



Statistical assessment of background levels for metal contamination from a subtropical estuarine system in the SW Atlantic (Paranaguá Estuarine System, Brazil)

José Lourenço Friedmann Angeli¹ · Bianca Sung Mi Kim¹ · Ítalo Martins Paladino² · Renata Hanae Nagai² · César C. Martins² · Michel Michaelovitch de Mahiques¹ · Rubens Cesar Lopes Figueira¹

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Abstract

Trace metal background levels determination is essential for the proper assessment of the contamination status of a region. This study aims to integrate geochemical and statistical methods for the reliable determination of background levels, applying it to the sediments of the Paranaguá Estuarine System (PES), a large subtropical estuarine system of international importance since it is considered a World Heritage Site and Biosphere Reserve and it harbors the main South American grain shipping port. Prediction Interval (PI) was applied as a chemometric tool to evaluate metal enrichment without a reference level and assess a regional background. Moreover, the sources and concentrations of major and trace elements were assessed in surface sediments from 135 sampling sites located in the Paranaguá Estuarine System (PES). PES surface sediment elements concentrations may be considered lower than those found in other anthropized environments indicating no significant contamination for most of the studied elements (Cr, Cu, Ni, Pb and Zn). The levels of As in the PES may be related to the geochemical characteristics of the adjacent drainage basin and the occurrence of phosphate rocks, which contain As in their composition. However, As was also influenced by anthropogenic inputs either from agricultural activities or fertilizer industries working with mining phosphate in the region.

Keywords Major and trace elements · World Heritage Listed area · Background levels · Chemometric tool

1 Introduction

Estuaries are enclosed water bodies that connect land and ocean and are influenced by both marine conditions and by freshwater inflow (Hobbie 2000). They have a major importance in sediment transfer between fluvial and marine

systems and on the biogeochemical cycle. Mobility, partitioning and reactivity of elements are affected by physical and chemical gradients that occur in this mixing environment (Machado et al. 2016). Moreover, due to their nature and strategic position between terrestrial and marine environments, estuaries have been a center of attention for a variety of human activities including urban, industrial and port developments (Ridgway and Shimmield 2002; Pregolato et al. 2018). Consequently, effective management of such environments is crucial for achieving Sustainable Development Goals (SDG) set by the United Nation, and in particular SDG 14: Conserve and sustainably use the oceans, seas and marine resources for sustainable development (UN 2015).

In the last decades, geochemical research of surface sediments along estuaries, have been extended, due to the growing awareness of coastal pollution and its impact on the marine ecosystem (e.g., Kim et al. 2016; Kelly and Rudd 2018; Unda-Calvo et al. 2019; Díaz Morales et al. 2019a, b). Currently, this contamination is more significant due to

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✉ José Lourenço Friedmann Angeli
louangeli14@gmail.com; louangeli@usp.br

¹ Instituto Oceanográfico, Universidade de São Paulo (IO/USP), Praça do Oceanográfico, 191, 05508 120, São Paulo, SP, Brazil

² Centro de Estudos do Mar, Universidade Federal do Paraná, Av. Beira-Mar, s/n, Pontal do Paraná, PR 83255-976, Brazil

increasing urbanization in coastal areas and, therefore the increase in domestic and industrial effluents discharges, fossil fuel burning, surface runoff and soil erosion, mining and mobilization of contaminated sediment by dredging activities (Bai et al. 2015; Machado et al. 2016; Angeli et al. 2019).

The Paranaguá Estuarine System (PES) is a subtropical ecosystem that features great biological heterogeneity and importance for environmental conservation (Denardin et al. 2008), with anthropogenic influence due to harbor activities at the Paranaguá, Antonina, and Ponta do Félix terminals, dredging, fishing, aquaculture, and effluent inputs (Cabral and Martins 2018). Potentially harmful products such as petroleum and by-products, fertilizers, minerals, and grains are massive handled in the harbor areas. Furthermore, the channel that connects the shallow continental shelf and the inner estuary requires dredging in order to maintain navigable depth for vessels (Mayerle et al. 2015). As consequence, the assessment of organic and inorganic contaminants has been constantly required as part of monitoring and conservation programs.

In recent years, the sediment of PES has been used as indicator of environmental quality face to the anthropogenic impacts, such as the input of metals (Sá et al. 2006; Choueri et al. 2009), sewage (Cabral and Martins 2018), petroleum hydrocarbons (Cardoso et al. 2016; Garcia et al. 2019; Damasio et al. 2020) and halogenated organic contaminants (Combi et al. 2013). Nevertheless, none of these studies established natural concentrations for contaminants in this environment or purposed new strategies to evaluate chemical pollution in other subtropical estuaries of the world.

Since trace elements have natural and anthropogenic sources it is necessary to distinguish if the elements are lithogenic from weathering and sedimentation or anthropogenic (e.g. Cunha et al. 2018; Pinto et al. 2019). In environmental studies, natural concentrations are called background levels (BGs) and different approaches have been developed to determine geochemical background concentrations. These methods can be divided into direct (empirical and geochemical) or indirect (statistical or theoretical) (Hernández-Crespo and Martín 2015). Thus, to provide basic data for environmental management, the assessment of background concentrations of hazardous substances in sediments and the use of statistical approaches are required to improve the evaluation of human impact in coastal zones (Fukue et al. 2006; Birch 2017).

In this context, the main objectives of this study were: (a) to evaluate geochemical factors that control the distribution pattern of major and trace elements; (b) to establish regional background equations using a chemometric tool, promoting new insights to the evaluation of metals in estuarine environments, and; (c) to estimate the anthropogenic input and

assess the pollution status of this subtropical South Atlantic coastal area. The research outcomes are expected to provide a step improvement in knowledge on the sources and dynamics of pollutants that can pose risks to human health. This will contribute to the formulation of effective measures to improve estuarine and marine conservation, and thereby to enhance the sustainable development of these systems.

2 Study area

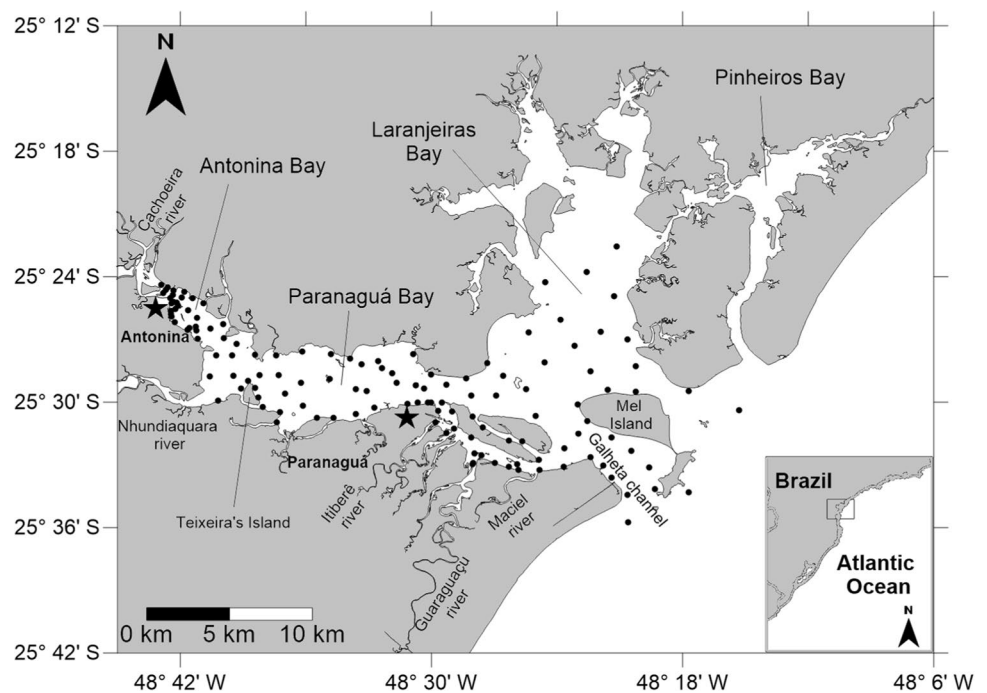
The PES is located in southern Brazilian coast, which is situated on the South Atlantic (Fig. 1). It has a water volume of approximately 2×10^9 m³, an area around 612 km² and is divided into two main sections: (a) the western section, which is formed by Paranaguá and Antonina Bays, and; (b) the northern section, which is formed by the Pinheiros and Laranjeiras Bays (Lana et al. 2001).

The region is environmentally significant once it is encompassed by a large fraction of the preserved Atlantic rainforest (207,169 ha), which is a significant trademark characteristic that adds to its status as a World Heritage Site and Biosphere Reserve (UNESCO 1999). Nevertheless, it has been under to rapid, hazard human occupation and urban development (Martins et al. 2010), particularly in the urban areas of Paranaguá and Antonina, which house 65% of the population of the coastal area of the Paraná State, with 149,467 and 19,414 inhabitants, respectively (IBGE 2014). Fishing and aquaculture, urban development, petrochemical facilities, and the ports of Antonina and Paranaguá are among the main economic activities in the region. The Paranaguá port is the main South American grain terminal and is the third most important port in terms of loading and unloading operations, with 8,540,000 tons transported in 2009 (Choueri et al. 2009; Martins et al. 2010).

In general, the western axis of the PES is affected by small, short, and steep drainage basin which descend from the Serra do Mar mountain complex. The most volumetric river, with an average discharge of 21.13 m³/s, is the Cachoeira river, followed by the Nhundiaquara River, with an average discharge of 15.88 m³/s (Bigarella et al. 1978). The organic matter composition of this ecosystem is affected by marine input seaward and continental supply through these main rivers, which flow at the inner estuary and adjacent margin runoff (Mantovanelli et al. 2004).

The maximum turbidity zone (MTZ), lying between Teixeira's Island and the Port of Paranaguá cross section (Rocha et al. 2017), features an important role in the processes of deposition, erosion and resuspension of fine particles, once the increased concentration of suspended particulate material as well as regular mixture between continental and marine waters (Noernberg 2001; Cattani and Lamour 2016) lead to intensive physical, chemical and biological reactions

Fig. 1 Map of the study area and sampling sites in the Paranaguá Estuarine Complex. Stars indicate harbor areas



between dissolved and particulate species (Gebhardt et al. 2005).

Based on the mean grain size of the bottom sediments of Paranaguá and Antonina bays, three distinct types of depositional environments are found in the region (Cattani and Lamour 2016). Within the sector under the marine influence, the sediments are moderate to well sorted and mainly composed by fine to medium sands (0.125–0.500 mm; Lamour et al. 2004). At the middle part of the estuary, where the mixing processes occur, very fine sands (0.063–0.125 mm) and fine silt (0.008 mm) are poorly selected. Within the inner sector, the mean grain size varies between silt and clay (0.062 to 0.004 mm), except at the river mouths, where sand predominates (Cattani and Lamour 2016). Meanwhile, sediments in the bottom of the Laranjeiras Bay range from medium silts to fine sands, most of which are poorly selected, and the organic matter content is approximately 5% (Lamour et al. 2004).

3 Materials and methods

3.1 Sampling

To evaluate major and trace metal inputs from natural and anthropogenic sources in the PES, a total of 135 surface sediment samples (0–3 cm) were collected along the western axis (Paranaguá and Antonina Bays) and the northern axis (Laranjeiras Bay) (Fig. 1; Table S1) using a stainless *Van Veen* grabber. All samples were frozen, freeze-dried,

macerated, and homogenized for major and trace element analysis.

3.2 Grain size analysis

The grain size was determined using a Malvern Mastersizer 2000 laser sedimentometer, after calcium carbonate and organic matter removal of samples. In this study, results are presented as mud (sum of the silt and clay fractions) percentage (Mud %).

3.3 Major and trace element analysis

Major elements such as Ca and Sr were determined by a portable EDXRF (Energy Dispersed X-Ray Fluorescence—the instrument is abbreviated henceforth as pXRF) analyzer DELTA Professional, manufactured by Olympus. Soil Geochem mode was used for all measurements. Every data read was performed for a period of 3 min using a beam generated by 40 kV.

XRF analyses were performed using dry samples that were ground into a powder with an agate mortar and pestle. They were then packed in an SCP Science® plastic container, with a circular Mylar® polyester film, 6.3 cm in diameter and 6.0 μm (0.24 mil) thickness. The lower orifice of the container was covered with the polyester film and, with the help of two rings of the same material, a taut wrinkle-free sample support window was created. The container was then filled with the sample material through the upper orifice, gently pressing it to obtain a compact sample. Lastly, the

upper orifice was covered with the same type of Mylar[®] polyester film and closed with a lid of the same material as the container.

Even in the case of a semi-quantitative analysis in which the analysis had more qualitative purpose, a reference material SS-2 (EnviroMAT Contaminated Soil) from SCP Science, was analyzed with the aim of improving the data in the future, based on the calibration of the XRF results as a function of ICP-OES values. The results of this reference material can be found in Supplementary Material Table S2. It was possible to observe that the analyzed elements presented values within the tolerance limits of the certified reference material and high precision values, represented by the coefficient of variation (CV).

A partial digestion technique was performed, according to the method US EPA 3050B (USEPA 1996). Briefly, about 1.0 g of dried sediment aliquot was taken in a 50 mL beaker and then 5 mL of HNO₃ (65%, v/v), 2.5 mL of H₂O₂ (30%, v/v), and 5 mL of HCl (37%, v/v) were added. Digestion was performed at 90 °C. Subsequently, all treated samples were filtered and diluted to 50 mL with ultrapure water (Milli-Q[®]). The elements Al, As, Cr, Cu, Fe, Ni, Pb, Sc, V, and Zn were measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Varian MPX 710ES model) according to the procedure described in Method 6010c (USEPA 2007).

The quality control was made considering, recovery and Method Detection Limit (MDL) and Method Quantification Limit (MQL). A certified reference material (CRM) SS-2 EnviroMAT Contaminated Soil from SCP Science (140-025-002) and blanks were submitted to the same analytical procedure. Once the confidence interval was within the certified value, the relative standard deviation below 20% and recovery values within 75–125% (Supplementary Material S3) as recommended by USEPA (1996), it was possible to validate the method since it presented veracity and precision.

3.4 Assessment of background levels and evaluation of sediment contamination

This particular study applied the Prediction Interval (PI) given by Kim et al. (2017) to establish background concentrations equations for the PES. According to the authors, PI is an estimate of an interval in which upcoming observations would fall within 95% of probability given what has already been observed. In order to assess background concentrations in a study area, using chemometric tools, many samples must be gathered covering a broad spatial area. The prediction interval requires that metal concentrations in sediment fluctuate linearly with the grain size and, for each and every sample, there is a corresponding different background. Moreover, this tool can differentiate between possible natural or anthropogenic sources and allows the assessment of

metal enrichment. This type of approach permits background ranges to be estimated, in fact, it is more realistic to view background as a range rather than an absolute value (Reimann and Garrett 2005).

The use of sediment quality guidelines (SQG) has been applied in environmental studies to evaluate the biological effects and the degree of contamination of sediments (Kim et al. 2016; Angeli et al. 2019). In this study, trace metal concentrations were compared to the Effects Range Low (ERL), an indicative of concentrations below which adverse effects on organisms rarely occur, and the Effects Range Median (ERM), representative of concentrations above which adverse effects frequently occur. These limits were specified as indicators of biological effects by the National Oceanic and Atmospheric Administration (U.S. NOAA) sediment quality guidelines under the National Status & Trends Program (NS&T) (Long et al. 1995).

Furthermore, the Brazilian legislation for the classification of sedimentary materials (CONAMA 454/2012) was used in this study, since the permitted levels of As in the environment have been increased (using EPA SW 846: 3050B method) via a Brazilian legislation amendment in 2012 to facilitate economic activities. The CONAMA 454 (2012) designates the level below which there is low probability of a negative effect of As exposure to biota as level 1; it was increased from 8.2 to 19 mg kg⁻¹. Level 2 (70 mg kg⁻¹) is the level above which the probability of negative effects is high and it remained the same.

4 Results and discussion

4.1 Distribution of major and trace elements in sediments of the PES

The levels of major and trace elements and statistical parameters, such as Mean, Standard deviation, minimum and maximum are presented in Supplementary Material Table S1.

Data were subjected to simple statistical analysis in order to explore the possible association existing between different variables. Table 1 shows a Pearson correlation matrix for the surface sediments major and trace elements. Most elements are correlated ($p < 0.001$), the most noticeable positive correlation were Cr vs Cu ($r = 0.933$); Cr vs Ni ($r = 0.984$); Cr vs Pb ($r = 0.959$); Cr vs Zn ($r = 0.989$); Cu vs Ni ($r = 0.935$); Cu vs Pb ($r = 0.966$); Cu vs Zn ($r = 0.935$); Ni vs Pb ($r = 0.954$); Ni vs Zn ($r = 0.974$) and Pb vs Zn ($r = 0.961$). The significant correlation between Al and Sc and the other elements (except Ca and Sr) confirms that these elements are associated with aluminosilicate minerals.

The chemical composition of sediments changes with the grain size as well as with mineralogical composition (Rubio et al. 2000). Usually, the trace metal concentrations increase

Table 1 Pearson correlation matrix for the studied major and trace elements and Mud % in the surface sediments (0–3 cm) at PES, South Atlantic

	Al	As	Ca	Cr	Cu	Fe	Mn	Ni	Pb	Sc	Sr	V	Zn	Mud %
Al	X													
As	0.713**	X												
Ca	0.135	0.088	X											
Cr	0.949**	0.768**	0.112	X										
Cu	0.903**	0.598**	0.119	0.933**	X									
Fe	0.951**	0.755**	0.192	0.947**	0.884**	X								
Mn	0.887**	0.719**	0.135	0.889**	0.829**	0.891**	X							
Ni	0.950**	0.686**	0.110	0.984**	0.935**	0.938**	0.889**	X						
Pb	0.910**	0.678**	0.098	0.959**	0.966**	0.906**	0.874**	0.954**	X					
Sc	0.952**	0.774**	0.130	0.987**	0.945**	0.945**	0.897**	0.967**	0.962**	X				
Sr	0.300**	0.232**	0.667**	0.312**	0.280**	0.349**	0.308**	0.341**	0.295**	0.303**	X			
V	0.933**	0.720**	0.122	0.970**	0.958**	0.933**	0.895**	0.970**	0.970**	0.978**	0.342	X		
Zn	0.942**	0.781**	0.123	0.989**	0.935**	0.953**	0.897**	0.974**	0.961**	0.985**	0.320**	0.972**	X	
Mud%	0.856**	0.678**	0.233	0.902**	0.878**	0.845**	0.810**	0.878**	0.911**	0.914**	0.561**	0.893**	0.905**	X

* $p < 0.01$

** $p < 0.001$

with decreasing grain size of the material, as a consequence of changes in host minerals of the elements and the surface area of the particles making up the sediments (Loring and Rantala 1992). It is generally acknowledged that some elements such as Al, Fe, Sc, V or Li are associated with clay minerals and, thus fit as grain size proxies (UNEP 1995). In this study, we used Sc as a particle-size proxy, once it presented good correlation with mud% ($r=0.914$; $p<0.001$) and its distribution is presented in Fig. 2. Furthermore, since Sc correlated well with most of the analyzed metals, its spatial distribution can be used to represent that of the other metals studied in the PES.

The spatial distribution of the mean values of Sc in the PES surface sediment samples shows a clear distinction between samples from the Paranaguá and Laranjeiras Bays (Fig. 2). Higher values of Sc were found in the inner sector of the PES (Antonina bay), associated with the shallow depths of this sector. In general, the sediments in the Antonina Bay, the silt fraction is predominant, except in the river mouths, where sand is the main sediment component (Angulo et al. 2006). Near the southwest margin of the PES, the mean sediment diameter of sediments increases from medium to coarse sand, becoming smaller towards the Port of Paranaguá (Lamour et al. 2004).

Around the Port of Paranaguá cross-section, at the transition between riverine and proper estuarine zones, the increases in Sc contents and consequently other metals indicates resuspension/deposition processes associated with the maximum turbidity zone (MTZ) (Rocha et al. 2017), that

apparently is acting as a barrier for the transport of fine particles towards the coast (Cattani and Lamour 2016).

A decrease in Sc values in the sediments retrieved from the mouth of the estuarine system indicates the presence of coarser sediments and stronger hydrodynamics conditions. Currents (mainly tidal currents) associated with the flood-tide delta formed at the margins of Mel Island control the dynamics of this particular sector (Lamour et al. 2007). Bottom sediments around the Galheta channel and in the outer sector of Paranaguá Bay are mainly composed of medium fine and very fine sand (Lamour et al. 2007).

Geochemical proxies have a wide application in environmental studies and a continuous and accurate measurements are a prerequisite for obtaining meaningful environmental data. Several factors may influence the geochemical composition of sediments, such as source rocks type and weathering, transport, depositional conditions and diagenesis (Weltje and von Eynatten 2004). Terrigenous elements (i.e., Fe and Al) are typically land-derived from erosion of continental rocks and commonly applied as indicators of continental to the deep-sea sediment input. Fe and Ca commonly anti-correlate or have weak correlation and Fe/Ca quantifies relative proportions or terrigenous fluxes vs marine carbonate deposition (Rothwell and Croudace 2015). The Fe/Ca ratio distribution is presented in Fig. 3.

Higher Fe/Ca values were found in the inner and middle sector of the estuary. The first is characterized by the presence of the Cachoeira and the Nhudiaquara rivers, which together, according to Rocha et al. (2017), contribute 82%

Fig. 2 Concentrations of Sc as a particle-size proxy along the PES, South Atlantic

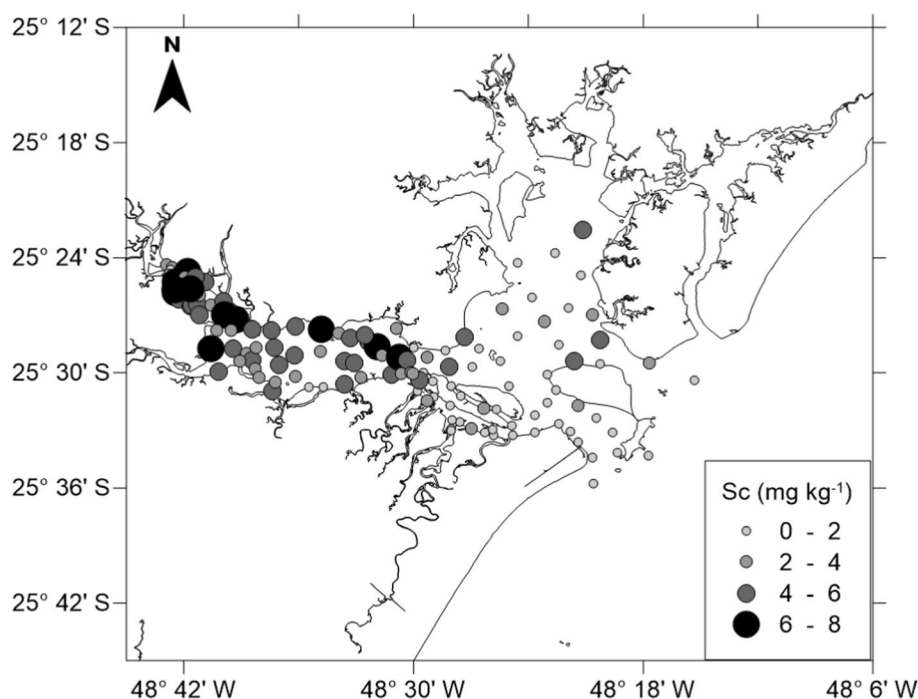
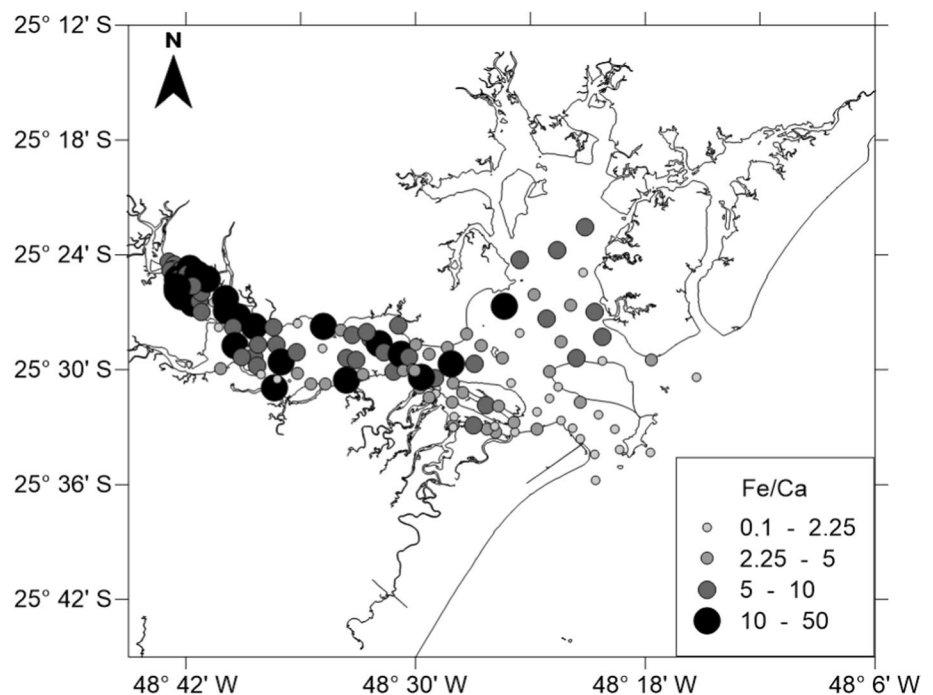


Fig. 3 Fe/Ca ratio in sediments along the PEs, South Atlantic



of the total discharge of continental water into the estuarine system.

Meanwhile, in the second sector, the primary freshwater contributors are the Itiberê, Guaraguaçu and Maciel rivers. The Itiberê river is 14 km long and receives most of the untreated sewage production in the city of Paranaguá (Cabral et al. 2018). The Guaraguaçu river is 60 km long and is the largest river that discharges freshwater into the PES, contributing with a great input of terrigenous material washed down from the Serra do Mar Mountains directly into the Cotinga sub-estuary (Abreu-Mota et al. 2014). The Maciel river is 10.6 km long and its edges are bordered by mangrove, with essentially very low human presence in the banks (Kolm et al. 2002). It is important to state that the continental sediments from the mountain ridges are trapped in the estuary heads (Angulo et al. 2006). Furthermore, the limited dispersion of continental sediments is controlled by trapping of suspended sediments in the MTZ, which is located in this sector.

Fe/Ca values are very low next to estuary mouth. This sector, as detailed above, has strong hydrodynamic conditions controlled primarily by tidal currents, associated with the flood-tide delta formed at the margins of Mel Island (Lamour et al. 2007). The deposition of sediments near the Galheta channel is essentially from the longshore sediment transport along the coast caused by the southeasterly waves in the Atlantic Ocean (Noernberg et al. 2006). TOC/TN ratio for the sedimentary organic matter in sediments within this region is as low as 2.9 (Cabral and Martins 2018) which reflects a predominantly marine input (Meyers 1997).

4.2 Assessment of regional background and evaluation of sediment contamination

The background has been defined as the “properties, location and distribution of geochemical samples that represent the natural variation of the material being studied in a specific area that is not influenced by exotic processes, such as chemical forming (diagenetic processes) or anthropogenic contamination” (Filzmoser et al. 2005).

Prediction Interval (PI) and linear regression of V were plotted, to verify if the chosen chemometric tool equation would be fitted for this proposal. Due to its similar features and well-correlated levels with Sc ($p < 0.001$), V was used as a normalizer element (Kim et al. 2017). The relationship between Sc and V is given in Fig. 4. A t test was used to compare the equation of the linear regression of all values of the PES and the V levels. Since there are no significant differences between those values ($\alpha = 0.05$), V was considered a good normalizer and the equation is well fitted to calculate background levels.

For the trace element analyses (Fig. 5), it was possible to observe a high linear correlation and a low error associated with the PI. This is a strong indication that, in general, there is no severe contamination in the region since samples with anomalous values would fall above the curve.

Enrichment factors estimation is based on the background data (Loring and Rantala 1992). The world average shale and the world average soils are among the materials frequently used to provide background levels. Nonetheless, these global levels do not take into consideration mineral

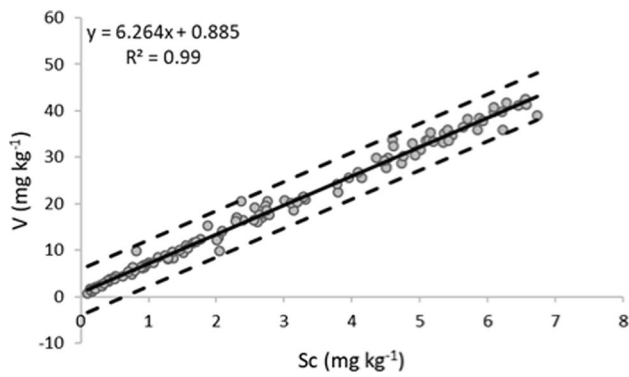


Fig. 4 Prediction interval (PI) and linear regression line for V vs Sc in the PES samples, South Atlantic

and chemical heterogeneity and regional variability (Birch 2017), that explain why it is preferred using regional background levels. Thus, we propose the following background equations for the studied area (Table 2).

The Enrichment Factor (EF) of As, Cr, Cu, Ni, Pb and Zn were calculated using the background equations from Table 2 and are presented in Fig. 6. By convention, a value of $0.5 < 1.5$ is taken as an indication that the trace metal is entirely provided from crustal contribution (e.g. weathering product), and a value of $EF > 1.5$ is considered to be indicative that an important proportion of trace metals is delivered from non-crustal materials, for example, biota and/or pollution drainage (Zhang and Liu 2002).

In general, the PES surface sediment samples presented EF values lower than 1.5, suggesting that they were entirely

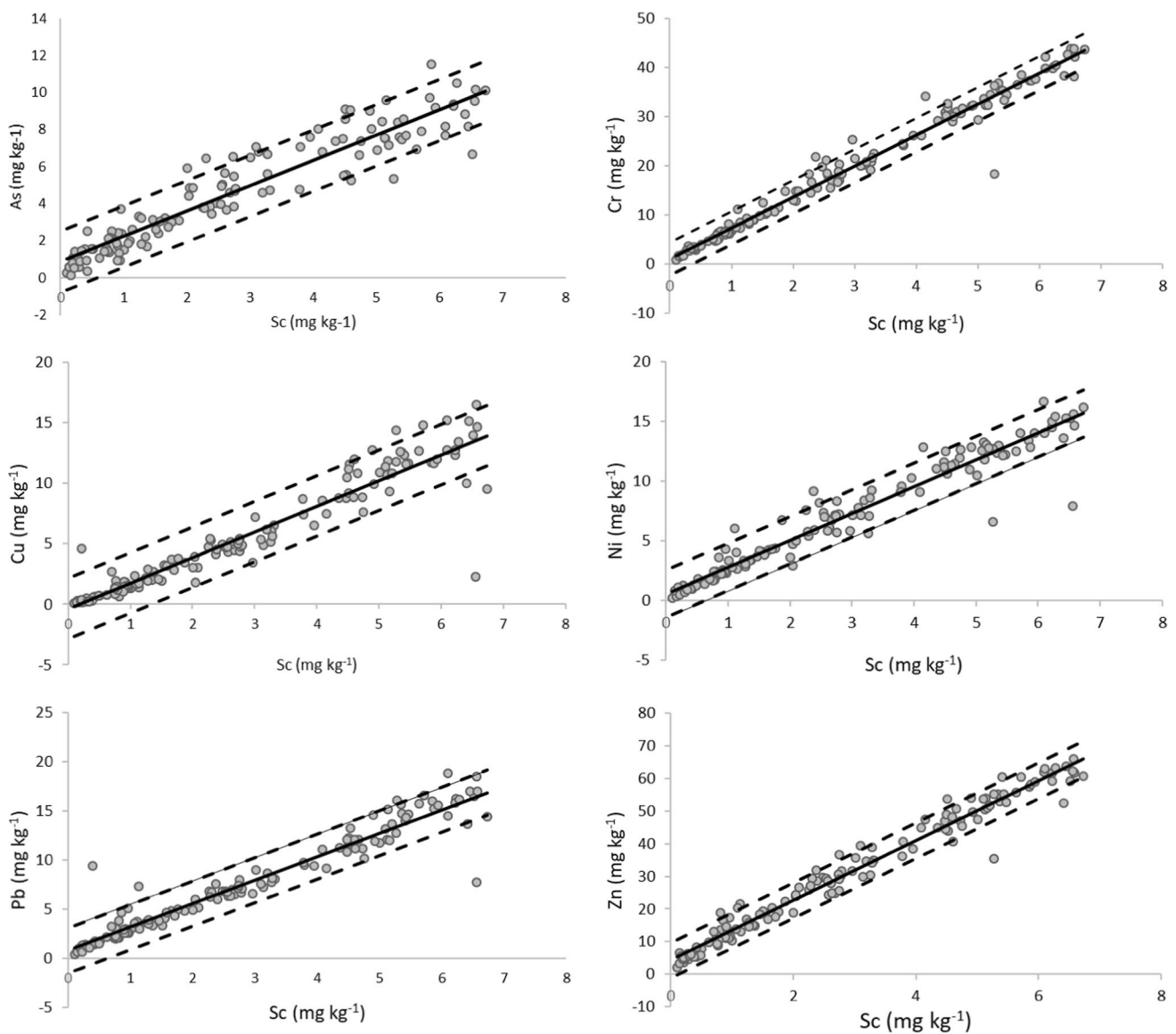


Fig. 5 Linear regression (full line) with prediction interval (PI) (dashed line) of As, Cr, Cu, Ni, Pb, and Zn in the PES samples, South Atlantic

Table 2 Background equations for trace elements for the PES (this study) established considering the regression line and Prediction Interval, compared to worldwide background references

Element	Background equations for the PES	Global ^a	Global ^b	Global ^c
As	$y = 1.365x + 0.865$ ($r^2 = 0.89$); $p < 0.05$ [As] _{bg} = $y \pm 1.65$	13	13	nd
Cr	$y = 6.626x + 0.986$ ($r^2 = 0.99$); $p < 0.05$ [Cr] _{bg} = $y \pm 2.55$	90	90	90
Cu	$y = 2.290x - 0.720$ ($r^2 = 0.96$); $p < 0.05$ [Cu] _{bg} = $y \pm 1.55$	45	250	nd
Ni	$y = 2.320x + 0.447$ ($r^2 = 0.97$); $p < 0.05$ [Ni] _{bg} = $y \pm 1.45$	68	225	68
Pb	$y = 2.494x + 0.452$ ($r^2 = 0.97$); $p < 0.05$ [Pb] _{bg} = $y \pm 1.46$	20	80	95
Zn	$y = 9.248x + 4.21$ ($r^2 = 0.98$); $p < 0.05$ [Zn] _{bg} = $y \pm 4.86$	95	95	n.d

nd not defined

^aShales, presented by Turekian and Wedepohl (1961)

^bDeep-sea sediments, presented by Turekian and Wedepohl (1961)

^cAverage shale, presented by Wedepohl (1971)

from crustal material or natural origin; nevertheless, several sampling areas presented enriched samples for As demonstrating that anthropogenic activities contributed to them partially.

Stations in the Antonina bay displayed the highest As enrichment. In this city, cultivation of cassava, rice and bananas, are the main agricultural activities, such factors led to the increase of fine-grain sediment input and also contributed into the need for dredging activities in the navigation channel (Rocha et al. 2017). In this inner sector, metal enrichment has been related to the presence of Ponta do Félix Port, placed upstream in the estuary (Choueri et al. 2009). Moreover, the local topography facilitates the particles dispersion (Possatto et al. 2015), notably within the city of Antonina since it represents one of the largest drainage areas (Noernberg et al. 2006).

The level of chemical contamination was also assessed considering sediment quality guidelines (Long et al. 1995). Cr, Cu, Ni, Pb and Zn concentrations were below their corresponding ERLs, indicating no significant contamination by these elements in the study area (Table 3). The only element that showed concentrations above the ERL was As although when compared to the permitted levels set by the Brazilian legislation CONAMA 454 (2012), levels were mainly below level 1, indicating low probability of negative effects. Thus, regarding the inorganic contamination assessed by the calculation of the PI and EF and the comparison with values of ERL and ERM, the PES can be considered a pristine environment, nevertheless, special care is needed to interpret the levels of As in the region (Table 3).

In order to obtain a global perspective of the results detected in the PES surface sediments, a Principal Component Analysis (PCA) was conducted on the entire metal data set. The PCA permits the identification of the more

important processes that determine the sediment metal content. It was possible to reduce the dimensions of all data into three components that could explain the distribution in the study area, PC1 (75.2%), PC2 (14.0%) and PC3 (4.4%) which are not linearly correlated and accounted for 93.6% of the variations.

The first component (PC1) revealed higher loadings to virtually all elements (Fig. 7), representing metals with natural sources derived from parental rocks and linked to clay minerals, which could be observed by the high correlation between Al, Fe, and Sc. For that reason, PC1 was called a “lithogenic factor”, and Cr, Cu, Ni, Pb, and Zn were likely originated from rock weathering as well. The second principal component (PC2) showed strong loadings on Ca and Sr. The positive correlation ($p < 0.001$) among them could suggest a preferential association of these elements with carbonates as it has previously been reported (Rubio et al. 2000). The third principal component (PC3) accounted strong loading on As. The PI results suggested that As was influenced by anthropogenic inputs, corroborated by levels higher than ERL. Therefore, PC3 was regarded as an “anthropogenic factor”. However, As also showed moderate positive loading on PC1, suggesting that As could be from both natural and anthropogenic sources. The higher PC1 loading compared with that of PC2 and PC3 indicated that the lithogenic factor dominated the distribution of most considered metals in the study area, nevertheless, As was influenced by anthropogenic inputs.

High As content has been already reported in Brazilian shelf and estuarine sediments (Mirlean et al. 2012; Kim et al. 2016; Cagnin et al. 2017; Angeli et al. 2019) as well as in the PES (Sá et al. 2006; Martins et al. 2012). Marine environment is generally enriched in As (Reimann et al. 2009). The average content in marine shale is as much as 13 mg kg^{-1}

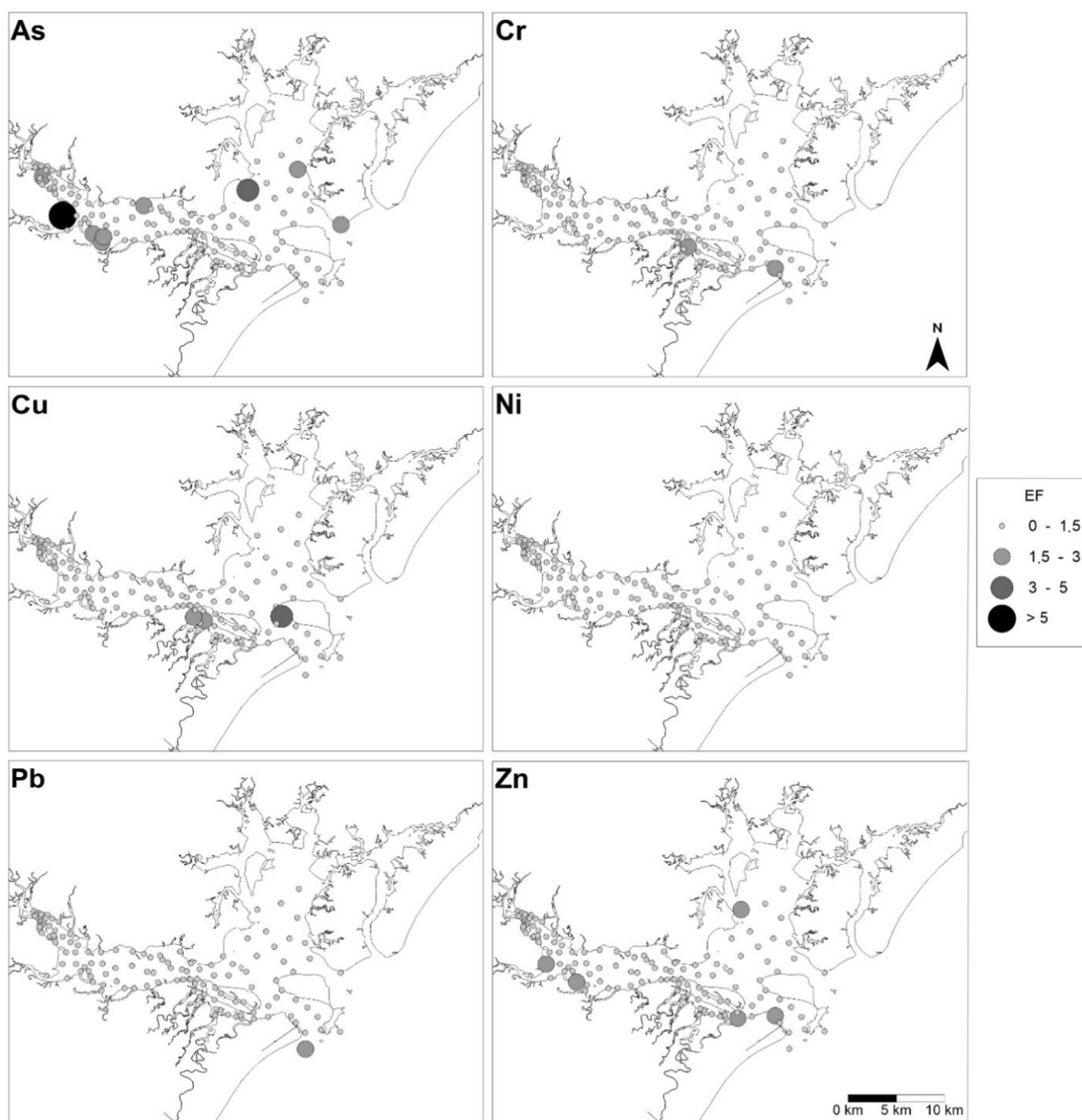


Fig. 6 Spatial distribution of the enrichment factors (EFs) along the Paranaguá Estuarine System

Table 3 Mean trace element concentrations (min–max), in mg kg^{-1} , determined in the samples from PES together with ERL and ERM values (Long et al. 1995)

Element (mg kg^{-1})	This study	ERL	ERM	Level 1	Level 2
As	5.20 (0.13–32.33)	8.2	70	19	70
Cr	18.87 (0.74–43.75)	81	370	81	370
Cu	5.67 (0.10–16.54)	34	270	34	270
Ni	6.94 (0.20–16.63)	20.9	51.6	20.9	51.6
Pb	7.56 (0.39–18.77)	46.7	218	46.7	218
Zn	30.37 (2.04–66.01)	150	410	150	410

(Chester 1990). In contrast to continental deposits, the elevated concentrations of As in marine sediments might be explained by the preservation of charged As species (arsenites and arsenates) by iron oxyhydroxides under oxidizing, low alkaline conditions (Mirlean et al. 2011).

Phosphoric fertilizers are among the principal sources or arsenic pollution in certain surroundings (Mirlean and Roisenberg 2006) with major attention usually directed at sources of contamination like phosphogypsum storages or warehouses of phosphoric fertilizers (Rutherford et al. 1994). Sediments from Patos and Mirim lagoonal systems, located in southern Brazil, contain on average between 2.5 and 7.7 mg kg^{-1} of total arsenic (Mirlean et al. 2003). In the downstream area of Patos lagoon, next to the port terminals,

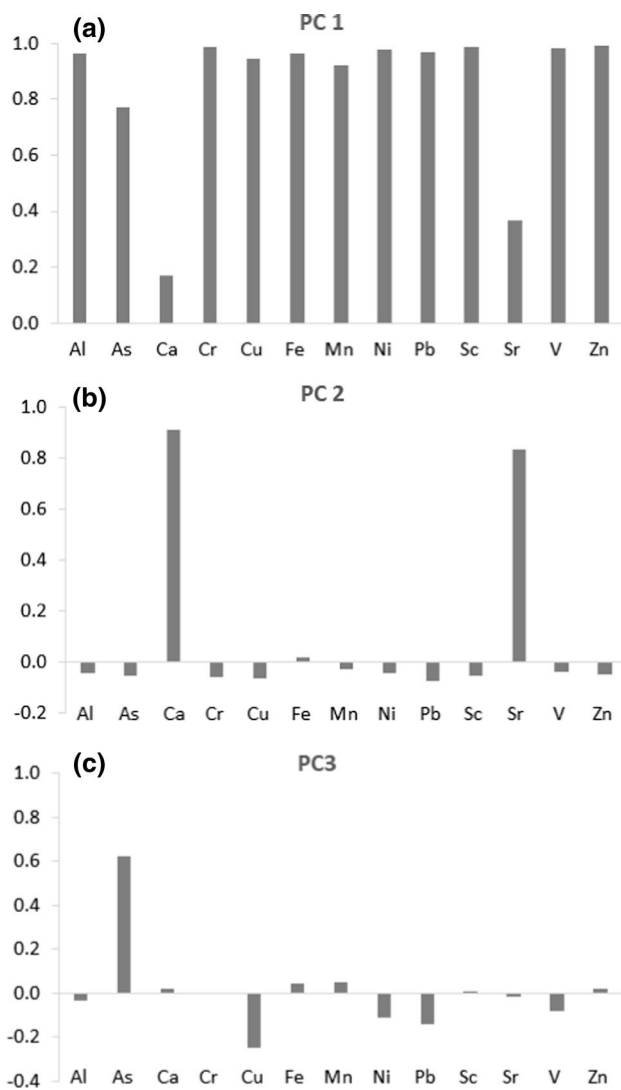


Fig. 7 Loading plots of **a** PC1; **b** PC2 and; **c** PC3 from the PCA to the PES samples

in which a complex of fertilizer production plants is located, As concentrations in superficial horizon of soil varies from 7.5 up to 27.5 mg kg⁻¹. Moreover, the anomaly of arsenic in these soils appears at a significant distance from the factories, and this distribution is probably linked to a gravitational separation of differently sized particles and, as a result, As migrates further from the emission source, being present in finer particles of the sediment (Mirlean and Roisenberg 2006).

The levels of As in the PES samples may be related to the geochemical characteristics of the drainage area and influence of human activities (Sá et al. 2006; Choueri et al. 2009; Anjos et al. 2012). Variation in the As levels may be due to the presence of a potential pollutant sources in the Paranaguá region, such as the agricultural activities present in the inner sector or port activities, including dredging activities

and an active fertilizer industry located at the middle sector of the estuarine system (Sá et al. 2015).

It is reasonable to say that the natural weathering of soils and rocks of the region could release As to the aquatic environment. Moreover, PES sediments may be inherently rich in As, because of the existence of phosphate rocks in the region, which might contain As in their composition (Anjos et al. 2012). Phosphate (PO₄³⁻) and arsenate (AsO₄³⁻) are considered chemical analogs, due to their similar chemical speciation, implying that they could substitute each other in chemical reactions (Strawn 2018). Nevertheless, fertilizer industries working with mining phosphate are also found in this region. The only Superphosphate Simple industry in the state of Paraná has its own port terminal, located next to the Port of Paranaguá and accounts for about 10% of the national production of this input for agriculture, being the main supplier for the Port of Paranaguá. Therefore, it seems that this contaminant is physically transported (e.g. by currents, tides, waves) to inner sectors of the estuary, currently being trapped in the finer sediments of this low energy zone.

5 Conclusions

The determination of background levels of metals for the sediments of the Paranaguá Estuarine System performed in this study is an important step in assessing the degree of sediment contamination and consequently proposing appropriate measures for the sustainable development of estuarine systems. Moreover, the integrated use of geochemical and statistical methods has been demonstrated to be useful for reliably determining background levels without the use of reference levels and/or sampling of sediment cores and is applicable to other estuarine systems worldwide.

Major and trace elements, such as Al, Fe, As, Cr, Cu, Ni, Pb, Sc and Zn were associated with natural sources and were predominant in sites located in the inner region of the Paranaguá Estuarine System (PES), which is subject to terrestrial inputs. Alternatively, the marine influence, reflected by elements, such as Ca and Sr, was stronger in the outer regions of the study area. Multivariate statistical analysis (PCA) ratified the correlation between the metals.

The results of trace elements enrichment and the comparisons with established Sediment Quality Guidelines showed that, in general, most of the elements presented enrichment relative to the background values and average concentrations below ERL, except for As, which presented enriched samples and levels, primarily between ERL and ERM. However, when compared with the permitted levels set by the Brazilian legislation the levels were primarily below level 1, thus As levels should be viewed with caution.

The levels of As in the PES samples may be due to the geochemical characteristics and the presence of phosphate

rocks of the drainage area, which may contain As in their composition. Nonetheless, As was also influenced by anthropogenic inputs, which could be related either to the presence of agricultural activities or ports and fertilizer industries working with mining phosphate in the region, however, it seems that this contaminant is physically transported (e.g. by currents, tides, waves) to internal parts of the estuary, being trapped in the finer sediments of these low energy zones.

The PES is an important estuarine region of South Atlantic that supports diverse human activities and ecological characteristics that evoke environmental management challenges. While it is clear that the area can be classified as uncontaminated for most metals, the As behavior requires further monitoring programs to determine trends, to prevent anthropogenic impacts and to promote the health and achieve a sustainable development of the last preserved Atlantic rainforest areas in South America.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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