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RECONSTRUÇÃO HISTÓRICA DE ELEMENTOS TRAÇOS EM TESTEMUNHOS SEDIMENTARES DA BAÍA DE TODOS OS SANTOS EMPREGANDO UM SCANNER DE FLUORESCÊNCIA DE RAIOS-X (ITRAX).

SALVADOR
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Este manuscrito representa o trabalho de graduação do Curso de Graduação em Oceanografia, Instituto de Geociências, Universidade Federal da Bahia, como requisito parcial para obtenção do grau de Bacharel em Oceanografia.

Orientadora: Profa. Dra. Vanessa Hatje

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APRESENTAÇÃO

Este trabalho tem como objetivo principal a reconstrução histórica da distribuição dos elementos traço na Baía de Todos os Santos (BTS). Na primeira etapa do estudo foi realizada a reconstrução histórica da contaminação e fontes de Hg na BTS, que resultou em um artigo publicado na Marine Pollution Bulletin, intitulado: “Historical records of mercury deposition in dated sediment cores reveal the impacts of the legacy and present-day human activities in Todos os Santos Bay, Northeast Brazil” (HATJE et al., 2019), no qual sou coautora. Minha participação neste trabalho foi o preparo das amostras, bem como tratamento dos dados e construção das figuras. Ademais, contribui com a redação do artigo. Com o intuito de abranger um maior número de elementos, a segunda etapa deste estudo constituiu na análise dos testemunhos sedimentares com auxilio de um scanner de fluorescência de raios-X (ITRAX) e com análises de amostras discretas usando técnicas convencionais (espectrometria). No entanto, problemas com o forno de micro-ondas causaram o atrasou das análises químicas que complementariam os resultados obtidos com o ITRAX e que ainda estão em andamento. O presente trabalho é apresentado na forma de um manuscrito que será submetido para a revista Marine Pollution Buletin.

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Abstract

In this study a comparison between ITRAX results and data from quantitative measurements (ICP-OES and DMA-80 Tri Cell) from previous studies was performed, in order to explore the ITRAX capabilities as a tool for assessing the historical evolution of trace elements in Todos os Santos Bay (BTS). The sediment cores were collected from several locations in BTS, covering a diverse range of environmental conditions and anthropogenic pressures. The total Hg concentrations (T-Hg) showed a good relation with intensities of Al, Si and Ti ($r = 0.66$, $r = 0.65$ and $r = 0.68$, $p < 0.05$, respectively) in Iguape Bay, corroborating previous indications that T-Hg is relatively unaffected by anthropogenic sources. On the other hand, in Ribeira Bay, T-Hg concentrations did not show a significant correlation with these elements, which suggests anthropogenic input associated with a decommissioned chlor-alkali industry, as the main source of Hg for this region. Samples from Ribeira Bay also presented good correlations between T-Hg concentrations and normalized intensities for Mn ($r = 0.65$, $p<0.05$), Pb ($r = 0.70$, $p<0.05$), and Cu ($r = 0.60$, $p<0.05$), suggesting the contamination by other elements associated with the the chlor-alkali industry. In the Aratu Harbor, normalized Cu intensities show a decreasing trend as a consequence of a reduction in the number of ships traffic after the 2008 financial crisis, moreover, Cu and Zn intensities presented good correlations with T-Hg ($r =0.58$ and $r = 0.67$, $p<0.05$, respectively), these metals have been used in antifouling paints. In general, the ITRAX system is sensitive to perform a semi-quantitative trace element analyses, being an analytical and efficient tool to evaluate contamination at screening level. When more accurate results are necessary, the initial detailed characterization provided by ITRAX allows a better selection of the interest sections of the core, before applying conventional techniques.

Keywords: ITRAX, sediment core, anthropogenic activities, Todos os Santos Bay, contamination, trace elements.

1. Introduction

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The chemical composition of seawater is largely controlled by biogeochemical processes. The elements once in solution can be adsorbed, precipitated and incorporated into the bottom sediments, which act as a sink (SALOMONS, 1980, 1985; WARREN, 1981). Sediments are a good tool to monitor aquatic and costal environments because: i) they are the main reservoir of contaminants; ii) sediments provide spatially and temporally integrated information; iii) element concentrations are orders of magnitude higher in sediments than in water, being more easily collected and accurately determined; iv) sediments may act as an important secondary source of pollutants (BIRCH, 2003; BRULAND et al., 1974; BUBB; RUDD; LESTER, 1991; CUNDY; CROUDACE, 2017).

Marine and coastal sediments record the oceans past environmental conditions. They have the ability to integrate long-term information, which make them attractive for the assessment of the anthropic impacts on the aquatic environment (ANDRADE et al., 2017; BIRCH et al., 2000; BIRCH; TAYLOR, 1999; BRULAND et al., 1974; LI et al., 2001; VALETTE-SILVER, 1993; WANG et al., 2015).

The advent of X-ray fluorescence (XRF) core scanners in the early 2000s led to a geoanalytical revolution. A new automated multi-function core scanning instrument, named ITRAX, emerged as an alternative to the analytical traditional methods commonly employed in studies of sediment profiles, which are time-consuming, involve incremental sampling to obtain significant quantities of material and additional processing before analysis (CROUDACE; RINDBY; ROTHWELL, 2006). ITRAX is a non-destructive scanner that incorporates XRF analysis, providing fast, useful and high-resolution geochemical records, detecting variations along sediment cores (JANSEN et al., 1998; RODRÍGUEZ-GERMADE; RUBIO; REY, 2014; ROTHWELL et al., 2006; THOMSON; CROUDACE; ROTHWELL, 2006).

For a given sediment core, ITRAX produces optical and micro radiographic images and elemental profiles by a micro-X-ray fluorescence (μXRF) spectrometry. It can operate on sediment cores or rocks with a maximum length of 180 cm and up to 12 cm diameter (CROUDACE; RINDBY;

ROTHWELL, 2006). X-ray fluorescence spectrometry utilizes the X-ray emission process, so each atom emits its own energy characteristic and wavelength spectrum. The ITRAX data are output as counts and can be considered semi quantitative in nature, and as such need to be interpreted with caution. The magnitude of the signal for each depends usually on excitation performance produced by the X-ray primary radiation, the energy of the elemental X-rays and abundance of the element (JANSEN et al., 1998; ROTHWELL et al., 2006). Sample preparation is very simple and results are produced in a few hours (depending on core length, step size and X-ray exposure time) (RODRÍGUEZ-GERMADE; RUBIO; REY, 2014). Croudace et al., (2006) evaluated the sensitivity of the XRF system using several international reference samples (USGS-MAG and USGS-SGR1), and found detection limits ranging from 5 ppm to 22 000 ppm, for Sr and Al respectively.

Errors may arise due to particle size, mineral surface heterogeneity, density (porosity changes), poor peak discrimination in the X-ray spectra, as well as, variations in water and organic matter content (HENNEKAM; LANGE, 2012; ROTHWELL et al., 2006). In spite of that, ITRAX elemental profiles can be obtained for a large range of elements. The sections of interest can also be analyzed more accurately (although with less spatial resolution) using well-established and destructive methods. Studies have shown that semi-quantitative data correlate well with quantitative analytical data (traditional destructive methods), and have shown that there are similar trends between the profile pattern obtained with the two techniques (CROUDACE; WARWICK; MORRIS, 2012; CUNDY; CROUDACE, 2017; HENNEKAM; LANGE, 2012; LEPLAND et al., 2010; RODRÍGUEZ-GERMADE; RUBIO; REY, 2014; THOMSON; CROUDACE; ROTHWELL, 2006).

Over the years the majority of samples analyzed by core scanners have been sediments, as a tool for investigating the geomorphological, palaeoclimatology, palaeoceanography and contaminant history of environmental systems (CROUDACE; WARWICK; MORRIS, 2012; LEPLAND et al., 2010; PENNINGTON et al., 2019; RODRÍGUEZ-GERMADE; RUBIO; REY, 2014). However, the versatility of these scanners provides new uses, and they are now being applied to investigate other materials such as coral, tree sections, sedimentary nodules, environmental remediation and even in art conservation or restoration (AGNEW et al., 2011; CRONAN; ROTHWELL; CROUDACE, 2010; ELLIS et al., 2019; JANSSENS et al., 2000; SÁNCHEZ-SALGUERO et al., 2019).

The objective of this study is to explore the ITRAX capabilities as a tool for assessing the historical evolution of trace elements in Todos os Santos Bay, Bahia, Brazil. We compared the ITRAX results and data obtained from quantitative measurements by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Direct Mercury Analyzer DMA-80 Tri Cell from previous studies (ANDRADE et al., 2017; HATJE et al., 2019).

2. Materials and methods

2.1. Study Area

Todos os Santos Bay (BTS; Fig. 1), the second largest bay in Brazil (1,223 km^2), is an extremely diverse environment (coral reefs, estuaries, mangroves, islands, tidal flats and seagrass), with tropical climatic characteristics. The BTS has ecological, historical and socio-economic importance, and is located in the vicinity of Salvador, the third largest city in Brazil with a population over 2.7 million (IBGE, 2010).

Human activities at BTS started around the 1550s, with the cultivation of sugar cane. But the most significant change occurred in 1950, due to the broad industrial growth, after the construction of the Landulpho Alves Refinery (RLAM) and the development of the largest petrochemical complex of the southern hemisphere. Currently there is a myriad of anthropogenic activities arround the bay, which includes metal smelting, chemical industries, shrimp farming, harbors, and sewage discharges. These anthropogenic activities have caused environmental pressures, negatively impacting ecological services, the environmental quality of the bay and the lives of traditional communities (ANDRADE et al., 2017; CARVALHO et al., 1984, 1989; CRA, 2004; DE SOUZA; WINDMÖLLER; HATJE, 2011, 2014; HATJE et al., 2006, 2016, 2019; HATJE; BARROS, 2012; RIBEIRO et al., 2016).

2.2. Sampling and pretreatment

In July of 2017, sediment cores were acquired using a corer (UWITEC, Austria) designed to collect undisturbed sediment profiles. The sediment cores were collected from several locations in Todos os Santos Bay, Bahia, northeast Brazil (Fig. 1): i. Core CI6 (5 m depth) was collected in Iguape Bay, downstream the dam of the Paraguaçu River; ii. Core CI7 was collected in the vicinity of the harbor and the Industrial Complex of Aratu (4.5 m depth); iii. Core CI8 was collected in Ribeira Bay (6 m depth); and iv. Core CI9 was collected in the adjacencies of the Subaé estuary (6.5 m depth). Cores CI7 and CI9 were sliced into 0.5 cm sections for the top 10 cm, at 1 cm sections for the 10–20 cm interval, and then at 2 cm for the sections until the bottom. Dry bulk density was calculated dividing the dry weight of the slice by its volume. Details of sample collection and slicing of cores CI6 and CI8 has been previously described (HATJE et al., 2019).

For grain size analysis, 2 g of homogenized sediments were treated with hydrochloric acid (HCl). For the determination of the particle size, ~1 g of each sample was sieved through stainless steel sieves for the size fractions larger than 500 µm. Particle sizes < 500 µm were determined by a particle analyzer by laser diffraction (model Cilas 1064).

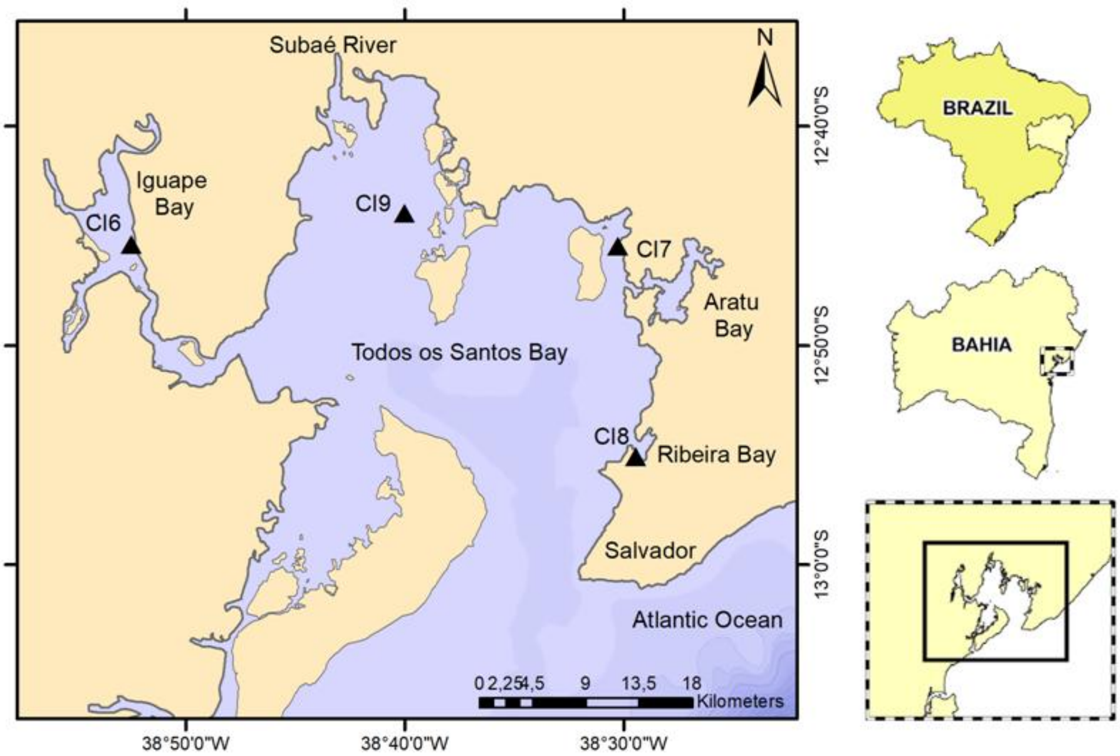

Figure 1. Sampling location of 4 sediment cores (CI6, CI7, CI8 and CI9) in black triangles in the Todos os Santos Bay, Bahia, Brazil.

2.3. ^{210}Pb analyses

We determined ^{210}Pb concentrations through the measurement of its granddaughter ^{210}Po (its decay product) by alpha spectrometry after addition of ^{209}Po as an internal tracer and microwave-assisted acid digestion (SANCHEZ-CABEZA; MASQUÉ; ANI-RAGOLTA, 1998). The concentrations of excess ^{210}Pb ($^{210}Pb_{ex}$) used to obtain the age models were determined as the difference between total ^{210}Pb and ^{226}Ra (supported ^{210}Pb), which was determined for selected samples along each core by low-background liquid scintillation counting (Wallac 1220 Quantulus) (MASQUÉ et al., 2002). These concentrations were confirmed with ^{226}Ra measurements by gamma spectrometry and found to be in agreement with the concentrations of total ^{210}Pb at depths below the excess ^{210}Pb horizons in each core. To calculate the sedimentation rates (SAR, cm y^{-1}) and mass accumulation rates (MAR, g cm^{-2} yr^{-1}) we used the Constant Flux:Constant Sedimentation (CF:CS) model (KRISHNASWAMY et al., 1971).

2.4. ITRAX procedures

Cores were analyzed using an ITRAX XRF core scanner, this permitted the rapid and automatic recording of a range of trace metal. X-rays, in this study were generated by a Mo tube at 30 kV and 55 mA, in the ITRAX system (Cox Analytical Systems, Sweden), focused to a 200 µm x 4 mm rectangular beam (size of irradiated area) with the long axis perpendicular to the axis of the sediment core. The XRF logging was done using a 1 mm step size, 10s counting time, and the measurement time for each 1 m was about 3 hours. Because X-ray absorption varies with sediment type, radiographic images were made to allow the recognition of sedimentary structures and texture variations along the cores. In addition, an optical image was made for correlation of radiographic and XRF data with the visual color characteristics of the sediment.

Element data recorded by the ITRAX are semi-quantitative, and are expressed as total counts (cnts), that is the integrated peak area, denoting the number of total counts collected by the detector during the measurement time (OHLENDORF; WENNRICH; ENTERS, 2015). The resulting data represent element intensities expressed as counts per second (cps), determined by the division between the peak area for the element and XRF count time (JARVIS; CROUDACE; ROTHWELL, 2015). Counts per second allow to see data trends, remove the artifacts of core topography and density differences.

2.5. Numerical procedures

Contaminant concentrations, frequently associated with the fine fraction of sediments, are influenced by the texture of sediments. To eliminate the grain size effect, the intensities of trace elements from ITRAX were normalized to a conservative element that is a proxy of the sediment texture and/or continental source (BIRCH, 2003; BIRCH; SNOWDON, 2004; GRANT; MIDDLETON, 1990). Pearson correlation between the trace elements (S, Mn, Fe, Ni, Cu, Zn, La, Ce, Pb, Al and Ti) in the sediments was used to select the best normalizing element for this study. On the basis of the correlation coefficients, Ti was chosen as the normalizing, conservative element. Ti has been previously used as a conservative element, characteristic of the detrital phase, in replacement of Al (ROTHWELL et al., 2006; THOMSON; CROUDACE; ROTHWELL, 2006).

The Pearson correlation was also used to compare intensities data (from ITRAX) with Total Mercury (T-Hg) and grain size provided by a previous study (HATJE et al., 2019).

3. Results and discussion

The results will be discussed for each sampled region of Todos os Santos Bay, Bahia, Brazil, namely: i. Iguape Bay, downstream a dam in the Paraguaçu River (CI6); ii. nearby the Aratu harbor (CI7); iii. Ribeira Bay (CI8); and iv. in the adjacencies of the Subaé estuary (CI9).

Iguape Bay – CI6

The sediment core CI6 was collected in Iguape Bay (Fig. 1), downstream the Pedra do Cavalo dam in Paraguaçu River. About 95% of the BTS catchment (56,300 km^2) is drained by Paraguaçu River, which is the main freshwater input to this bay, in the western side of the BTS (CIRANO; LESSA, 2007; GENZ; LESSA; CIRANO, 2006). Sediment characteristics, grain size and sedimentation rates for this core have been previously discussed by HATJE et al. (2019). The dry bulk density (DBD; Fig. 2) of core CI6 (HATJE et al., 2019) was stable from the base of the core to around 22 cm (~1.2 g cm^{-3}) and then decreased towards the surface (0.56 g cm^{-3}). Excess ^{210}Pb concentrations decreased with depth from the surface layers (Fig. 3), and the ^{210}Pb horizon was reached at 14 cm. The core CI6 presented the lowest average sedimentation rate (SAR, 0.11 ± 0.02 cm yr^{-1}) and mass accumulation rate (MAR, 0.12 ± 0.02 g cm^{-2} yr^{-1}) (HATJE et al., 2019).

ITRAX intensities normalized by Ti for core CI6 (Fig. 4) exhibit a constant depth profile for all elements, although La presented substantial variability. Iron shows a slight increase trend from the base up to ~5 cm and sulfur shows an increase from base of the core up to 22 cm followed by a decrease towards surface. Fe and S normalized intensities profiles were well correlated ($r = 0.73$, $p<0.05$).

Normalized intensities profiles of micro nutrients (Ni, Cu, and Zn) were positively correlated ($0.68 \leq r \leq 0.74$, $p < 0.05$) and presented low and constant intensities (Figure 4). The stable and low intensities of these elements in sediments may be associated with relatively low anthropogenic inputs to the bay (ANDRADE et al., 2017; BARROS et al., 2008; CRA, 2004). Depth profiles of the normalized intensities (Fig. 4) showed a very similar behavior with concentrations of trace elements along time found by ANDRADE et al. (2017). However, the slight increase in Cu, Pb, Fe and Zn concentrations in surface sediments observed by ANDRADE et al. (2017) could not be identified by the ITRAX. This discrepancy could be associated with the location of the CI6 sampling site, which is further upstream to the installation of the the Enseada Indústria Naval Shipyard (EIN), the main source of contaminants for the Paraguaçu river. Alternatively, ITRAX may not present the required sensitivity to measure variability at this low level.

Comparing intensities obtained using ITRAX with Hg concentrations provided by a previous study (HATJE et al., 2019), it was observed that total mercury (T-Hg) shows good corelation with Al, Si and Ti ($r = 0.66$, $r = 0.65$ and $r = 0.68$, $p< 0.05$, respectively). These elements are the main constituents of clay minerals and customarily associated with the aluminosilicate fraction (GRANT; MIDDLETON, 1990; THOMSON; CROUDACE; ROTHWELL, 2006; WANG et al., 2015). This good correlation corroborates the hypothesis that Hg concentrations in Iguape Bay are relatively unaffected by anthropogenic activities over the past 150 years (HATJE et al., 2019).

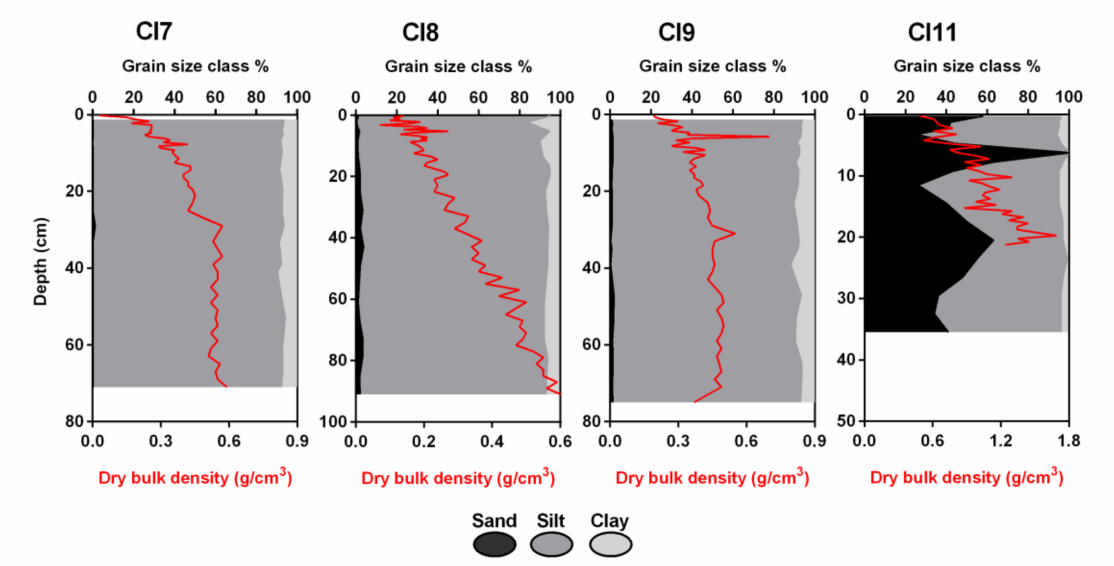

Figure 2. Depth profiles of grain size classes (gray scale areas) and dry bulk density (red line) for each sediment core. There were no available samples for grain size analysis for core CI6, which was collected near core CI11. For comparison purpose, the DBD for core CI6 (blue line) is shown with CI11 (red line). Data for cores CI8, CI6 and CI11 are from HATJE et al. (2019).

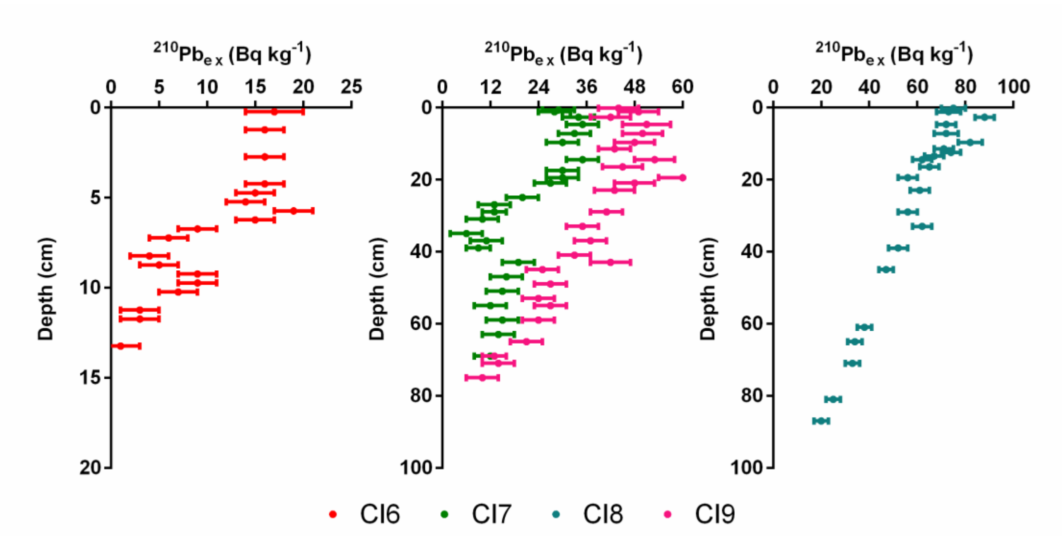

Figure 3. Excess ^{210}Pb concentration profiles for sediment cores CI7 and CI9. Data for cores CI6 and CI8 are from HATJE et al. (2019).

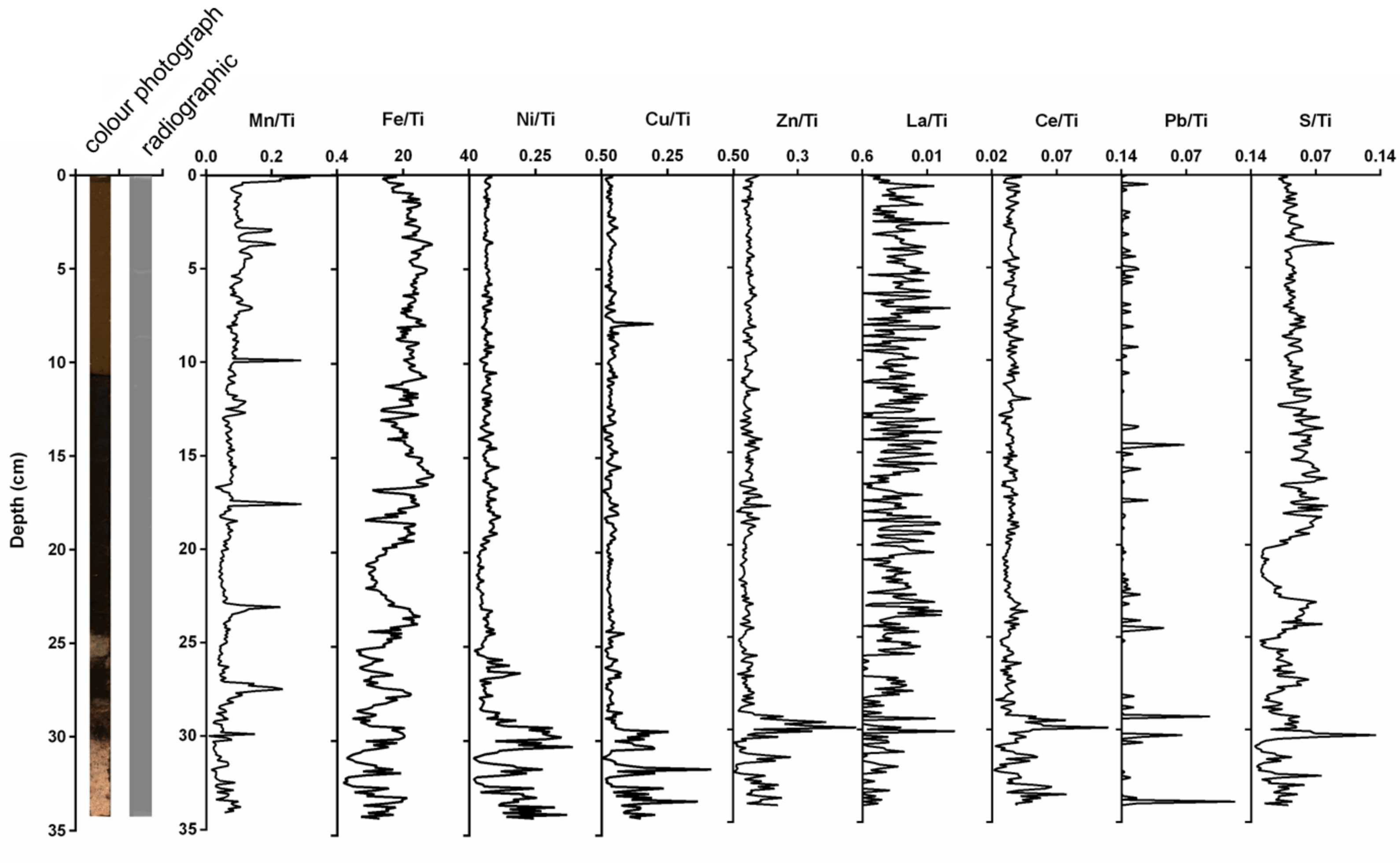

Figure 4. Non-destructive ITRAX core scanning data, showing colour photograph, radiographic image and elemental intensities normalized by Ti intensities along depth for core CI6, located in Iguape Bay, downstream a dam in the Paraguaçu River.

14

Nearby the Aratu harbor – CI7

The sediment core (CI7) was collected nearby the Aratu Harbor (Fig. 1), which opened in 1975. This port is crucial for commodity transportation from the Camaçari Industrial Center, and the Aratu Industrial Complex (CODEBA, 2014; CRA, 2004). Sediment characteristics along the CI7 (Fig. 2) were homogeneous and consists principally of fine sediments (> 98% of silt+clay), reflecting the drainage basin composed of fine-grained sedimentary rocks (CIRANO; LESSA, 2007). Dry bulk density (DBD; Fig. 2) increased with depth through the core and tended to stabilize towards the base at approximately 0.51–0.59 g cm^{-3}. The concentrations of $^{210}Pb_{ex}$ (Fig. 3) decreased with depth, but the horizon of excess ^{210}Pb was not reached. An average sedimentation rate was estimated below the mixed layer (between 15- 20 and 35 cm) of 0.15-0.20 g cm^{-2} yr^{-1} (or 3-4 mm yr^{-1}). However, this estimate is an upper limit and subject to a large uncertainty because of the presence of the thick layer of mixed sediments, and using this estimate the deeper sections (40-70 cm) cannot be modeled. An alternative interpretation would be to estimate a sedimentation rate below the mixed layer and down to 70 cm, but without including the 26-40 cm section. The Sedimentation rate would be of about (SAR, 1.6 ± 0.02 cm yr^{-1}) and mass accumulation rate (MAR, 0.8 ± 0.02 g cm^{-2} yr^{-1}), which is very similar to previous values determined for the region (ANDRADE et al., 2017).

The ITRAX core scanning of the core CI7 (Fig. 5) shows that from the base of the core up to 40 cm normalized intensities exhibit homogeneous behavior. In the top section of the core (first ~20 cm), the intensities became homogeneous again for most elements, although with some variability, especially for Mn. Zinc and Cu normalized intensities were highly correlated ($r = 0.84$, $p<0.05$) and presented an increase trend from 40 up to 20 cm depth. Niquel and Pb exhibited scatter intensities for this interval, where peak concentrations could be observed, and also presented a good correlation ($r = 0.77$, $p<0.05$). Normalized intensities of Ni, Cu, Zn and Pb were also significantly correlated ($0.61 \leq r \leq 0.84$, $p < 0.05$). The intensities data obtained with the ITRAX were compared with concentrations provided by a previous study (ANDRADE et al., 2017) and observed that profiles show a similar behavior.

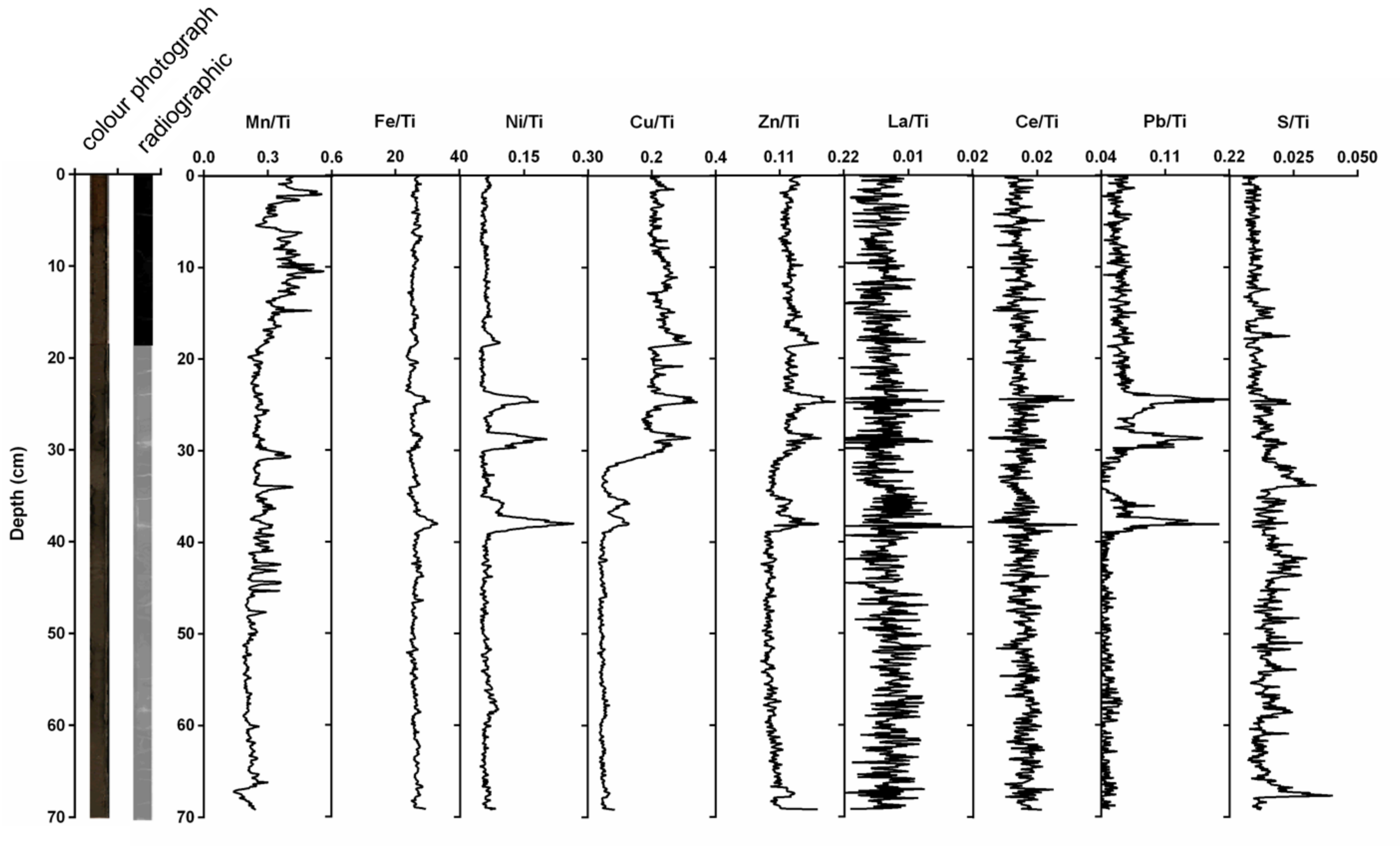

Figure 5. Non-destructive ITRAX core scanning data, showing colour photograph, radiographic image and elemental intensities normalized by Ti intensities along depth for core CI7, located nearby the Aratu Harbor.

ANDRADE et al. (2017) explained that metal inputs, especially Cu and Zn are associated with boating activities at the Aratu harbor that started in 1975. Metals have been used to protect ship hulls from marine fouling (ALMEIDA; DIAMANTINO; DE SOUSA, 2007). The main antifouling products changed since ancient times (wax, tar and asphalt) to present day (Cu, As, Zn and Hg dispersed in a polymeric binder) (ALMEIDA; DIAMANTINO; DE SOUSA, 2007; WOODS HOLE, 1952). ANDRADE et al. (2017) found a significantly correlation between Cu concentrations and the number of vessels docked in the Aratu harbor. The ITRAX data reflect this correlation. After reaching maxima in 20-30 cm depth (early 2000s), the normalized Cu intensities show a decrease trend, consequence of a decrease in the number of ships after the 2008 financial crisis. Besides that, we obtained good correlations between Hg concentrations provided by a previous study (HATJE et al., 2019) and metals intensities from ITRAX data for Zn ($r = 0.67$, $p<0.05$) and Cu ($r = 0.58$, $p<0.05$). The Pb inputs in this region are most likely linked to the burning of fossil fuels (terrestrial sources and maritime traffic), besides other sources such as the textile and metal industries, shipyards, and also past time burning of coal to produce gas and steam. The patterns of these elements show the impacts of the Port of Aratu and also the Industrial Complex of Aratu (CIA) in Aratu Bay.

Manganese normalized intensities from ITRAX data (Figure 5) are relatively constant in the bottom section of the core up to 20 cm, with the exception of the 30-50 cm zone that showed some intensity peaks. In the top section of the core (first ~20 cm), the intensities presented an increasing trend. There is a ferro-manganese alloy production plant in the Aratu Industrial complex, that produces 280,000 ton of SiMn and FeMn alloys per year, since the begin of operations in 1970 (MENEZES-FILHO et al., 2009). The ITRAX depth profile is very similar with the Mn concentrations found by ANDRADE et al. (2017), that suggested that the Mn emitted through by the chimneys of the ferro-manganese production plant is contributing to the contamination of the sediments.

Normalized intensities of Fe, La, Ce and Ni (Fig. 5) show a relatively constant profile, although presented some variability, especially between 30-50 cm.

The results indicate that ITRAX is sensitive to perform a semi-quantitative trace element analysis, being an efficient and quick option to monitor contamination. However, in a specific zone (20-40 cm depth), there is a difference between ITRAX data and data from the destructive method used by ANDRADE et al. (2017). Depth profiles by ANDRADE et al. (2017) show an increasing trend, whereas in normalized ITRAX data we only can see peaks of intensity.

Ribeira Bay – CI8

The sediment core CI8 was collected in Ribeira Bay (Fig. 1), which is surrounded by disorderly human occupation, and small-size industries. Sediments were mostly fine. The dry bulk density (DBD; Fig. 2) was 0.60 g cm^{-3} at the base, and decreased towards the surface as previously described (HATJE et al., 2019). Excess ^{210}Pb concentrations decreased with depth from the surface layers (Fig. 3), and the ^{210}Pb horizon was not reached (HATJE et al., 2019). The core CI8 presented the highest average sedimentation rate (SAR, 2.22 ± 0.15 cm yr^{-1}) and mass accumulation rate (MAR, 0.81 ± 0.05 g cm^{-2} yr^{-1}) (HATJE et al., 2019).

The ITRAX scanning of the core CI8 (Fig. 6) exhibit a constant depth profile for all elements, although La and Ce presented substantial variability. Only Mn and S show a slight increase trend from ~40cm towards surface. Normalized intensities profiles of Ni, Cu and Fe were positively correlated ($0.66 \leq r \leq 0.81$, $p < 0.05$).

Pearson Correlation was applied to compare intensities data from ITRAX and Total Mercury (T-Hg) concentrations provided by a previous study (HATJE et al., 2019). The T-Hg did not show a significant correlation with Al, Si or Ti. The T-Hg concentrations shows a good correlation with S normalized intensities ($r = 0.82$, $p< 0.05$). The chlor-alkali process produces caustic soda and Cl_2 in addition to hydrochloric acid (HCl) and liquid sodium hydrosulfite ($Na_2S_2O_4$) (KINSEY et al., 2004). The sludge generated in this process precipitates $CaCO_3$, $Mg(OH)_2$ and sulfates (CRA, 2004). The good correlation between Hg and S, indicates that the chlor-alkali industry Companhia Química do Recôncavo (CRQ) was the main source of sulfur for this region. The CRQ,

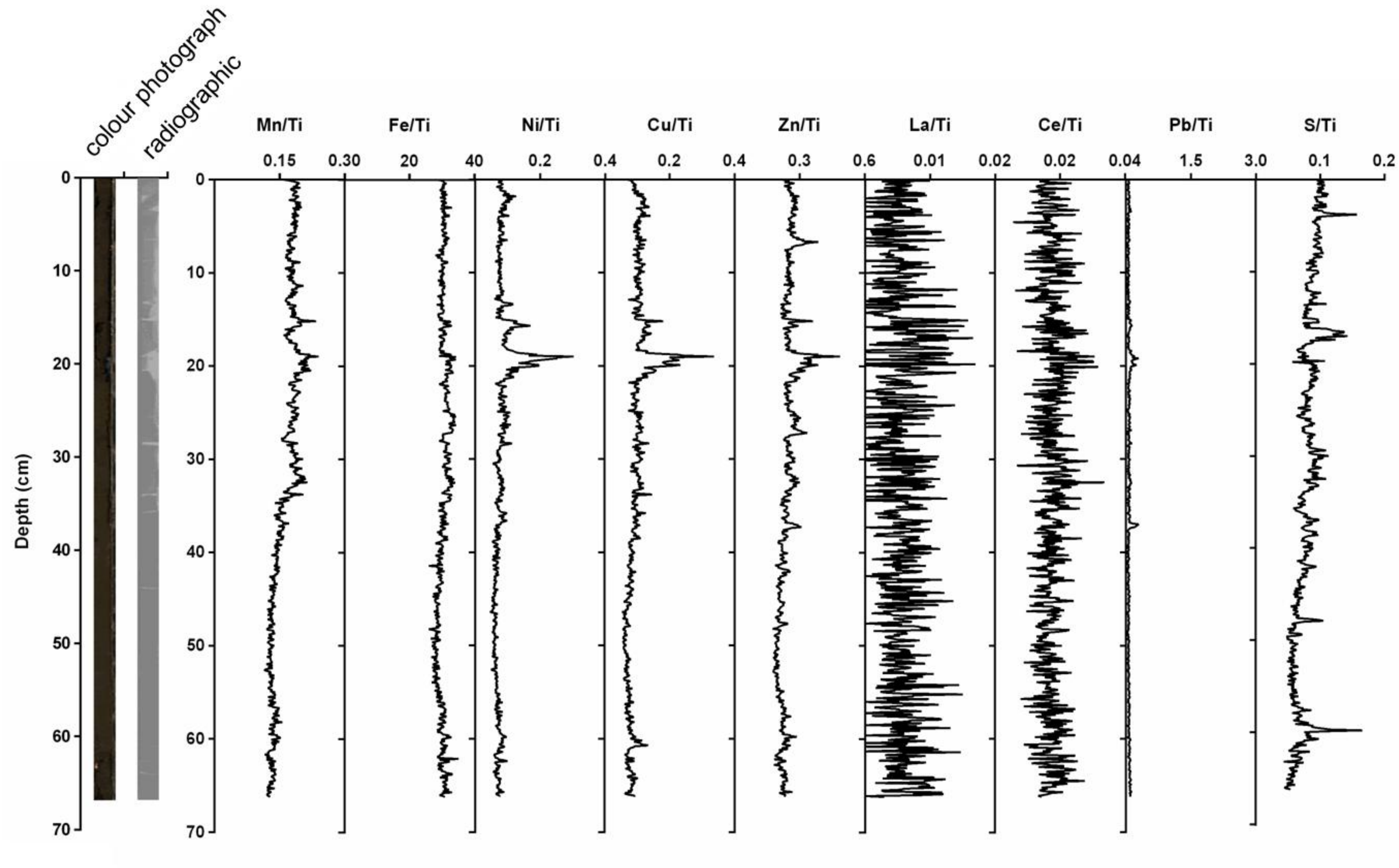

Figure 6. Non-destructive ITRAX core scanning data, showing colour photograph, radiographic image and elemental intensities normalized by Ti intensities along depth for core CI8, located at Ribeira Bay.

now operating at the Camaçari Petrochemical Complex, operated for 12 years on Itapagipe Bay (1966 to 1978), being the largest source of mercury for the region (CRA, 2004; DE SOUZA; WINDMÖLLER; HATJE, 2011, 2014; HATJE et al., 2019).

Good correlations were obtained between T-Hg concentrations and normalized intensities for Mn ($r = 0.65$, $p<0.05$), Pb ($r = 0.70$, $p<0.05$ r), and Cu ($r = 0.60$, $p<0.05$). A previous study evaluated the concentration of trace metals in sediments in Ribeira Bay and found high concentrations for Hg, Pb, Cu and Zn (CRA, 2004). The main sources of contamination for this region, besides the legacy of the chlor-alkali plant, are surface runoff and raw sewage from disorderedly occupied hillsides for the last decades (CRA, 2004; HATJE et al., 2019).

Although the correlation suggest that there is an anthropogenic input of trace elements in the region, which is corroborated by previous studies (CRA, 2004; DE SOUZA; WINDMÖLLER; HATJE, 2011, 2014; HATJE et al., 2019), the elemental intensities normalized by Ti did not illustrate that. If only ITRAX had been used to detect contamination, the impact of certain elements would not have been identified.

Adjacencies of the Subaé estuary - CI9

The sediment core (CI9) was collected near the mouth of the Subaé river (Fig. 1), the second most important source of freshwater and suspended material to the BTS (CRA, 2004; HATJE; BARROS, 2012). Grain sizes along the sediment core CI9 were vertically homogeneous and consisted mainly of fine sediments (> 95% of silt+clay) over the entire sediment core (Fig. 2), reflecting the drainage basin mainly composed of fine-grained sedimentary rocks. Sediment characteristics indicates low energy sediment transport, and deposition processes favorable to good sediment preservation. The dry bulk density (DBD; Fig. 2) of core CI9 was stable from the base of the core to around 23 cm (~0.43 g cm^{-3}) and then decreased towards the surface (0.19 g cm^{-3}). The concentration profile of $^{210}Pb_{ex}$ (Fig. 3) shows that the horizon of $^{210}Pb_{ex}$ was not reached, indicating that sedimentation rates are substantial in this site. There is evidence of mixing (or high sedimentation) in the upper 20 cm, from which the concentrations of excess ^{210}Pb decreased with depth. The sedimentation rate (SAR, 1.4 ± 0.15 cm yr^{-1}) and mass accumulation (MAR, 0.67 ± 0.07 g cm^{-2} yr^{-1}), below the mixed layers, were high, compatible with the high inventory of $^{210}Pb_{ex}$ (10 x 10^3 Bq m^{-2}), and comparable with previous values determined for the region, although slightly lower (ANDRADE et al., 2017).

ITRAX scanning of normalized intensities (Fig. 7) shows that from the base of the core CI9 up to 10 cm, profiles of Mn, Ni, Cu, Zn, and S were homogeneous, followed by an increase towards surface. Normalized intensities profiles of Ni, Cu, Zn were significantly correlated ($0.75 \leq r \leq 0.89$, $p < 0.05$). Iron also presented a positively correlation with Cu ($r = 0.69$, $p < 0.05$), Ni ($r = 0.66$, $p < 0.05$), and Zn ($r = 0.64$, $p < 0.05$). We have compared intensities obtained with the ITRAX with concentrations depth profiles provided by a previous study (ANDRADE et al., 2017) and observed that profiles followed the same trends. However, for the most recent period, where we identify an increasing trend, the ANDRADE et al. (2017) lack data. These results indicate that the ITRAX is an efficient and fast option for the screening of contamination, serving to provide an initial characterization of sediment cores.

Lead normalized intensities (Figure 7) are relatively constant in the bottom section of the core until the 46 cm, then they increase and reach a maximum at 32 cm, followed by a decrease. In the top section of the core (first ~10 cm), the intensities increased again up to around 5 cm and then they were quite variable. The Subaé estuary is one of the most contaminated areas of BTS due to the Pb smelter which operated in Santo Amaro between 1960 and 1993, producing 11–32 × 106 kg yr^{-1} of Pb. The smelter is still considerate a source of contamination through atmospheric dust, runoff, and groundwater dispersion due to a large waste reservoir that is poorly maintained (HATJE et al., 2006, 2019; HATJE; BARROS, 2012; MACHADO et al., 2013), and is responsible for promoting a decrease in the abundance and richness of benthic macrofauna assemblages, impairing the ecological services (HATJE et al., 2006; KRULL et al., 2014), and exposing local people to high levels of trace elements (CARVALHO et al., 1984, 1989; TAVARES et al., 1989). ANDRADE et al. (2017) used Pb stable isotopes to link the increase in Pb concentrations to the activities of this currently decommissioned Pb smelter. They observed that after the control of atmospheric dust emissions, an increase in Pb isotopic ratios was observed, reflecting the decrease in dust discharges and the dilution of the smelter signal recorded in sediments. This agrees with ITRAX data, that also shows the decreasing behavior of Pb intensities from 31 cm. Other anthropogenic activities are also contributing to metal contamination, for example, paper and food industries and, especially, several point sources of untreated sewage discharge.

Normalized intensities of Fe, La and Ce (Figure 7) show a relatively constant profile, although La and Ce presented substantial variability.

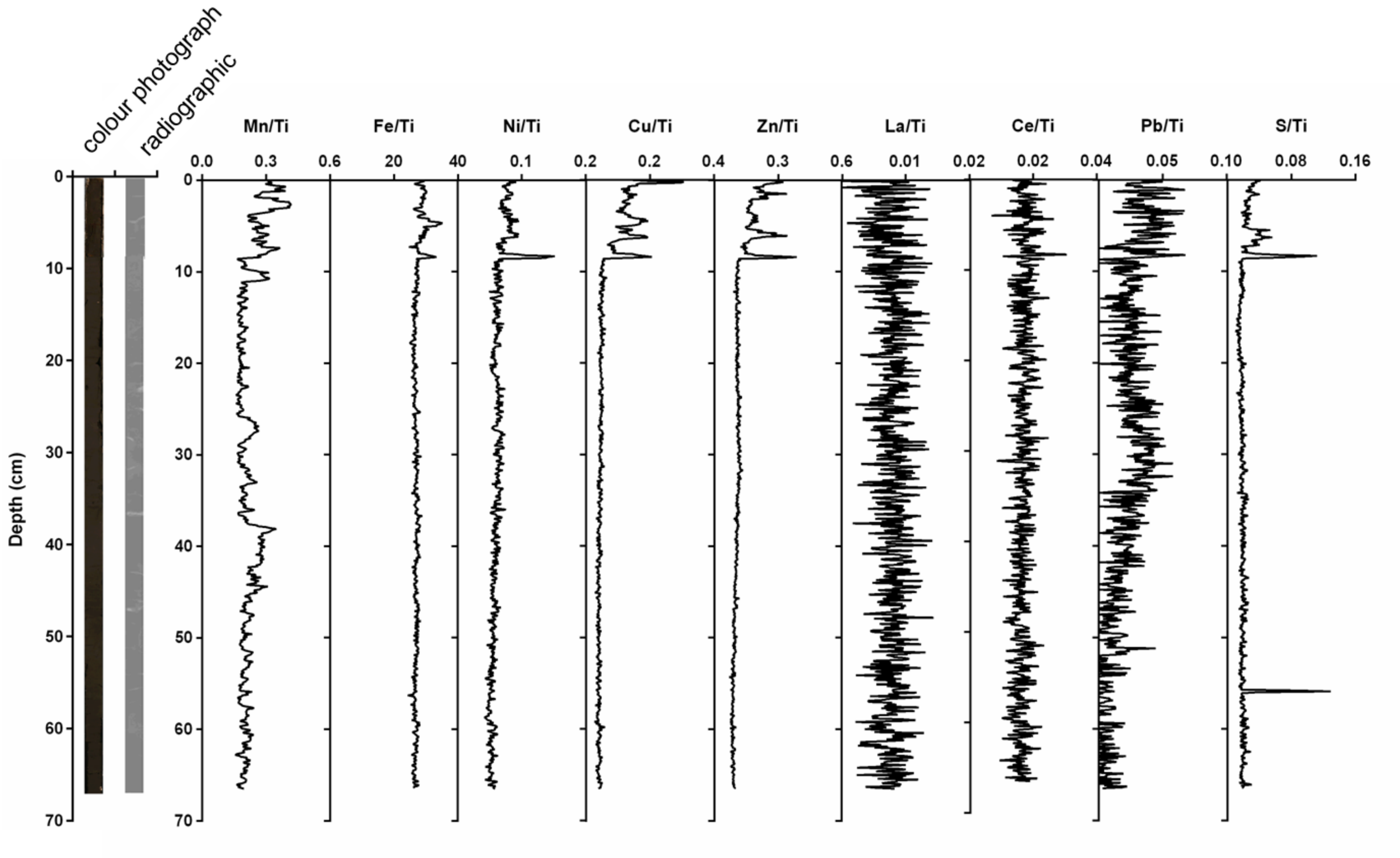

Figure 7. Non-destructive ITRAX core scanning data, showing colour photograph, radiographic image and elemental intensities normalized by Ti intensities along depth for the core CI9, located in the adjacencies of the Subaé estuary.

4. Conclusions

Similar patterns and good correlations observed between ITRAX data and concentration profiles validate ITRAX's efficiency in identifying anthropogenic inputs in Todos os Santos Bay from punctual sources (e.g. chlor-alkali industry, Pb smelter, harbor, ferro-manganese alloy production) and general sources (e.g. maritime traffic, untreated sewage discharge). We concluded that the ITRAX system is sensitive to perform a semi-quantitative trace element analysis, being an analytical and efficient tool to evaluate contamination, serving to provide an initial, non-destructive, quick and high resolution characterization of sediment cores. We found that when concentrations are low, it is easier to identify temporal variability employing discrete samples than with ITRAX. The later is a good tool for acquiring an initial detailed characterization, allowing a better selection of the interest sections of the sediment core for further discrete sample analysis at higher accuracy (although generally at poorer spatial resolution) using conventional techniques (destructive traditional methods).

The main feature of scanner systems is their analytical rapidity and the high-resolution capability to provide information not possible with conventional methods where the scale is usually centimeters. However, more advancement are required to improve XRF core scanning, including better determination of accuracy and precision of XRF core scanners, methodological adjustments to deal with variations in water and organic matter contents.

The ITRAX has been widely used to acquire geochemical data in different matrices (e.g. sediments, rocks, coral, tree sections, sedimentary nodules) evidencing great versatility. It can be installed inside a container, which facilitates its use on board research vessels, being an auxiliary instrument during several sea expeditions.

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