid digestion technique following the SW 846 US EPA 3050B method (USEPA, 1996). This method dissolves the "environmental available" elements, such as those bound to the organic matter, carbonates, and Fe/Mn oxides and adsorbed onto fine-grain

Fig. 1 Sampling locations (S1, S2, S3 and S4) and possible pollution sources along the Santos and São Vicente estuarine system

particles, excluding those linked to the silicate structure. Trace elements (As, Cr, Cu, Ni, Pb, Sc, V, and Zn) were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES), and their levels are presented in Table S2, S3, S4, and S5 of the Supplementary Material. A certified reference material (SS-2 from EnvironMAT™ CRM SPC Science) was used to validate trace element determination's precision and accuracy, and the results are given in Table 1.

The activities of ^{210}Pb and ^{226}Ra were determined by high-resolution gamma spectrometry in low-background high pure Ge gamma spectrometer (EG&G ORTEC. model GMX25190P). According

Table 1 Confidence interval, mean, relative standard deviation and recovery from the CRM

Element	Certified confidence interval (mg kg^{-1})	Mean (mg kg^{-1})	Relative standard deviation (%)	Recovery (%)
As	65–85	76.4	6	101.88
Cr	30–38	32.5	3	95.58
Cu	182–200	188.9	3	98.92
Ni	50–58	54.4	2	100.85
Pb	116–136	125.7	3	99.83
V	31–37	29.9	7	87.91
Zn	444–490	467.4	4	100.09

to previous works (Ferreira et al., 2013; Figueira et al., 2007), sedimentation rates and core dating were calculated from $^{210}Pb_{xs}$.

Dating model, MAR, and trace element fluxes

The CRS (Constant Rate of Supply) model (Appleby & Oldfield, 1978) was used to determine the age models and mass accumulation rates (MARs, g cm^{-1} $year^{-1}$). This model assumes that a constant rate of $^{210}Pb_{xs}$ is supplied, and the sedimentation is time-dependent. Corroboration of the ^{210}Pb chronology was achieved using the weapon fallout ^{137}Cs. The activity levels of each core are given in Table S6, S7, S8, and S9 in the Supplementary Material.

Based on the excess ^{210}Pb ($^{210}Pb_{xs}$) activity profiles, MARs were determined. The mass accumulation rates can be shown in the following formula:

$$\varphi(z) = \frac{1}{\lambda}\left[\frac{I(A)_{tot} - I(A)_z}{(A)_z}\right]$$

where φ is the mass accumulation rate at depth z; λ is the constant decay for ^{210}Pb (0.0311 $year^{-1}$); $I(A)_{tot}$ is the total inventory; $I(A)_z$ is the inventory from the top until depth z; and $(A)_z$ is the $^{210}Pb_{xs}$ activity at depth z.

According to Cochran et al. (1998), we calculated element fluxes through the multiplication of the mass accumulation rate by the element concentration with the following formula:

$$Fi = Si[Me]$$

where Fi = metal flux at i interval (μg g^{-2} cm^{-2} $year^{-1}$), Si = the accumulation rate derived from ^{210}Pb method (g cm^{-2} $year^{-1}$) for the i interval, and Me = metal concentration (μg g^{-1}).

Assessment of contamination

Sediment quality guidelines (SQGs), such as the Brazilian legislation for classifying dredged sedimentary materials CONAMA 454/2012 (CONAMA, 2012), were used in this research, to assess the quality of the sediments. The threshold levels are given in Table 2, where level 1 is the level at which no harmful effect on the biological community is detected, and level 2 is the level at which adverse effects might arise within the biological community.

The evaluation of the contamination status of the SSVES was determined through the calculation of the enrichment factor (EF) (Zoller et al., 1974). The EF is calculated as follows:

$$EF = \frac{\left(\frac{M}{X}\right)_{sample}}{\left(\frac{M}{X}\right)_{background}}$$

where M is the concentration of the element of concern, and X is the concentration of the normalizing element. By convention, if $0.5 \leq EF \leq 1.5$, the trace element is provided as a weathering product from crustal rocks; meanwhile, an $EF > 1.5$ indicates an anthropogenic contribution (Zhang & Liu, 2002).

Differences in grain size and mineralogy were compensated by normalization with a conservative element (i.e., Li, Al, Ti, Fe or Sc). The element Sc was selected as the reference element for normalization due to its lithogenic and conservative nature and strong association with the fraction of fine-grain sediments (UNEP, 1995) (Table 3). Background levels (BLs) were assessed by using the mean trace element contents of the 5 deepest samples from the bottom of each core. These samples, considering the chronology, represent pre-industrial conditions.

Statistical analyses

Chemometrics can be a valuable tool in environmental studies, especially considering the large amounts of data generated with the geochemical analyses and the complexity of the processes under investigation. Thus, to study the relationship between the elements and identify processes that affect the sediment trace element contents, Pearson's correlation coefficients and principal component analysis (PCA) were carried out on the dataset of each sediment core. The PCA was conducted to investigate the interrelationships between variables and evaluate the possible sources of trace elements. Many researchers (Angeli et al., 2020; Filgueiras et al., 2004; Geng et al., 2015; Hosokawa et al., 2020; Rubio et al., 2000; Varol et al., 2020) have used this technique in the evaluation of

Table 2 Mean ± standard deviation, range of concentration, and background levels (BLs) (mg kg^{-1}) for trace elements from this study, range of concentrations from other studies in the same region, and threshold effect and probable effect levels from the Brazilian legislation (CONAMA 454/2012)

Location	As	Cr	Cu	Ni	Pb	Sc	V	Zn	Reference
S1	8.94 ± 2.33 (4.33–13.40) BL = 7.31 ± 2.33	27.12 ± 6.04 (11.05–34.68) BL = 31.15 ± 6.04	7.43 ± 0.90 (4.83–9.44) BL = 7.85 ± 0.90	10.62 ± 2.19 (4.64–13.49) BL = 11.93 ± 2.19	11.72 ± 1.51 (7.56–14.43) BL = 12.22 ± 1.51	4.85 ± 1.22 (1.73–5.73) BL = 5.81 ± 1.22	28.21 ± 5.73 (13.11–36.72) BL = 32.06 ± 5.73	45.35 ± 5.02 (32.94–53.17) BL = 49.68 ± 5.02	This study
S2	16.45 ± 4.81 (5.29–23.66) BL = 19.22 ± 2.42	39.93 ± 5.33 (27.97–50.50) BL = 45.66 ± 3.23	28.19 ± 4.65 (15.56–33.65) BL = 30.76 ± 2.02	19.57 ± 2.78 (13.48–26.07) BL = 21.79 ± 2.58	14.49 ± 2.66 (8.96–18.64) BL = 16.17 ± 0.67	6.77 ± 1.20 (4.09–8.81) BL = 8.09 ± 0.51	50.50 ± 8.91 (29.54–63.36) BL = 59.98 ± 2.84	70.45 ± 9.92 (46.05–88.19) BL = 75.73 ± 3.86	This study
S3	7.27 ± 1.94 (2.58–12.20) BL = 5.16 ± 1.74	21.65 ± 4.20 (10.81–31.24) BL = 18.39 ± 6.28	5.76 ± 2.02 (2.64–12.69) BL = 4.42 ± 1.37	8.60 ± 1.62 (4.28–12.19) BL = 7.30 ± 2.39	7.86 ± 1.72 (3.70–12.13) BL = 6.33 ± 2.22	3.03 ± 0.67 (1.44–4.75) BL = 2.56 ± 0.95	23.56 ± 4.88 (11.42–34.22) BL = 19.57 ± 6.87	34.22 ± 10.06 (15.24–75.81) BL = 26.84 ± 9.37	This study
S4	3.16 ± 0.91 (1.48–6.02) BL = 2.81 ± 0.21	8.51 ± 2.91 (5.42–18.09) BL = 5.98 ± 0.61	3.83 ± 1.57 (1.65–8.13) BL = 1.830.18	3.62 ± 1.39 (2.17–8.06) BL = 2.47 ± 0.25	5.64 ± 2.38) 2.58–12.65 BL = 2.87 ± 0.26	1.29 ± 0.47 (0.78–2.84) BL = 0.90 ± 0.09	10.05 ± 3.25 (6.51–20.63) BL = 7.87 ± 0.76	23.16 ± 9.33 (9.52–48.35) BL = 11.03 ± 1.31	This study
SSVES. Brazil	0.70–11.51	3.93–44.78	1.26–48.78	1.67–17.12	2.30–64.02	0.63–5.90	4.61–36.62	10.04–912.56	Kim et al., 2018
Paranaguá Bay, Brazil	0.13–32.33	0.74–43.75	010–16.54	0.20–16.63	0.39–18.77	n.d	n.d	2.04–66.01	Angeli et al., 2020
Guanabara Bay, Brazil	n.d	18–297	18–423	11–41	18–287	n.d	n.d	23–698	Aguiar et al., 2016
Caravelas Estuary,Brazil	2.76–34.24	9.18–62.85	1.40–6.67	1,40–7.37	2.87–23.26	n.d	n.d	10.98–53.29	Angeli et al., 2019
Todos os Santos Bay, Brazil	0.80–26.3	5.58–17.7	2.52–33.7	1.48–23.7	10.9–325	n.d	n.d	20.1–667	Hatje & Barros, 2012
Cuñani Estuary, Brazil	7.10–22.10	n.d	6.00–26.50	12.30–28.50	8.60–27.10	6.00–18.00	54.00–151.00	46.00–93.00	Xavier et al., 2020
Level 1	19	81	34	20.9	46.7	n.d	n.d	150	CONAMA., 2012
Level 2	70	370	270	51.6	218	n.d	n.d	410	CONAMA., 2012

Table 3 Correlation matrix of mud content and the analyzed elements in the sediment cores

	%Mud	As	Cr	Cu	Ni	Pb	Sc	V	Zn
a (S1)									
% Mud	1								
As	0.45	1							
Cr	0.93**	0.48**	1						
Cu	0.14	0.21	0.39*	1					
Ni	0.93**	0.54**	0.99**	0.42*	1				
Pb	0.55**	0.40*	0.68**	0.73**	0.70**	1			
Sc	0.92**	0.38*	0.99**	0.39**	0.98**	0.65**	1		
V	0.86**	0.51**	0.96**	0.33	0.95**	0.57**	0.95**	1	
Zn	0.75**	0.44**	0.90**	0.67**	0.92**	0.78**	0.90**	0.87**	1
b (S2)									
%Mud	1								
As	0.82**	1							
Cr	0.84**	0.84**	1						
Cu	0.93**	0.81**	0.93**	1					
Ni	0.69**	0.79**	0.93**	0.85**	1				
Pb	0.75**	0.63**	0.73**	0.75**	0.58**	1			
Sc	0.89**	0.86**	0.96**	0.92**	0.86**	0.66**	1		
V	0.91**	0.88**	0.97**	0.93**	0.86**	0.72**	0.99**	1	
Zn	0.47**	0.41**	0.62**	0.62**	0.63**	0.81**	0.46**	0.51**	1
c (S3)									
%Mud	1								
As	0.55	1							
Cr	0.81**	0.78**	1						
Cu	0.37**	0.84**	0.60	1					
Ni	0.82**	0.80**	0.99**	0.65**	1				
Pb	0.67**	0.88**	0.89**	0.85**	0.91**	1			
Sc	0.83**	0.68**	0.98**	0.44**	0.96**	0.79**	1		
V	0.75**	0.84**	0.96**	0.66**	0.97**	0.87**	0.93**	1	
Zn	0.48**	0.83**	0.71**	0.96**	0.75**	0.91**	0.56**	0.71**	1
d (S4)									
%Mud	1								
As	0.74*	1							
Cr	0.88**	0.90**	1						
Cu	0.85**	0.80**	0.96**	1					
Ni	0.87**	0.90**	0.99**	0.96**	1				
Pb	0.88**	0.87**	0.98**	0.97**	0.97**	1			
Sc	0.88**	0.89**	0.99**	0.96**	0.99**	0.97**	1		
V	0.84**	0.90**	0.99**	0.94**	0.99**	0.96**	0.99**	1	
Zn	0.86**	0.84**	0.95**	0.98**	0.95**	0.98**	0.94**	0.93**	1

**Pearson's correlation significance at the 0.01 level; *Pearson's correlation significance at the 0.05 level

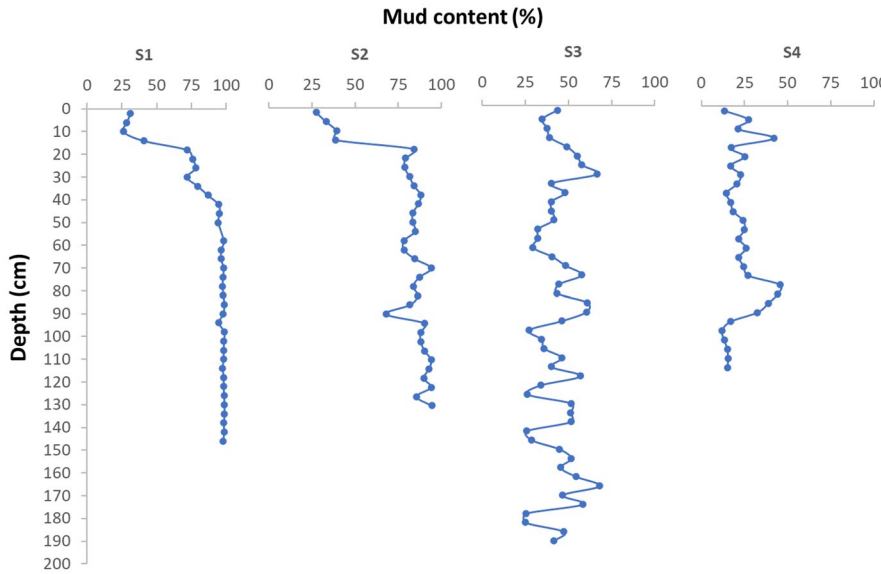


Fig. 2 Vertical distribution of mud content (%) along with the sediment cores

environmental data. Statistical analyses were conducted in R Software (RCoreTeam, 2017).

Results and discussion

Mud content distribution

The mud content (defined as the sum of silt + clay) shows that the core from Santos (S1) is almost entirely composed of mud with slight variation in content (86.95% on average) from the bottom of the core until 42 cm depth, where a marked decrease is observed, reaching levels of approximately 25% in the top sediment layers (Fig. 2). The core from the upper estuary, next to Cubatão (core S2), was predominantly mud (79.50% on average) and showed a marked decrease in mud content at 20 cm toward the top. These changes in the depositional characteristics in both cores can be related to the hydrodynamics properties of the area. Dredging operations in the early 1970s resulted in stronger current activity, favoring the deposition of coarser sediments in the area (Jesus et al., 2020). In São Vicente, cores S3 and S4 present a percentage of sands higher than muds. In these cores, the content of mud was 43.8 ± 11.5 and 23.2 ± 11.5, respectively.

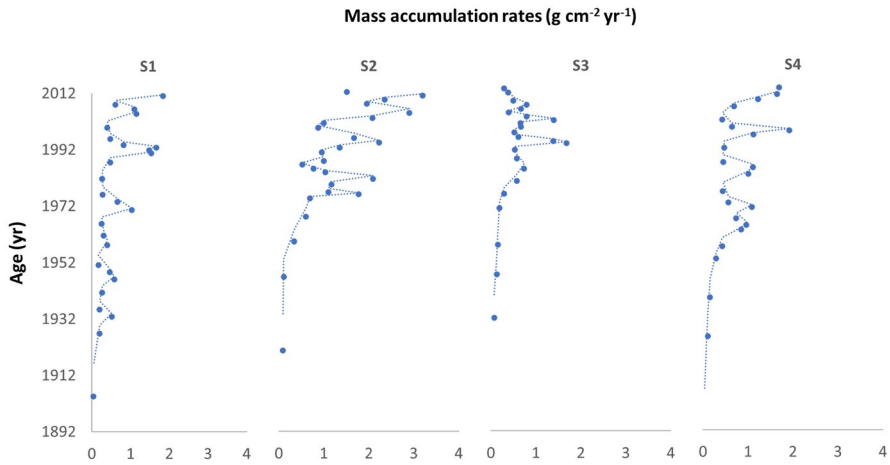


Fig. 3 Mass accumulation rates (g cm^{-2} $year^{-1}$ *vs* dating of cores from the SSVES

Mass accumulation rates and trace elements fluxes

The results obtained from the calculation using the CRS model for ages and accumulation rates in the cores from the SSVES are presented in supplementary tables S2, S3, S4, and S5. The CRS model was applied until 130 cm depth for core S1, until 100 cm for S2, 90 cm for S3, and 90 cm for core S4. The sedimentation rates varied from 0.06 to 2.10 cm year^{-1} in core S1, from 0.07 to 1.96 cm year^{-1} in core S2, from 0.10 to 2.56 cm year^{-1} in core S3, and from 0.01 to 1.47 cm year^{-1} in core S4.

The evolution of MARs for all cores is presented in Fig. 3. The MARs varied from 0.04 to 1.83 g cm^{-2} year^{-1} in core S1, from 0.09 to 3.19 g cm^{-2} year^{-1} in core S2, from 0.07 to 1.68 g cm^{-2} year^{-1} in S3, and from 0.01 to 1.92 g cm^{-2} year^{-1} in core S4.

The results indicate that the deposition of sediments varied between both sampling stations and time. The core S2, located next to the Cubatão Industrial Complex, showed the highest sediment flux (3.19 g cm^{-2} year^{-1}) around 2010. The conversion of the mass accumulation rate to sedimentation rate results in approximately 1.69 cm year^{-1}. This value is higher than in previous studies in the same area (Gonçalves et al., 2013; Tessler et al., 2006). The increased sedimentation since the early 1970s may be attributed to the Cubatão Industrial Complex accelerated urbanization and industrial growth and the expansion of port operations (Bordon et al., 2011; Luiz-Silva et al., 2008).

Next, we assessed trace element fluxes using MAR and element concentration to gain insights into the accumulation of the elements over time (Fig. 4). To achieve this, we used only dated layers of the cores (130 cm depth for S1, 100 cm for S2, 90 cm for S3, and 80 cm for S4) spanning time intervals from 1905, 1920, 1932, and 1887 to the present, allowing us to measure these fluxes. In general, all cores showed an increased trend in trace element fluxes.

Both human influence and storms or other high flow occurrences, such as landslides, might reflect the high mass accumulation rates. Heavy rainfall is typical in the studied area leading to many landslides

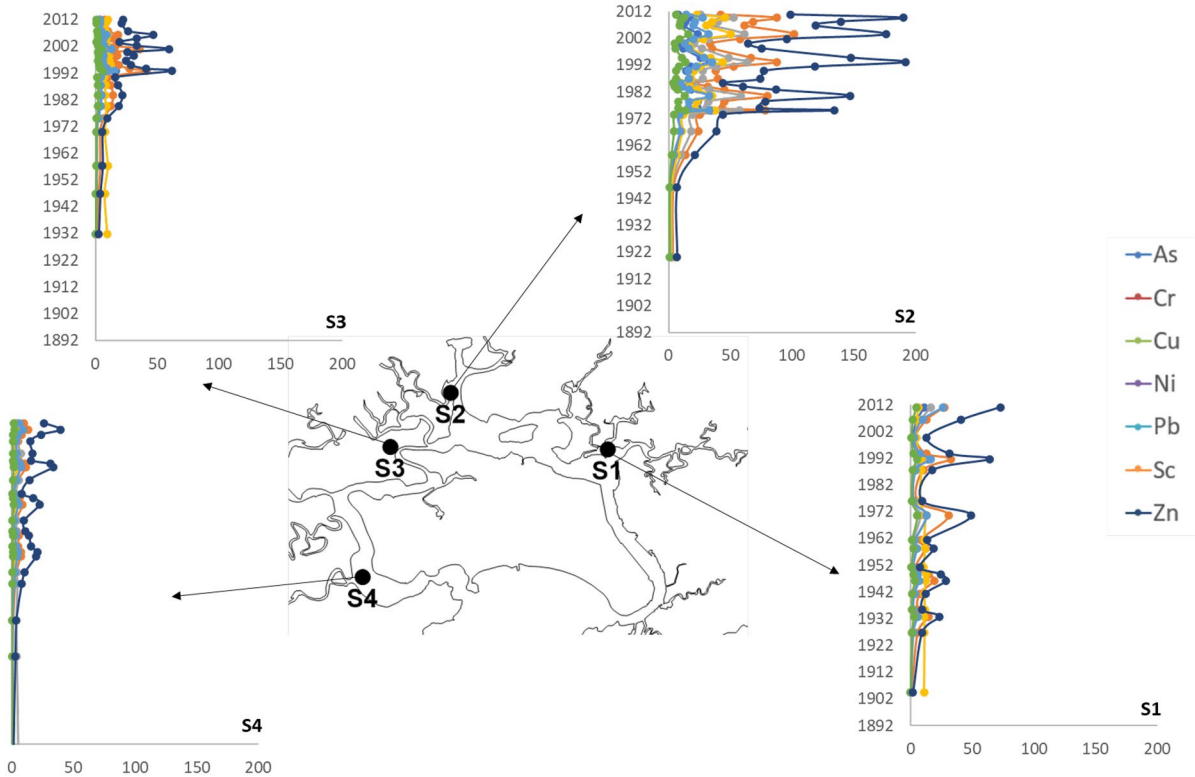
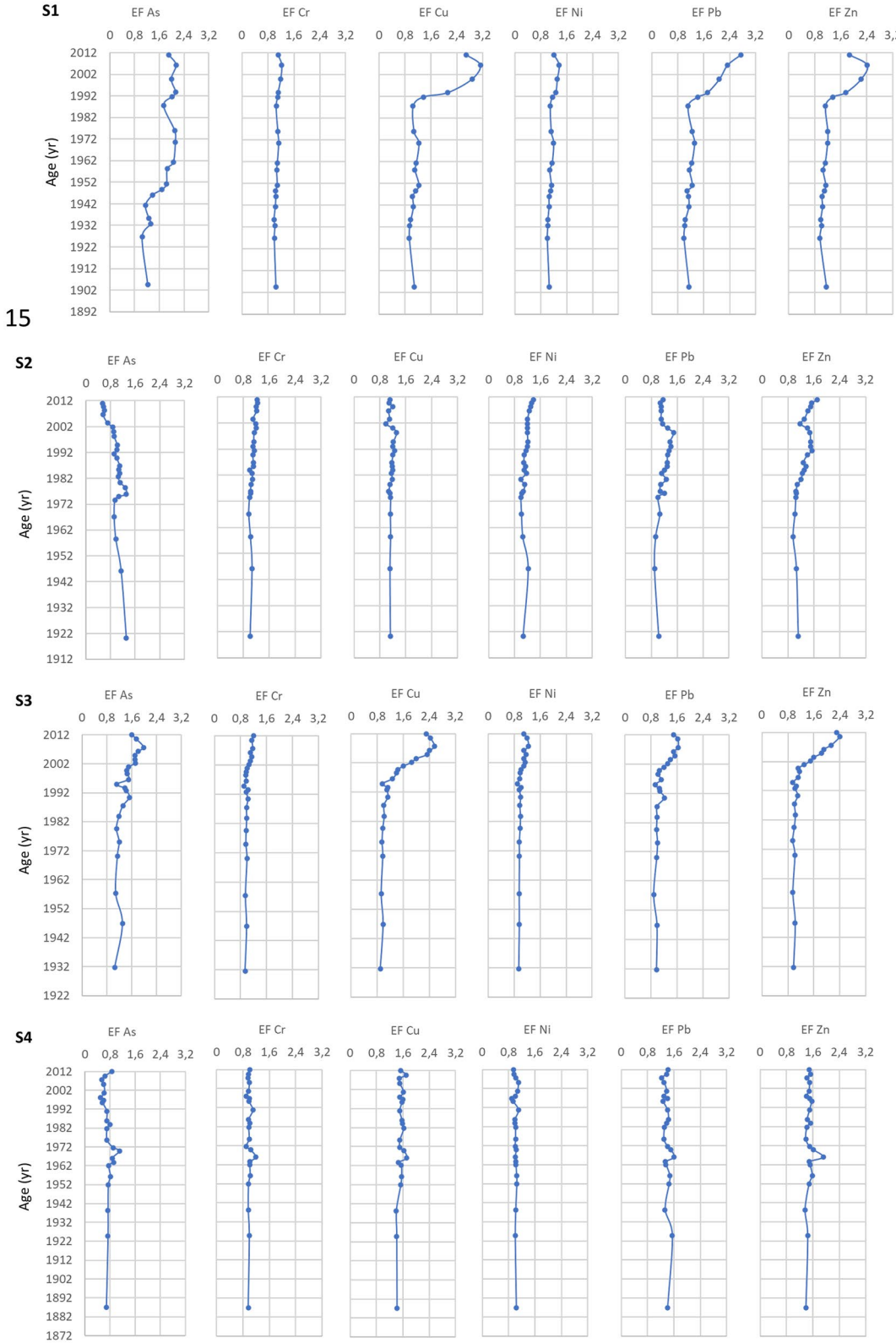


Fig. 4 Trace element fluxes (mg cm^{-2} year^{-1}) along the sediment cores of the SSVES.15


S1
EF As
EF Cr
EF Cu
EF Ni
EF Pb
EF Zn
0 0,8 1,6 2,4 3,2
Age (yr)
2012
2002
1992
1982
1972
1962
1952
1942
1932
1922
1912
1902
1892
S2
1912
S3
1922
S4
1872
1882

◂**Fig. 5** Enrichment factor (EF) of trace elements from the SSVES sediment cores

in the Serra do Mar Mountain chain, as recorded in 1967, 1971, 1976, and 1999 (Gramani et al., 2001; Kanji et al., 2003). Since core S2 is close to the Serra do Mar, sediment deposition appears to have been influenced by these mass movements. Moreover, fluvial waters from the rivers of the Serra do Mar arrive specifically in the port channel, where cores S1 and S2 are located (Tessler et al., 2006).

The marked peaks in trace element fluxes in the cores closest to the Port of Santos (S1 and S2) in the early 1970s coincide with the port expansion. In the early 70 s, a significant expansion in the Port of Santos took place. In comparative terms, 2314 m of docks were built in the previous 60 years, while from 1969 to 1976, the port expanded 3812 m (Zundt, 2006). In the 1980s, the relatively lower trace element fluxes are associated with the implementation of emission controls in the SSVES by most industries. It is plausible that pollution management has resulted in better waste treatment and decreased input of inorganic pollutants into this region.

Despite the trace element flux decrease in the 80 s, these fluxes rose during the following decades, caused by the growing number of industries and urbanization. By 1999, the cities of Santos and São Vicente had approximately 800,000 inhabitants (IBGE, 2000), of which approximately 10% emitted their untreated effluents directly into the estuary. Additionally, tourism doubles the number of inhabitants in the summer (Martins et al., 2007). Thus, after successive rainfalls, the runoff from this region contributes to the input of inorganic contaminants to the SSVES.

Evaluation of trace element contamination

The mean, standard deviation, and range of concentration for all analyzed elements, along with a comparison with studies performed in other regions and the thresholds established by the Brazilian legislation (CONAMA 454/2012) (CONAMA, 2012), are presented in Table 2, as well as the regional background levels (BLs). The background was calculated as the average of the last five samples of the bottom of each sediment core. These samples are representative of natural concentrations and therefore can be considered pre-industrial levels.

The element concentrations (mg kg^{-1}) showed a moderate variation. Compared to metal concentrations reported in surface sediments and sediment cores in other Brazilian coasts (Table 2), the present concentrations were relatively low. Trace element concentrations found in this study were comparable with previous works conducted in the SSVES (Kim et al., 2018) and Paranaguá Bay (Angeli et al., 2020), another important port impacted area. The trace element concentrations were also comparable to the levels found in the Caravelas estuary (Angeli et al., 2019) and Todos os Santos Bay (Hatje & Barros, 2012), both located on the Northeastern Brazilian coast and considered relatively preserved, despite the latter showing significant levels of Zn contamination. Furthermore, despite the differences in analytical methods used, trace elements in the SSVES were much lower than in Guanabara Bay (Aguiar et al., 2016), considered one of the most impacted estuaries of Brazil.

Since the sediment samples are composed of bulk sediment samples, they present different granulometric features. Thus, it is customary to report a significant level of variation. Moreover, the range of variation of background levels found in this study confirms the importance of assessing regional BLs, rather than use global values, since the latest does not account for regional variability and chemical heterogeneity (Birch, 2017).

The measured concentrations were compared with the predicted values for dredging material established by Brazilian legislation (CONAMA, 2012). The levels of Cr, Cu, Ni, Pb, and Zn were below level 1. Therefore, based on these results, we may assume that these sediments are not potentially harmful to the biota. Nonetheless, the highest levels were found the upper estuary (S2) core samples next to the industrial complex. The levels of As were highest in the upper estuary, presenting values greater than the level 1, but below level 2.

In general, no significant enrichment was observed in the cores from SSVES, with EF values around 1.5 (Fig. 5), indicating no significant contamination by trace elements in the SSVES. Core S1 showed a moderate enrichment for As in the early 1950s toward the top of the core. Cr and Ni showed no enrichment in any of the sediment.

Elements whose biogeochemical cycles can be influenced by anthropogenic activities in the estuarine system, such as Cu, Pb, and Zn, showed moderate enrichments at the top of the cores, corresponding to the early 1990s (except for core S4). The three metals showed similar behavior in all sampling stations. Despite the environmental programs conducted in the 1980s, the most likely answer for these profiles is the increase of anthropogenic inputs during the following years caused by intense urbanization and industrialization. Many authors have reported high concentrations of these elements coexisting in the environment due to similar chemical properties and use (e.g., Al Rashdi et al., 2015; Jiang et al., 2013; Liu et al., 2015).

Table 4 Results of principal component analysis (PCA) applied to the sediment cores of the SSVES

	Dim 1	Dim 2	Dim 3
Eigenvalue	7.36	0.26	0.19
%variance	92.11	3.30	2.40
Variable			
As	0.94	0.13	−0.12
Cr	0.97	−0.13	−0.13
Cu	0.91	0.36	0.12
Ni	0.98	0.055	−0.06
Pb	0.93	−0.25	0.21
Sc	0.96	−0.17	−0.13
V	0.98	0.04	−0.11
Zn	0.95	−0.02	0.24

Sources of trace elements in the SSVES

The correlation coefficients among the different elements (As, Cr, Cu, Ni, Pb, Sc, V, and Zn) and the mud content in all sediment cores are shown in Supplementary Table 3. In general, the cores showed significant positive correlations between Sc, V, and mud content. This high correlation is expected since these elements tend to be rapidly removed from the solution by interaction with the surfaces of sinking particles. The correlations between all metals were highest in core S4, indicating that the observed element deposition and accumulation in this region of the estuarine system were most influenced by the geochemical composition of the catchment area and the weathering of the rocks. Weaker positive correlation coefficients were found for As, Cu, Pb, and Zn, in cores S1, S2, and S3. The weaker correlation of As, when compared to the other elements, may be due to its metalloid nature. Meanwhile, the weaker correlation of Cu, Pb, and Zn with the conservative elements could represent a different source. Association between Cu, Pb, and Zn has also been identified in previous studies (Bordon et al., 2011; Buruaem et al., 2013; Kim et al., 2019; Salaroli et al., 2018; Tramonte et al., 2016, 2018) in the sediments of the SSVES and adjacent areas.

The multivariate technique of principal component analysis (PCA) was performed to the matrix of 8 variables (total concentration of As, Cr, Cu, Ni, Pb, Sc, V, and Zn) on all sediment cores, to minimize the data dimensions into three components that together explained 98% of the total variance. High loads for all elements were found in the principal component 1 (Dim1) (Table 4). This component was interpreted as lithogenic since a significant fraction of all metals is lithogenic, and their concentrations are controlled by parent rock composition (Rubio et al., 2000). The weathering and erosion of rocks containing minerals enriched in Al, Ni, Sc, and V is the primary source of sediments to the studied region (Abreu, 1973). Cr levels, EFs, and steady behavior along the sediment cores suggest its presence in weathering-resistant minerals such as migmatite and chromite. Ni present low mobility as well and is probably incorporated into the mineral structure (Moalla et al., 1998).

The relatively high concentrations of As and its presence, particularly in the PC1 (Dim 1), confirm that the weathering of rocks could be a significant source of this element. Arsenic is naturally enriched in the region (Gonçalves et al., 2013; Kim et al., 2018; Silva et al., 2011); several studies have found high arsenic background levels along the entire Brazilian coast (Mirlean et al., 2012; Cagnin et al., 2017; Baeyens et al., 2019; Angeli et al., 2019). Despite these high As background levels, several anthropogenic impacts along the coast, including releases from metallurgical industries, gold and iron mining, and phosphate fertilizer plants, are observed (Baeyens et al., 2019). In the Doce River continental shelf, on the Eastern Brazilian coast, high As enrichments were attributed to iron and gold mining exploitation (Cagnin et al., 2017). In estuarine and lagoonal systems located on Brazil's

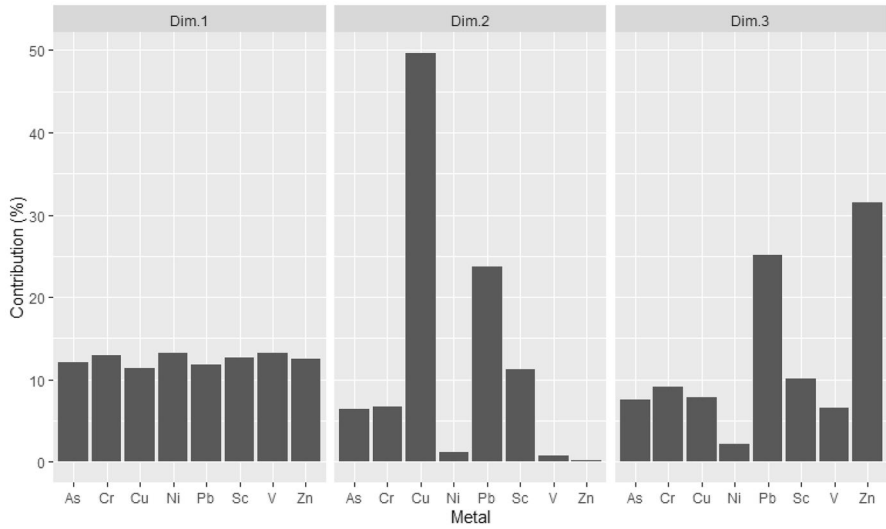


Fig. 6 Contribution (%) of each element in the first three components (Dim1, Dim2, and Dim3)

southern coast, As enrichments were found next to port terminals and related to the presence of fertilizer-producing plants (Mirlean and Roisemberg 2006; Sá et al., 2015; Angeli et al., 2020). In the SSVES, fertilizer plants, established in the 1970s, have been operating along the margins of some rivers and next to the port area, discharging a large quantity of phosphogypsum (approximately 400 ton per day) as piles in adjacent storage areas (Oliveira et al., 2007). Thus, it is possible that increasing As enrichments in the study

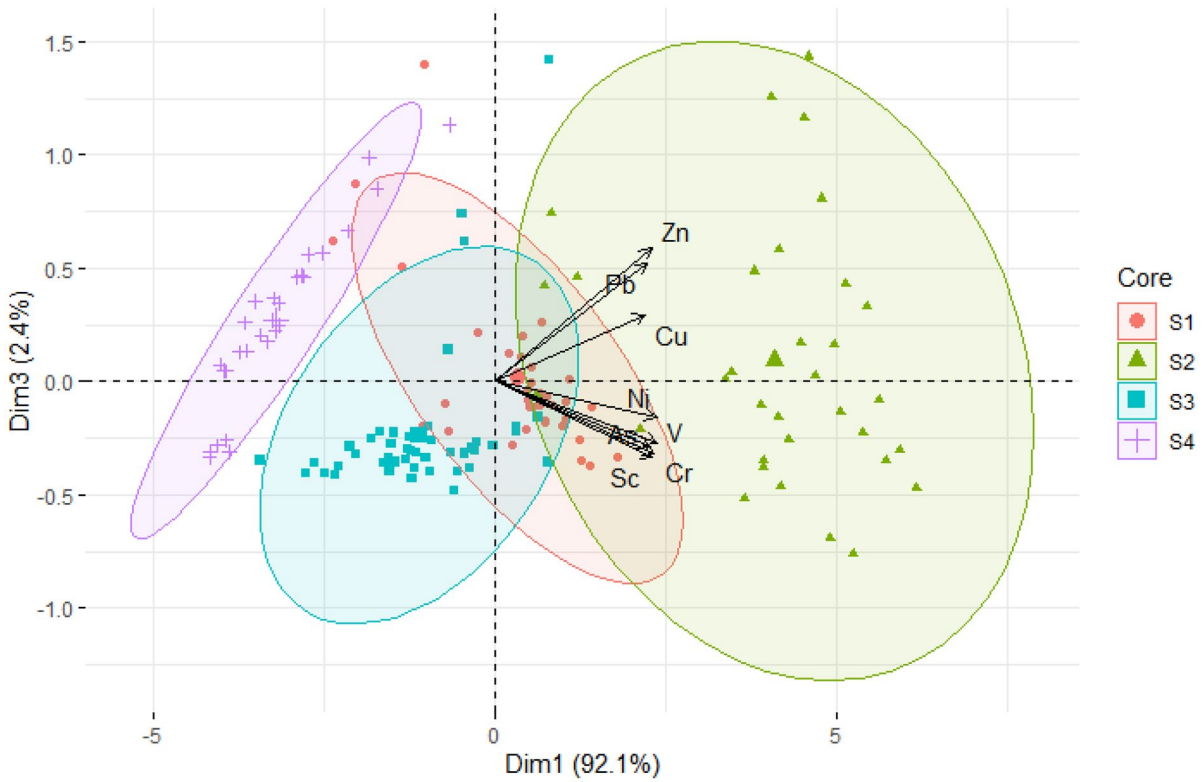


Fig. 7 Bi plot of PC1 (Dim1) with PC3(Dim3) of the SSVES sediment cores

area are related to the fertilizer plants and the phosphogypsum ponds.

The principal component 2 (Dim2) had a higher contribution of Cu and Pb, while PC3 (Dim3) showed higher Pb and Zn contributions (Fig. 6). These components express anthropogenic effects since they presented higher loadings of potentially pollutant elements. Interestingly, according to Fig. 7, it can be noted that the sediment cores S1 and S2, located next to the port and in the upper estuary, respectively, showed a stronger relationship with these potentially polluting elements.

Copper is found in effluents at the Cubatão Industrial Complex, from several industries and discharged into the estuary as untreated sewage (CETESB, 2001). Zinc can be employed in its metallic or salt form, and may have significant anthropogenic sources, since it can be found in the effluent of most industries in the region, in port terminals as well as in the domestic sewage (CETESB 2001; Gonçalves et al., 2013). Moreover, boat traffic and repair areas are significant causes of Cu and Zn release (Costa & Wallner-Kersanach, 2013; Turner, 2010). Several anthropogenic sources for Pb in the area including metal extraction, beneficiation and smelting, oil refining, petrochemical, steel, and fertilizer industries make the precise determination of the source of this metal difficult (Kim et al., 2018). Nevertheless, cores S1 and S2 are close to the Alemoa oil terminal, which has been supplied and exported since 1951. Moreover, since 1960, loading and unloading of chemical products have often occurred on the east side where storage tanks are found (Martins et al., 2010).

There is a well-documented record of historic emission trends worldwide (Steffen et al., 2007; Zalasiewicz et al., 2015; Water et al., 2016). These anthropogenic signals progressively gained strength during the mid-twentieth century and are associated with the extreme growth of human influence during the stage of the Anthropocene called the Great Acceleration (Ludwig & Steffen, 2018; Bibi et al., 2020). However, the potential markers for the onset of this activity are not synchronous and highly variable. Southern Hemisphere atmospheric ^{14}C suggest 1965 as the peak of radionuclides produced during nuclear bomb tests (Turney et al., 2018). Moreover, the radioactive record in sediment profiles in the South American coast of the South Atlantic suggests 1963 as a chronostratigraphic marker, regarding the deposition of fallout radioactivity (Ferreira et al., 2016). Therefore, the chronological and geochemical signals of the Santos and São Vicente estuarine system provide strong evidence that allow us to confirm the early 1960s (Ferreira et al., 2016; Turney et al., 2018) as the base of the Great Acceleration of the Anthropocene in the South Atlantic.

Conclusions

This research underlined the significance of using geochemical and chemometric approaches combined with the ^{210}Pb dating to understand the sources and evolution of trace elements and interpreting the anthropogenic influence.

The contamination assessment revealed that most of the analyzed trace elements did not present high contamination levels, with average values below thresholds established by Brazilian legislation. Enrichment factors (EFs) suggest contamination levels for As, Cu, Pb, and Zn, at the uppermost layers of the sediment cores located in the port area and upper estuary. The high levels of As at the bottom of the sediment cores, corresponding to pre-industrial levels, confirm this element's high natural background levels in the Brazilian coast. Nonetheless, the increasing enrichment trend could result from the development of fertilizer plants in the region during more recent years.

The sediment accumulation rates and trace element fluxes showed an accumulation tendency starting in the early 60 s. The increased accumulation of these trace elements can be associated with the mid-twentieth century "Great Acceleration." This process was accompanied by the increased urbanization and industrialization needs in that period resulting in the erosion and drainage of the urbanized area. Important to note, in the 1980s, a marked decrease in trace element fluxes was achieved due to the implementation of environmental programs. However, despite these efforts, the fluxes and enrichment of trace elements resumed the increasing trend in the following years.

According to the correlation and PCA analyses, most of the trace elements in the sediments of the SSVES have a natural lithogenic source, suggesting that they are transported and adsorbed into fine-grained particles through weathering and erosion

processes. On the other hand, Cu, Pb, and Zn results suggest anthropogenic influence, especially close to the port area and upper estuary. Our results also indicate that the region is not severely contaminated. These findings allow us to indicate that the contamination in the SSVES is closely related to the drainage from the adjacent urbanized area and the erosive processes rather than the disposal of inorganic contaminants.

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Data availability The authors declare that the data supporting the findings of this study are available within the article or its supplementary information.

Declarations

Conflict of interest The authors declare no competing interests.

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