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CRONOLOGIA DOS IMPACTOS ANTROPOGÊNICOS RECONSTRUÍDA A PARTIR DE REGISTROS SEDIMENTARES DATADOS DE METAIS TRAÇO E ISÓTOPOS DE Pb EM UMA BAÍA TROPICAL

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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. Este trabalho é apresentado na forma de um manuscrito que será submetido para a revista Science of the Total Environment.

Orientador: Profa. Dra. Vanessa Hatje

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APRESENTAÇÃO

Este trabalho é apresentado na forma de um manuscrito que será submetido para a revista Science of the Total Environment.

Chronology of anthropogenic impacts reconstructed from dated sedimentary records of trace metal and Pb isotopes in a tropical bay

Abstract

The mankind actions have lead us to the Anthropocene, a geological epoch when Nature is not alone conducting the biogeochemical cycles of many trace elements. The objective of this study was to use sediment cores to determine the chronological record of anthropogenic impacts in five regions of Todos os Santos Bay, Bahia, Brazil. Trace metals (Co, Cu, Mn, V, Pb, Zn, Fe, Al, Cr, Cd, Ni, and Ti) and Pb isotopes (^{208}Pb, ^{206}Pb, ^{207}Pb, and ^{204}Pb) were measured in five dated sediment cores (CI1-CI5). The sedimentation rates raged from (0.38 – 2.60 cm yr^{-1}). The grain size was homogeneous through time along all cores, and was mainly composed by silt sediments. Trace elements concentrations tended to increase especially after 1950, most of them showing low to moderate enrichment. Increases in concentrations of trace metals were associated to different anthropogenic activities: Pb smelting (CI2-CI3), burning of fossil fuels (all cores at some extend), maritime traffic (CI4), petroleum related activities (CI5), and changes in land uses (CI1). All metals, except Cu at CI4, presented concentrations bellow TEL, indicating that contamination in the studied areas are not prone to cause adverse effects to biota. Stable Pb isotopic ratios identify a decommissioned lead smelter and burning of fossil fuels as the main sources of Pb to the bay. The results of implementation of environmental policies to improve the waters of the bay could not be noted by the evaluated cores.

Keywords: Sediment cores; Pb isotopes; Geochronology; Trace elements; Todos os Santos Bay

1. Introduction

The world's population growth associated with the industrial and technological development; the astounding natural resources exploitation, intensive agriculture practices, production of new materials (*e.g.* plastics); the extinction of species and the proliferation of exotic species in several places have supported the designation of Anthropocene for the current geological epoch (Crutzen and Stoermer, 2000; Waters et al., 2016, 2014). In this period, the anthropogenic activities started to exert dominance over many geological surface processes, increasing substantially the scale of mankind negative impacts in the planet's environments (Halpern et al., 2008; Meybeck, 2003). Consequently, the anthropogenic fluxes of trace metals, which can act as contaminants to water bodies, were substantially increased, perturbing their biogeochemistry cycles (Boyle et al., 2014; Dean et al., 2014).

The costal zone is particularly important in this scenario, once it provides space, goods and services to human beings and highly diverse habitats to organisms. This region is one of the most densely populated and industrialized areas in the planet, what makes it extremely vulnerable to man-made changes to soil, atmosphere and waters both in local and global scales (*e.g.,* increase in sea level) (Jennerjahn, 2012). The coastal systems receive most of the fluvial inputs of water, as well as dissolved and particulate matter (Martin and Meybeck, 1979; Milliman and Farnsworth, 2013; Viers et al., 2009). A large part of the fluxes of the natural and anthropogenic materials introduced in coastal systems tend to accumulate in sediments, producing unequivocal geochemical signatures within sedimentary bodies, thus registering changes in time (Bruland et al., 1974). These anthropogenic geochemical signatures include elevated levels of contaminants such as metals (Bai et al., 2016; Begy et al., 2016; Garcia-Orellana et al., 2011), polycyclic aromatic hydrocarbons (PAHs) (Martins et al., 2015; Peng et al., 2008),

pesticides (Alonso-Hernández et al., 2015; Kaiser et al., 2016), polychlorinated biphenyls (PCBs) (Combi et al., 2016; Ruiz-Fernández et al., 2012), in addition to changes in Pb isotopic composition from leaded gasoline and other industrial processes such as non-ferrous metal smelting, coal burning, and waste incineration (Nriagu and Pacyna, 1988; Waters et al., 2016; Yu et al., 2016; Zhang et al., 2016).

The chronological history of environmental impacts can be assessed by dating sediment layers in the sediment deposit (Begy et al., 2016; Birch et al., 2013; Cantwell et al., 2015). ^{210}Pb is a natural occurring radionuclide from the ^{238}U series commonly used to determine the chronology of recent (~150 years) deposits (Appleby and Oldfield, 1978; Foster et al., 2015; Yang et al., 2016). Given that natural and anthropogenic processes may disturb the sedimentary record, the use of complementary tracers, such as Pb isotopic compositions (Cheng and Hu, 2010) and/or artificial radionuclides (*e.g.,* ^{137}Cs) becomes important for the validation of the ^{210}Pb derived chronology (Álvarez-Iglesias et al., 2007).

Lead is also a valuable geochemical tracer for contamination, because of its four naturally occurring stable isotopes: ^{206}Pb, ^{207}Pb, ^{208}Pb, and ^{204}Pb, which is the only non-radiogenic one. Though ^{204}Pb abundance on Earth has not varied in time, the abundances of ^{206}Pb, ^{207}Pb, and ^{208}Pb in an ore deposit depend on when it was formed, since they are products of radioactive decay (Bird, 2011; Doe, 1970; Ault et al., 1970). As Pb does not undergo significant isotopic fractionation in natural or industrial physicochemical processes, the isotopic composition only changes if mixed with a secondary source of Pb (Bird, 2011; Komárek et al., 2008; Cheng and Hu, 2010). Since many different sources of Pb have distinct isotopic signatures, lead isotopes are a suitable tool for tracing sources of Pb in different environmental compartments, as well

as studying its transport pathways (Cheng and Hu, 2010; Komárek et al., 2008; Oulhote et al., 2011).

The Todos os Santos Bay (BTS), located in northeast Brazil, is the second largest bay (1223 km^2) in the country and is considered a fluvial-marine depositional environment with tropical humid climate characteristic and diverse ecosystems (coral reefs, estuaries, mangroves, islands, and tidal flats) (Cirano and Lessa, 2007). In the northern section of the bay, sediments are mostly composed of mud, and in the southern section sand is prevalent (Lessa and Dias, 2009). The currents inside BTS are tidally driven and the tides are semidiurnal with a maximum range of 2.7 m (Lessa et al., 2001). Paraguaçu (56,300 km^2), Jaguaripe (2,200 km^2), and Subaé (600 km^2) rivers are the three major tributaries of the bay (Cirano and Lessa, 2007). The Paraguaçu River has had its hydrological regime artificially controlled since the construction of the Pedra do Cavalo dam in 1985 (Cirano and Lessa, 2007).

BTS is located in the vicinity of Salvador, the third largest metropolitan area in Brazil, with a population of 2.9 million of people(IBGE, 2016). In 1949, the construction of the Landulpho Alves Mataripe refinery (RLAM; Supplementary Material Figure S1) led to extensive industrial development, with the construction of the Camaçari Industrial Center, the largest petrochemical complex of the southern hemisphere, and the Aratu Industrial Complex (CIA). Since then, the anthropogenic pressures in BTS increased progressively and several activities have been influencing the environmental quality of the Bay, such as terrestrial run off, shrimp farming, inputs of industrial and untreated domestic effluents, solid wastes, mining and intense harbor activities (Beretta et al., 2014; de Souza et al., 2011; Hatje et al., 2006; Hatje and Barros, 2012; Ribeiro et al., 2016). The commercial port of Aratu, opened in 1975, is especially critical for the flux of commodities (*e.g.,* Cu, Fe and Mn ores; fertilizers; propylene; urea; naphtha) from the

Camaçari and the Aratu Industrial Complexes (CODEBA, 2016a). In 1995, the program Bahia Azul was implemented with the objective of improving the urban sewage system, to reduce inputs of solid wastes and contaminants to the bay (Borja et al., 2004). Later, the construction of a second ocean submarine outfall, off the coast of Salvador, added to the efforts to improve the quality of the waters and sediments of BTS.

The objective of this work was to determine sedimentation rates and to reconstruct the chronology history of the contamination by trace elements recorded in Todos os Santos Bay, northeast Brazil, by investigating the vertical profiles of ^{210}Pb dated sediment cores. Pb stable isotopes and trace element profiles were employed to constrain the importance and temporal variation of diverse anthropogenic sources that contributed to the metal contamination of the bay. The use of geochemical signatures employed here could then be related to new proposed Antropocene epoch.

2. Methodology

2.1. Sample collection and processing

In October of 2014, scuba divers collected five cores (Figure 1) by carefully introducing polycarbonate cylinders into the bottom sediments. Core CI1 was collected close to the mouth of the Paraguaçu estuary. Cores CI2 and CI3 were expected to be under the influence of Subaé estuary and TEMADRE, the harbour operated by RLAM. Core CI4 was collected in the vicinity of the harbour and the Industrial Complex of Aratu (CIA), whereas Core CI5 was collected nearby the refinery RLAM. Cores (~ 120 cm long) were sliced at 1 cm intervals for the top 20 cm and then at 2 cm intervals down core. Samples were stored frozen before being freeze-dried for further analysis. Dry bulk density was calculated dividing the dry weight of slices by its volume. Twenty slices of each core

were selected for analyses assuming that top sediments would be more impacted by anthropogenic activities. The analyses were performed in the bulk fraction of sediments. For grain size analysis, sediments were first sieved through a 2 mm mesh and 0.5 mm, to separate the gravel and coarse sand fractions. The fraction < 0.5 mm was then analysed by a Particle Size Analyser by laser diffraction (Cilas model 1064). Organic carbon (C_{org}) contents were determined by EA-IRMS after removal of $CaCO_3$.
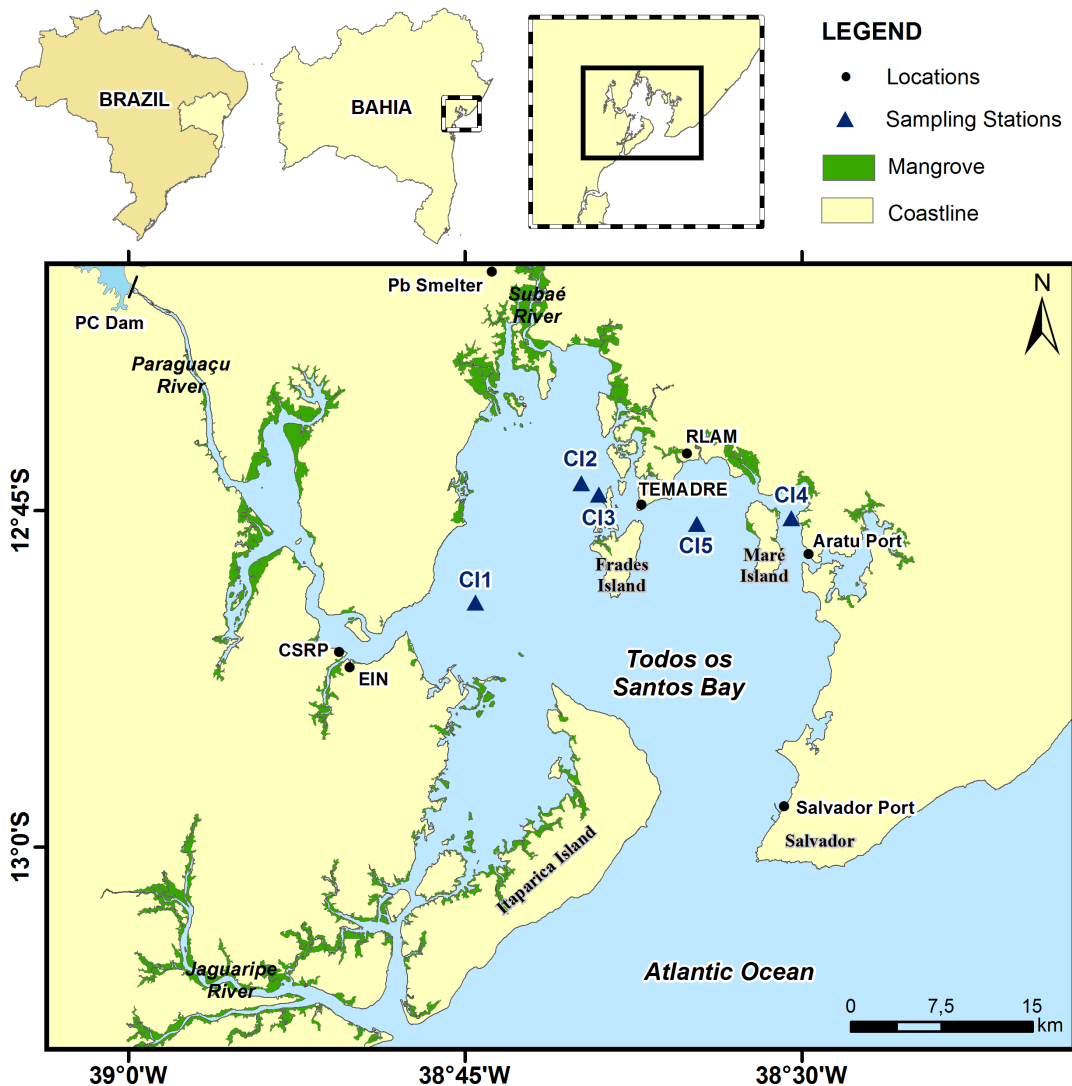

Figure 1 – Location of sample collection (Cores CI1-CI5) at Todos os Santos Bay, Bahia. The location of Enseada Indústria Naval Shipyard (EIN), São Roque do Paraguaçu Shipyard (CSRP), Pedra do Cavalo Dam (PC Dam), Landulfo Alves Refinery (RLAM), and Madre de Deus Waterway Terminal (TEMADRE) are showing for reference.

2.2. Trace element analysis

Homogenized and comminuted sediments were extracted employing 0.1 M HCl (30% suprapur, Merk, Germany) (Hatje et al., 2006). Concentrations of trace and major elements (Al, Co, Cr, Cu, Fe, Mn, Pb, V, and Zn) were determined by ICP OES with axially viewed configuration (PerkinElmer, Optima 7300 DV). Sediment extractions were carried out in triplicate and relative standard deviations (RSD) were lower than 5%. Blanks and certified reference material (MESS-3, National Research Council of Canada, Canada) were utilized to assess the accuracy of the analytical procedure. Recovery values ranged from 3 - 61% for Al and Pb, respectively. The dilute acid leach used solubilized only the more readily bioavailable fractions and left behind residual metals within the structure of silicate minerals (Bryan and Langston, 1992).

Sediments were also leached with 1.75 M HNO_3/3 M HCl employing ultrasonic bath for 90 minutes, following Graney et al. (1995). Samples then sat for 24 h before centrifuged to separate from supernatant, being diluted with 0.1 N HNO_3 (Optima, Fisher Chemicals, USA) and filtered through 0.45 μm PTFE syringe filter cartridges (acid cleaned). Spikes of 1 ppb In were used to correct for instrument drift. Lead concentrations were more precisely determined by isotope dilution (^{204}Pb spike). Concentrations of Pb, Cd, Ni, and Ti were determined by ICP-MS (PQ2+, Fisions Instruments, UK). Recovery values for MESS-3 ranged from 18 - 84 % for Ti and Pb, respectively.

The Pb isotope determination was a slight adaptation of the isotope ratio method of Reuer et al. (2003), as described below. The method included purification by column chromatography and isotope ratio analysis on a GV/Micromass IsoProbe Multicollector MC-ICP-MS with Tl addition for mass-fractionation correction, and a tailing correction established by measuring the monoisotopic ^{209}Bi spectrum at half-mass intervals. The

instrument was calibrated by running NBS SRM 981. Normalization to NBS SRM 981 used the absolute ratios performed by Baker et al. (2004). During the isotope ratio analysis, the data were collected in 20 cycles. The isotope ratios were edited for outliers, and averaged with standard errors estimated from the multiple cycles. Using this method for 12 determinations of an in-house standard ("BAB") shows that samples can be reproduced (1 s.e.) to ~0.05 permil for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ and ~2 permil for $^{206}Pb/^{204}Pb$. Samples SUB3 and SUB9 collected in the Subaé River estuary in a previous study (Hatje and Barros, 2012) also have had their stable Pb isotopic ratios determined.

2.3. ^{210}Pb analyses

Concentrations of ^{210}Pb were determined through the analysis of its decay product ^{210}Po by alpha spectrometry after addition of ^{209}Po as an internal tracer and microwave-assisted acid digestion (Sanchez-Cabeza et al., 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 some measurements by gamma spectrometry, and found to be in agreement with the concentrations of total ^{210}Pb at depth below the excess ^{210}Pb horizons.

3. Results

3.1. Grain size analysis

Vertical differences in sediment texture were small along all cores (Figure 2) that were mainly composed of silt (~ 91%). Mean clay percentage ranged from 5% in core CI1 to 10% in core CI5. Sand contents varied the most between cores. Cores CI4 and CI5 had

almost no sand through them. Core CI3 had about 3% of sand along all core. Cores CI1 (51%) and CI2 (5.1%) displayed the highest sand contents in the topmost slices and nearly no sand in the deeper layers. The sand in these cores contained mostly siliciclastic grains.
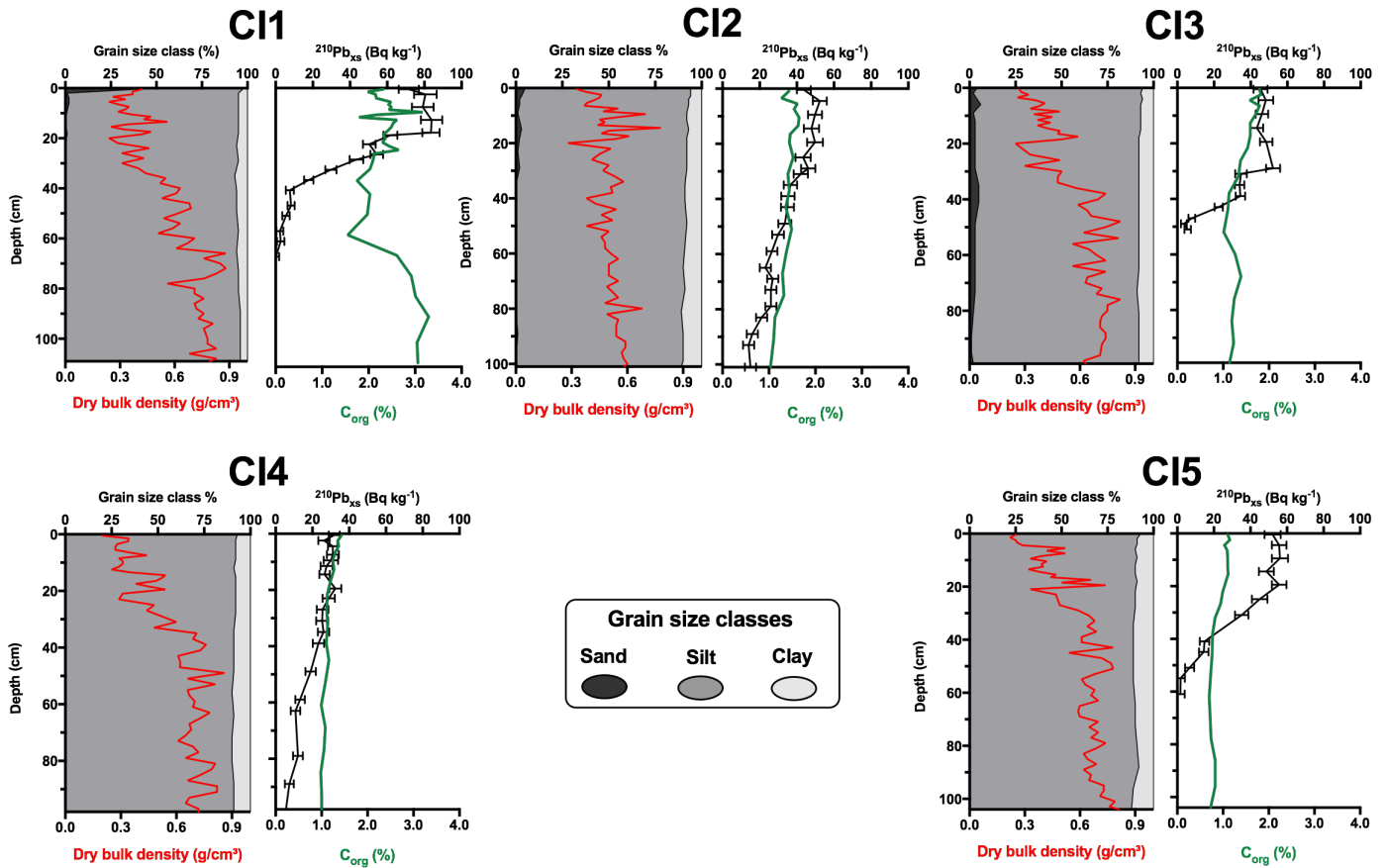

Figure 2 - Depth profiles of grain size classes (grey scale areas), dry bulk density (red line), organic carbon content (C_{org}, green line), and $^{210}Pb_{ex}$ and associated standard errors (black line and bars) for each sediment core.

3.2. DBD

Generally, dry bulk density oscillated from values around 0.2 g cm^{-3} at sediment-water interface of cores CI4 and CI5 up to 0.9 g cm^{-3} in core CI1 (Figure 2). The sediment cores showed an almost continuous transition from liquefied to denser mud. DBD increased

with depth through the cores and tended to stabilize towards the bottom at approximately 0.7-0.8 g cm^{-3}. The exception was core CI2, which DBD tended to stabilize around 0.6 g cm^{-3}.

3.3. ^{210}Pb geochronology

The concentration profiles of ^{210}Pb$_{ex}$ are shown in Figure 2, and main results derived from the data are synthesized in Table 1. The depths at which the horizon of ^{210}Pb$_{ex}$ was detected ranged from 55 to >100cm (for cores CI2 and CI4 it was not reached), indicating that sedimentation rates are substantial at all sites. Mixing of the surface layers was present in all cores, varying from 20 to 30 cm. Mean sedimentation rates, which are to be taken as upper limits, below the mixed layers, were determined using the CF:CS model (Benninger et al., 1979; Krishnaswamy et al., 1971). They were particularly high for CI2 (2.6 ± 0.2 cm yr^{-1}) and CI4 (1.50 ± 0.2 cm yr^{-1}), and considerably lower for CI1, CI3 and CI5 (0.35 - 0.43 cm yr^{-1}; Table 1).

Table 1 - Main ^{210}Pb parameters of sediment cores collected in Todos os Santos Bay.

Core	^{210}Pb$_{ex}$ horizon (cm)	SML (cm)	SAR (g cm^{-2} yr^{-1})	SR (cm yr^{-1})
CI1	70	20	0.19 ± 0.01	0.38 ± 0.02
CI2	>100	25	1.34 ± 0.09	2.60 ± 0.20
CI3	60	30	0.23 ± 0.02	0.35 ± 0.02
CI4	>100	20	1.00 ± 0.12	1.50 ± 0.20
CI5	55	20	0.24 ± 0.02	0.43 ± 0.04

^{210}Pb$_{ex}$ horizon = penetration depth of excess ^{210}Pb for each core; SML= surface mixed layer; SR= sedimentation rate; SAR= sediment accumulation rate.

The estimated SR for CI3 was not supported by the historical human occupation in the area and/or Pb isotopic and metal changes along the sediment profile. The similarities

between CI3 and CI2 profiles were then used to estimate a corrected SR to CI3 (about 1.24 cm yr^{-1}). These date will be further discussed in the next section (4.1).

3.4. Organic carbon (C_{org})

The organic carbon content in cores CI2 to CI5 exhibited only small changes through time, varying from 0.70 to 1.82 %. The only exception was the minimum value observed in CI5 profile that reached 0.17 % at 19 cm (1984). Organic carbon contents in core CI1 varied from 1.55 to 3.29 %. The later, showed an important decrease in C_{org} contents at 60 cm (1870), when it changed from around 2.99 ± 0.22 to 1.82 ± 0.22 % up to 1945. From 1960 on, the C_{org} contents increased again to 2.34±0.28.

3.5. Pb source identification and apportionment

The major potential sources of Pb to the study areas are anthropogenic, from a Pb smelter and from fossil fuels, and natural sources. These sources can be distinguished using Pb isotopes. The Pb isotopic changes for sediment profiles are showed in Figure 3, together with the signatures for the galena, used for about 30 years in a decommissioned lead smelter located upstream Subaé River (^{206}Pb/^{207}Pb= 0.96 ± 0.01, ^{208}Pb/^{207}Pb = 2.26 ± 0.04, and ^{206}Pb/^{204}Pb= 14.67 ± 0.20) (De Anrade Lima and Bernardez, 2011); the isotopic background (^{206}Pb/^{207}Pb= 1.19 ± 0.01, ^{208}Pb/^{207}Pb = 2.50 ± 0.11, and ^{206}Pb/^{204}Pb= 18.76 ± 0.02), estimated as the average ratios of the bottommost layers of sediment cores; and values for gasoline (Aily, 2001). All isotopic profiles of each core exhibited a similar pattern. Isotope ratios for CI1 showed only a slight change over the years. For ^{208}Pb/^{207}Pb this change was still within the estimated background range, whereas ^{206}Pb/^{204}Pb and ^{206}Pb/^{207}Pb ratios indicated that for the past 75 years gasoline also had a minor contribution to Pb signature in this region. CI2

and CI3 cores showed the greatest change, with a pronounced decrease in all isotopic ratios from around 1970 to 1980, then a slower increase until 2000, when the ratios stabilized. Cores CI4 and CI5 displayed changes in isotopic ratios between 1970-90, and 1940-1960, respectively, followed by the stabilization of the ratios.

There was a good linear correlation between ^{206}Pb/^{207}Pb ratios and 1/Pb for cores CI2-CI5 ($0.919 < r < 0.998$, $p < 0.05$). This indicates that there was a linear mixing of natural Pb (background) and anthropogenic Pb from one single source. No significative correlation was observed for core CI1 ($p > 0.05$).
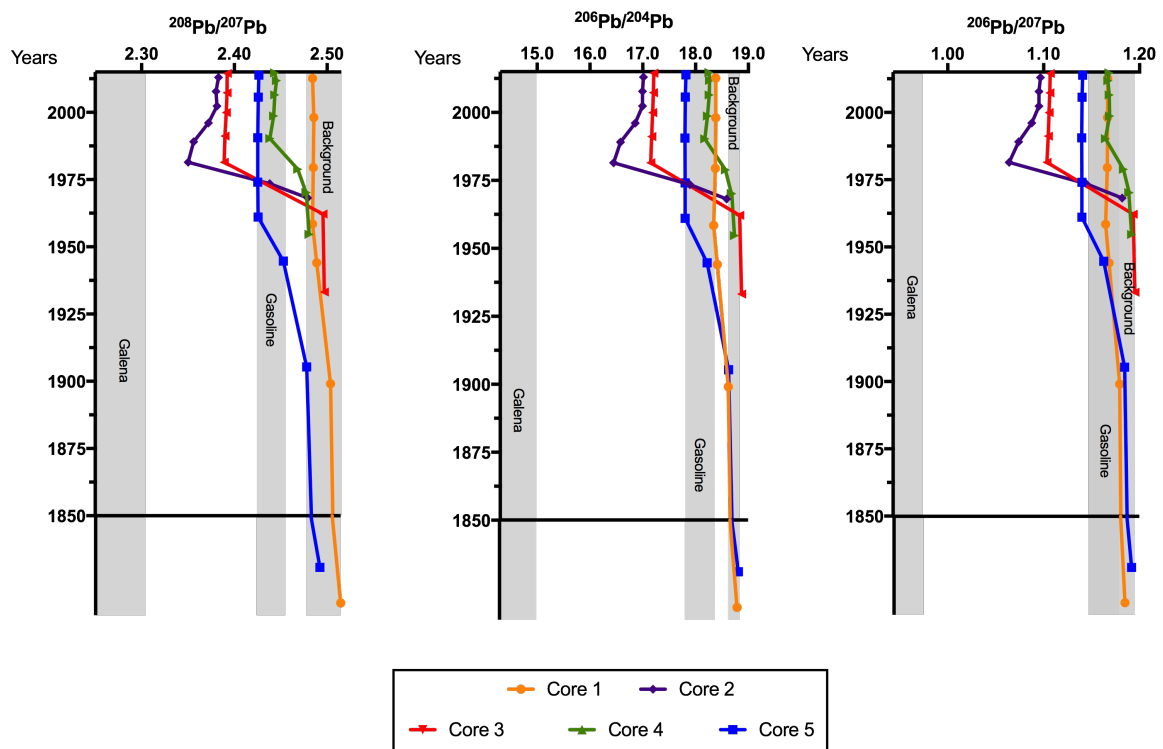

Figure 3 – Comparison of temporal trends for Pb isotopic ratios for sediment cores collected at Todos os Santos Bay. Galena and gasoline data are from de Andrade Lima and Bernardez (2011) and Aily (2001), respectively. The background was estimated as the range of values that samples from before 1900 exhibited.

The relative contribution of the anthropogenic and natural Pb sources can be evidenced by a triple isotope diagram of the samples (Figure 4). Samples showing background values fall within the same area, on the upper right corner of the plot, featuring high $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios. On the opposite side, the galenas (*i.e.*, lead ore, de Andrade Lima and Bernardez (2011)) sources feature low $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios. Between these endmembers there is a clear mixing line made out of CI2 and CI3 samples and surficial sediment samples from Subaé estuary (Sub 3 and Sub 9). In the context of these endmembers, sediments from northwest of BTS contain the highest contribution of anthropogenic Pb from the Pb smelter.

Cores CI1, CI4, and CI5 also present a mixing line, between background values, fossil fuels and gasoline soot isotopic ratios. Core CI5 presented relatively lower $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios, corresponding to an increased contribution of Pb from fossil fuels due to the proximity of the RLAM refinery. The CI4 features isotopic ratios greater than CI5, but still suggesting the contribution of fossil fuel as the main source. The distribution of CI1 samples in the triple isotope diagram was parallel to the CI4 indicating a minor contribution of fossil fuel.
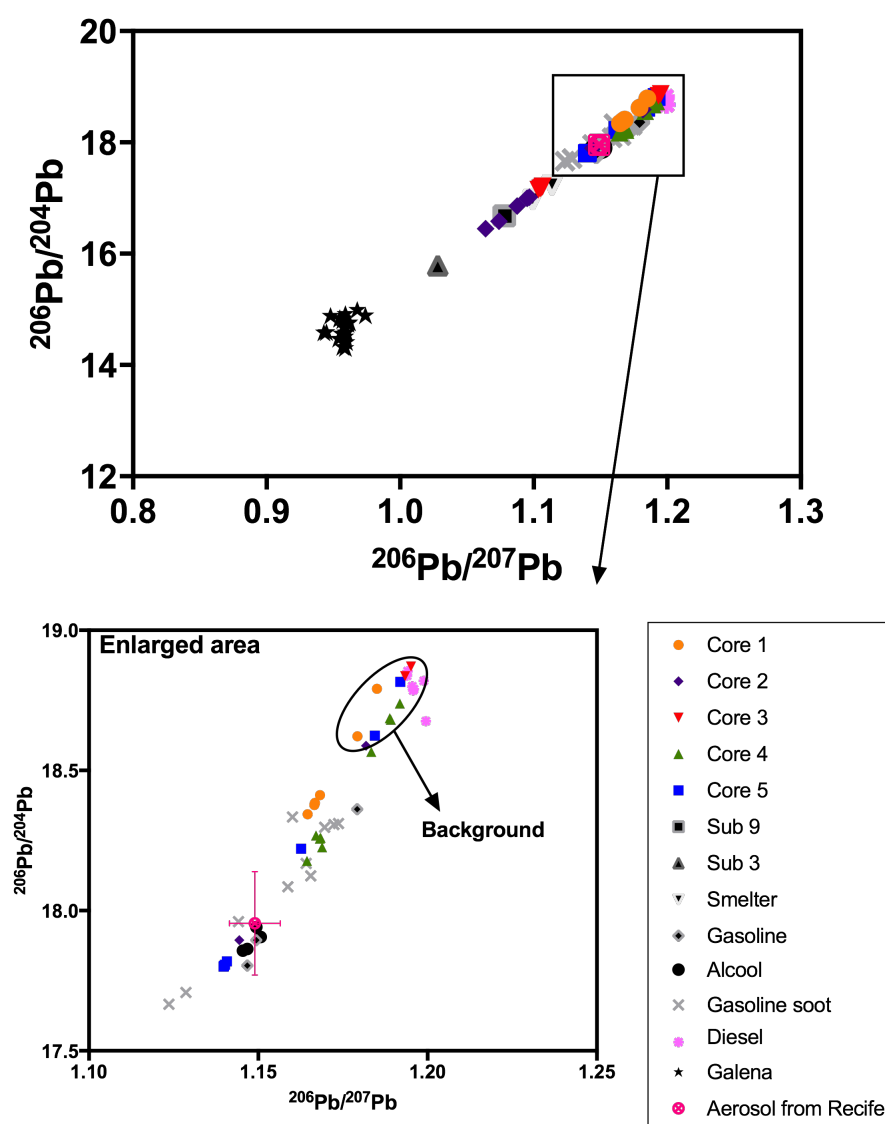
Figure 4 - Triple isotope diagram ($^{206}Pb/^{204}Pb$ *versus* $^{206}Pb/^{207}Pb$) for sediment cores and surficial samples from Subaé River (Sub 9 and Sub 3) obtained in this study. Data for gasoline, alcohol, gasoline soot (Aily, 2001), diesel (Gioia et al., 2005), galena (de Andrade Lima and Bernardez, 2011), and Recife's aerosol (Bollhöfer and Rosman, 2000) are plotted for reference.

3.6. Trace metals

Concentrations of trace elements are shown in Figure 5. For core CI1, Cu, Zn, Pb, and V concentrations reached a small peak around 1950 (5.79 ± 0.07 mg kg^{-1}, 24.4 ± 0.15 mg

kg^{-1}, 12.3 ± 0.16 mg kg^{-1}, 16.7 ± 0.29 mg kg^{-1}, respectively) and decreased afterwards. Iron also showed an increase in concentrations from the bottom of the core up to 1950, then a more substantial increase was observed from 1950 until 1980, when concentrations stabilized. Concentration profiles of Pb, Zn, Cu and Fe were highly correlated ($0.70 \leq r \leq 0.92$, $p < 0.05$). Manganese concentrations were stable throughout the core up until 1998, when it started to show a small increase, reaching 297 ± 7.06 mg kg^{-1}. Cadmium and Co also showed a slightly increase towards the surface. Concentrations of Co showed high variability in the last 60 years. Chromium and Ni did not vary substantially along the core, whereas Ti showed a slight increase in the past 60 years.

Concentrations of Pb, Cd, and Zn in CI2 increased from the lowest recorded levels (7.89 ± 0.21 mg kg^{-1}, 0.01 mg kg^{-1}, 21.3 ± 0.17 mg kg^{-1}, respectively) in 1967 to a maximum level at 1985 (28.6 ± 0.03 mg kg^{-1}, 0.44 mg kg^{-1}, 42.8 ± 0.17 mg kg^{-1}, respectively). Afterwards the concentrations of these elements decreased until 1996, when they stabilized. Lead and Zn concentrations were highly correlated ($r=0.97$, $p < 0.05$). Cupper and V also presented similar trends ($r=0.75$, $p < 0.05$). Cupper concentrations profile showed an increase between 1975 and 2012 (8.24 ± 0.07 up to 13.2 ± 0.19 mg kg^{-1}). Vanadium concentrations increased slightly from bottom (11.3 ± 0.04 mg kg^{-1}) up until 1990 (15.5 ± 0.29 mg kg^{-1}), when they stabilized for about ten years, then started to decrease. Vanadium was also correlated to Zn and Pb ($0.82 \leq r \leq 0.88$, $p < 0.05$). Chromium presented a small variability, reaching a minimum value of 8.84 ± 0.05 mg kg^{-1} at surface; and was significantly correlated to Al ($r=0.87$, $p < 0.05$). The concentrations of Mn were mostly constant, but presented peaks in 2010 and 2014. Manganese distribution was correlated with Fe ($r=0.73$, $p < 0.05$). Nickel and Ti did not vary substantially through time.

Lead, Zn, Cu, Cd, V, and Fe records in CI3 showed lowest concentrations (<0.01 mg kg^{-1}, 15.1 ± 0.06 mg kg^{-1}, 0.21 ± 0.01 mg kg^{-1}, 0.02 mg kg^{-1}, 6.51 ± 0.15 mg kg^{-1}, 5639 ± 35.2 mg kg^{-1}, respectively) at the beginning of the 20th century and started to increase significantly after 1975, followed by a stabilization of the concentrations after 1990 (13.1 ± 0.72 mg kg^{-1}, 31.5 ± 1.24 mg kg^{-1}, 10.8 ± 0.38 mg kg^{-1}, 0.05 ± 0.01 mg kg^{-1}, 10.4 ± 0.82 mg kg^{-1}, 8428 ± 296 mg kg^{-1}, respectively). All these elements were highly correlated (0.86 ≤ r ≤ 0.99, $p < 0.05$). Manganese concentrations record started to increase since 1975 to a maximum value of 520 ± 1.92 mg kg^{-1} in 2014, and was negatively correlated to Ti concentrations (r = -0.90 $p < 0.05$). Titanium, Cr, and Ni concentrations presented small variability along the core, and showed a small decrease towards surface. Cobalt concentrations fluctuated over the time, but concentrations were always below 18.0 ± 0.22 mg kg^{-1}. Aluminium and Cr were correlated (r=0.85, $p < 0.05$).

Trace metals, with the exception of V, presented minimum concentrations at the base of the core CI4. Small increases in the concentrations of Cu, Pb, and Zn started around 1978, then a noteworthy increase occurred in concentrations of Cu, Pb, Zn, and Cd between 1985 and 1990. The maximum concentration of Cu (122 ± 3.43 mg kg^{-1}), Pb (31.9 ± 0.35 mg kg^{-1}), and Zn (46.4 ± 1.53 mg kg^{-1}) were up to 11, 3.5 and 1.7-fold higher than concentrations at the base of the core, recorded in mid 20th century. The latter elements were highly correlated (0.83 ≤ r ≤ 0.99, $p < 0.05$). Nickel and V concentrations showed a slight decrease after 1980 to a minimum concentration in surface sediments (13.5 mg kg^{-1} and 14.9 ± 0.37 mg kg^{-1}, respectively). Manganese and Al profiles were correlated (r=0.83, $p < 0.05$), and exhibited an increase in concentrations in the last 15 years, with maximum values around the top of the core (664 ± 3.56 mg kg^{-1} and 6,810 ± 21.0 mg kg^{-1}, respectively). Chromium, Ti and Co concentrations did not change

significantly through time, though Co has shown a noteworthy increase in concentration in 2014 (24.8 ± 0.28 mg kg^{-1}).

Core CI5 showed increase in Cu, Zn, Fe, and Pb concentration profiles (Figure 5) since mid-20th century, reaching maximum values of 13.1 ± 0.08 mg kg^{-1}, 38.6 ± 0.80 mg kg^{-1}, $8,507 \pm 117$ mg kg^{-1}, 13.4 ± 0.56 mg kg^{-1}, respectively. From the 1975s, the concentrations of these elements remained relatively constant, with the exception of Pb that displayed a minor decrease towards surface. The above-mentioned elements were highly correlated ($0.95 \leq r \leq 0.99$, $p < 0.05$). Manganese showed a gradual increase in concentrations, reaching the highest values at surface sediments (612 ± 3.48 mg kg^{-1}). Co concentrations were constant (around 6.15 ± 0.65 mg kg^{-1}) until 1990s, then a gradual increase in concentrations was observed, reaching the highest values at surface sediments (12.2 ± 0.32 mg kg^{-1}). Cobalt and Mn were highly correlated (r=0.91, $p < 0.05$). Chromium, Ni, Cd, Cr, Ti, and V did not exhibit significant variability along the core. Cr was highly correlated to Al, Cu, Zn, Pb, and Fe ($0.71 \leq r \leq 0.92$, $p < 0.05$).

Enrichment factors (EFs) were calculated for trace elements through each core to assess the contamination degree over time. The EF was defined as follows:
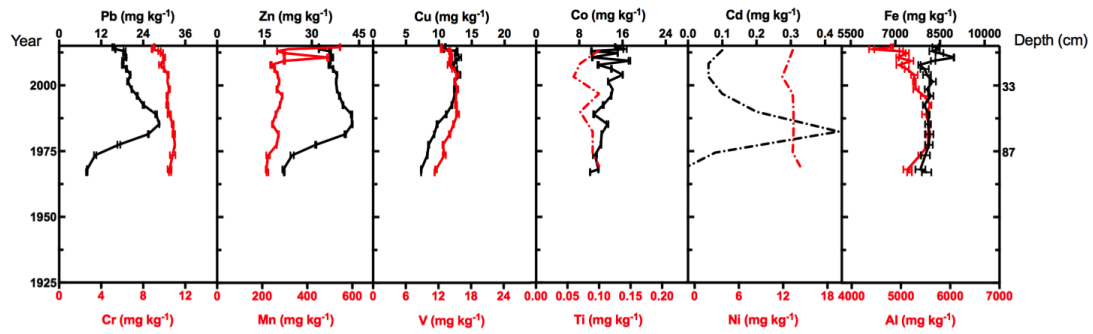
$$EF = \frac{(E/Al)Sediment}{(E/Al)Baseline}$$

Where E/Al is the ratio of the element to Al, which was chosen as the normalization element. Baseline values were estimated for each element using concentrations obtained from before 1900. The EFs were classified according to Wang et al. (2015) and are exhibited in Figure 6.
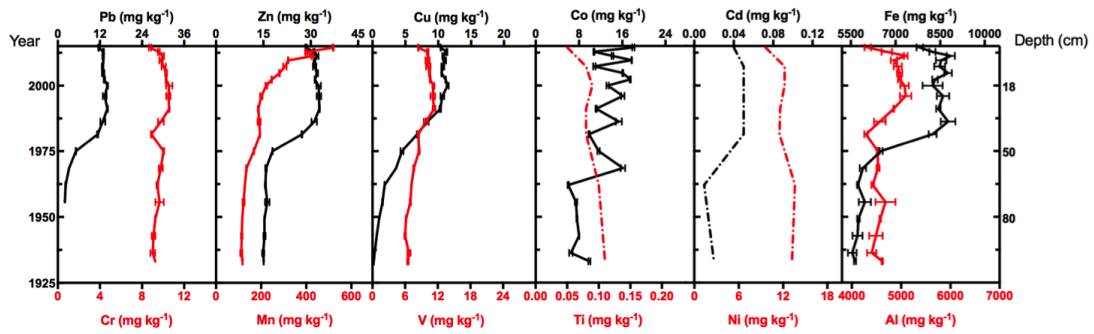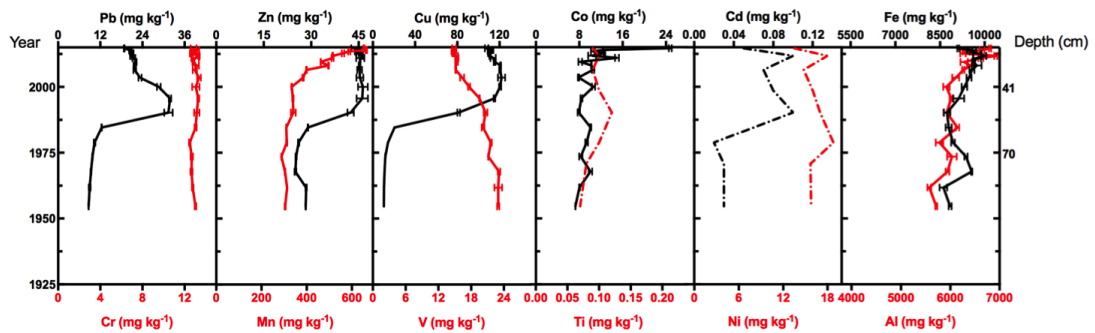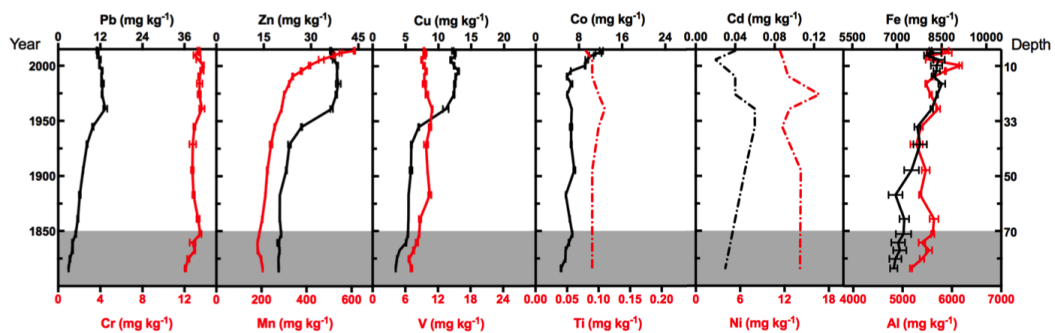
CI1

CI2

CI3

CI4
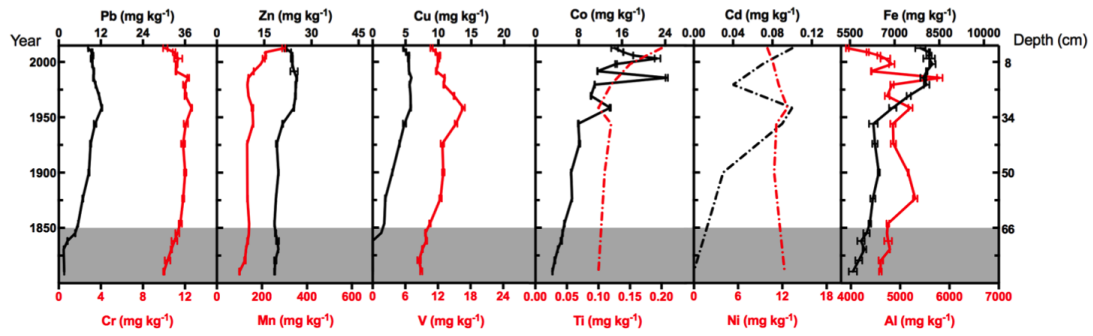
CI5

HCl 1M extraction

22

Figure 5 – Mean and standard deviation of trace elements profiles of cores CI1, CI2, CI3, CI4, and CI5. Lead, Zn, Cu, Co, Fe, Al, V, Mn, and Cr data are from the HCl 1M extraction, while Cd, Ni, and Ti data are from the pseudo-total digestions. The black lines are plotted in the upper scale and the red lines in the lower scale of each graph. The grey area represents sediments older than the age dateable by excess ^{210}Pb method.

In CI1, Zn and Cr presented no enrichment (EF < 1.5). Manganese, Fe, and V showed some enrichment (1.5 < EF < 2.5) in the top layers of CI1. Lead, Cu, and Co were moderately enriched (2.5 < EF < 5) since 1900, 1958, and 1926, respectively.

In the case of CI2, only Cr and Fe showed no enrichment (EF < 1.5) throughout the core. The other elements showed enrichments (EF < 4) either since the base of the core (1967), case of Pb, Co, and Cu, or starting at the end of 70's and 80's, case of Zn, Mn, and V. Lead reached significant anthropogenic enrichment (5 < EF < 20) between 1981 and 1989.

The CI3 was not enriched in Cr and V. Cobalt, on the other side, exhibited moderate enrichment since the base of CI3. Fe only presented enrichment in the 80's. Lead, Cu and Zn started to show moderate enrichment after 1980 and Mn after 2002.

Core CI4 presented moderate enrichment in Cu concentrations since its base (1955). By 1996, however, it showed a very high enrichment (20 < EF < 40). Manganese and Pb were also moderately enriched throughout CI4. Vanadium, from the base of the core up to 1979, and in Zn, from 1990 onwards also showed enrichments (EF up to 2.27 and 2.07, respectively). Enrichment was not observed Co, Fe and Cr.

The CI5 was not enriched in Fe, Cr, and V. Most pronounced enrichment for Pb, Zn, Cu, and Mn were observed since mid-20th century.
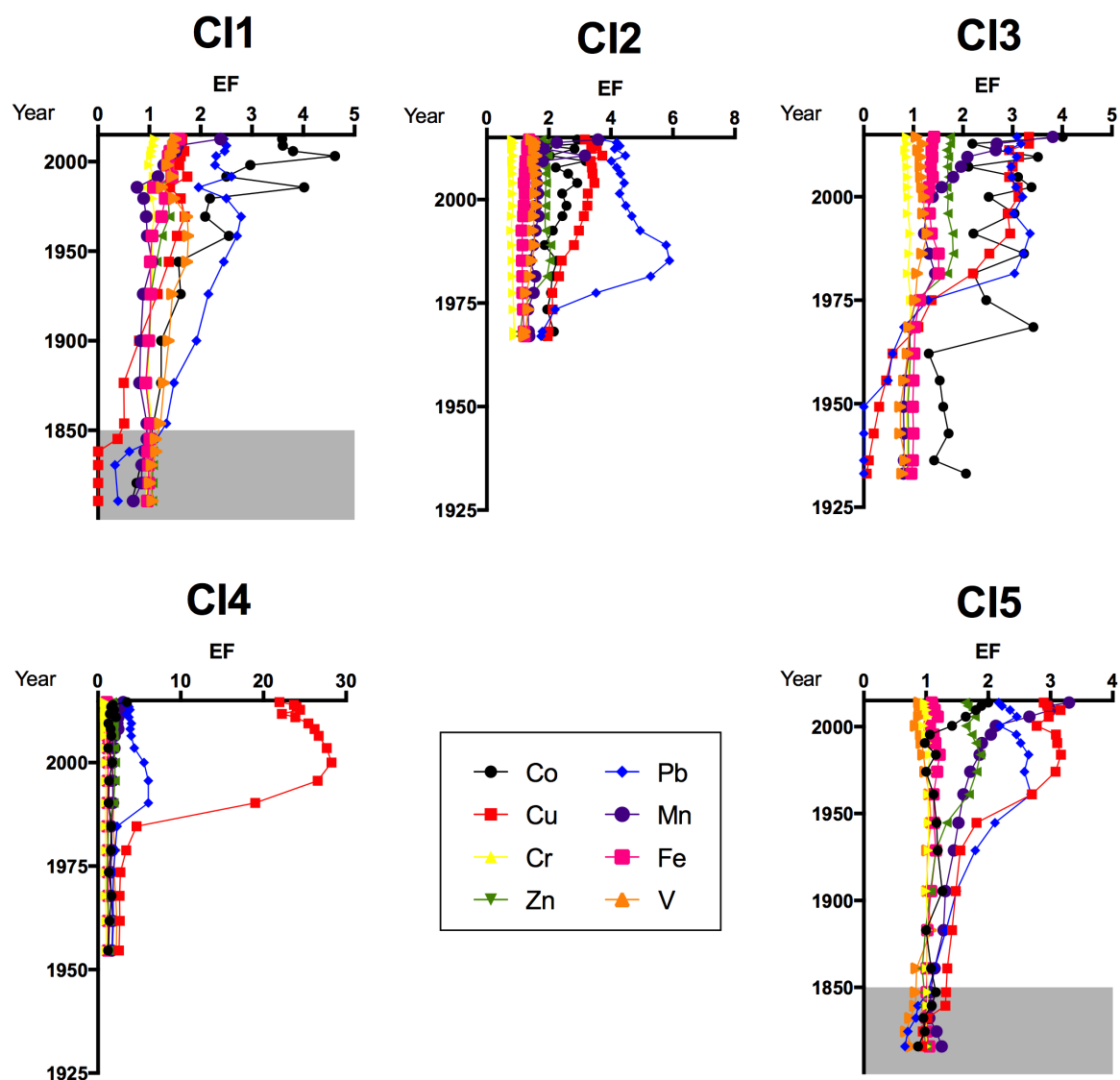
Figure 6 – Profiles of enrichment factors (EFs) of each element through time in cores CI1-CI5. The grey area represents sediments older than the age dateable by excess ^{210}Pb method.

4. Discussion

4.1. Sedimentation rates

The sedimentation rates estimated for the cores collected in BTS varied greatly, but did not change along the recorded time in each core. Nevertheless, the Pb isotopes and trace metals profiles validated the estimated ages for all cores, except CI3. Core CI1 exhibited

a remarkable change in the C_{org} at 60 cm deep, corresponding to 1870. At this period, there was a major shift in the land use in the Paraguaçu River basin, changing from sugarcane to tobacco farming (Figure S1). No clear change in the CI1 SR was observable over the time, which implies that even though the building of the Pedra do Cavalo Dam in 1986 significantly altered the fluvial water discharge and salinity field patterns in the estuary (Genz, 2006; Lima and Lessa, 2002), it did not cause significant modifications in the deposition of sediments at the mouth of Paraguaçu estuary, where CI1 was collected. This result can be explained by the presence of the Iguape bay, which may have buffered the impacts of a possible reduction of the transport of suspended particulate material due to the damming of the river. An alternative hypothesis, less likely (*i.e.,* the dating agreed well with the change in land use), is that the surface mixed layer in CI1 might be hiding a potential change in the SR.

For the CI2, the profiles of Pb isotopic signatures and concentrations of trace metals matched with the historical changes in the area, as will be discussed later (sections 4.2 and 4.3), corroborating the estimated dating results. Sedimentation rate for CI2 was higher than the other collected cores (0.38 - 1.5 cm yr^{-1}) in BTS, as well as sedimentation rates previously estimated for BTS (0.29 - 0.99 cm yr^{-1} (Argollo, 2001); 0.08 - 0.40 cm yr^{-1} (Lessa et al., 2000)), and other tropical bays in Brazil (*e.g.,* Guanabara Bay (0.14 – 1.25 cm yr^{-1}; Figueiredo et al., 2014), and Sepetiba Bay (0.08 – 1.03 cm yr^{-1}; Marques et al., 2006)). However, Chesapeake Bay (0.30 – 4.16 cm yr^{-1}; Zimmerman and Canuel, 2002) and Bohai Bay (0.1 – 3.0 cm yr^{-1}; Wang et al., 2008), among others, presented even higher sedimentation rates than the maximum observed in BTS. The position of CI2, relatively close to Subaé River mouth, and its depth, few meters deeper than CI3, is the probable explanation for the highest SR observed in this core. The Subaé River is a source of suspended particles and its deeper and closer position to the river when

compared to CI3 created better conditions for the deposition of particles. Also, no changes in the ^{210}Pb distribution through time were observed in this core to justify recent changes in land use or dredging as the source of these sediments.

Coastal land use as well as natural processes, such as littoral currents, bioturbation, and storms, may induce the mixing of sediments in coastal areas and disturb the ^{210}Pb activity in the top layers of a sediment core, which might lower sedimentation rate estimates through ^{210}Pb dating (Wang et al., 2008). In the case of core CI3, the surface mixing layer was 30 cm thick, which is about half of the penetration depth of excess ^{210}Pb, estimated in 60 cm. Moreover the ^{210}Pb inventory for this core (579 ± 48 Bq m^{-2}) was lower than for the other areas (*i.e.,* 631 ± 56 to 635 ± 57), suggesting possible erosion in the top layers of this core. These facts might have caused bias in the estimation of CI3 sedimentation rate, which was much lower than the observed in CI2, located nearby. Besides, the age model derived for CI3 (SR = 0.35 ± 0.02 cm yr^{-1}) is in disagreement with the historical human occupation of the area (*i.e.,* observing Pb isotopes and metal concentrations as will be discussed in sections 4.2 and 4.3). Considering the proximity between CI3 and CI2, the similarity of environmental settings of these areas, the Pb isotopes and the trace metal concentration profiles, the CI3 sedimentation rate was adjusted to fit the local historical events that were observable in CI2. It was assumed that the minimum value of ^{206}Pb/^{207}Pb in CI2 (74 cm deep, estimated age 1981) coincided in time with the minimum value in CI3 (42 cm). Considering that surface sediment was deposited in 2014, it was possible to estimate a SR of about 1.24 cm yr^{-1} and the age of each layer.

Argollo (2001) estimated relatively higher sedimentation rates for the Northeast part of the Bay (0.95 – 0.99 cm yr^{-1}) than for other areas. This result agrees with the high sedimentation rates obtained in CI4 (1.50 ± 0.20 cm yr^{-1}), collected in the vicinity of the

Aratu harbor. Nevertheless, previously reported temporal variation of SR (Argollo, 2001) was not observed in this study, possibly due to the larger distance from the Aratu Industrial Center, which nearby deforestation possibly caused increase in erosion and sedimentation rates.

Sedimentation rate for CI5 (0.43 ± 0.04 cm yr^{-1}) is in agreement with values obtained by Costa et al. (2016) for the surrounding region (0.53 ± 0.05 cm yr^{-1}), which was estimated using ^{210}Pb and ^{137}Cs data.

4.2. Pb sources

The relative contributions of the anthropogenic and natural Pb sources for the sediment cores collected at BTS could be evidenced in the triple isotope diagram (Fig. 4). This graph used the ^{204}Pb isotope as the denominator in one of the axes to assure that it could reliably reveal more than two sources (Ellam, 2010). The decommissioned Pb smelter in Santo Amaro that used galena from Boquira (de Andrade Lima and Bernardez, 2011), and the burning of fossil fuels were identified as the main anthropogenic sources of Pb.

Cores CI2 and CI3 were predominantly influenced by the deposition of Pb derived from the smelter, which produced isotopic ratios that were much less radiogenic than the background values, and also lower than fossil fuels. These cores are relatively close to the Pb smelter (Plumbum Mineração, Figure 1) that operated between 1960 and 1993 in Santo Amaro (Figure S1). Dust emissions are one the main pathways of contamination from smelters (de Andrade Lima and Bernardez, 2010; Ettler, 2015; Shotyk et al., 2016). A clear peak in the isotopic ratios in CI2 and CI3 (Figure 3) coincided with the end of the period of uncontrolled atmospheric emissions of the lead plant (1980), when the main chimney was extended to 90 m and filtration started to be applied (Machado et al.,

2012). Since then, an increase in Pb isotopic ratios was observed, reflecting the reduction in atmospheric emissions from the smelter.

Given the isotopic ratio profiles and the relatively large distance between the smelter and the other studied locations, the Pb presented in CI4 and CI5 are more likely derived from the ongoing atmospheric deposition of industrial Pb and from the burning of fossil fuels from both terrestrial and maritime traffic. As leaded gasoline was phased out in the beginning of 1990s in Brazil (Gioia et al., 2006), the observed signature in the most recent sediments is presumably due to Pb emissions from industrial sources and legacy Pb from fossil fuels. Even so, it is important to note that the data on Pb isotopic signatures of fossil fuels (Aily, 2001) is very recent and does not include leaded petrol.

Atmospheric data on Pb isotopes for BTS would be of fundamental importance to a better interpretation of the results. However this information is not available. Bollhöfer and Rosman (2000) studied the Pb isotopic signatures of atmospheric particles of some Brazilian cities. As Recife is more similar to Salvador concerning its industrial development, population, and also geographic position than other studied cities, its Pb atmospheric data was plotted in the triple isotope diagram (Fig. 4). The Pb isotopic ratios ($^{206}Pb/^{207}Pb$= 1.1401 ± 0.0004 and $^{206}Pb/^{204}Pb$= 17.806 ± 0.008 for the period since around 1960) in CI5, close to RLAM, and the signature of the atmospheric particulate material from Recife ($^{206}Pb/^{207}Pb$= 1.141-1.156 and $^{206}Pb/^{204}Pb$= 17.77–18.14) (Bollhöfer and Rosman, 2000) were similar. This result suggested that the sources of Pb to CI5 area are comparable to the industrial and vehicular emissions observed in Recife. The isotopic signature of CI5 in 1944 was positioned around the gasoline and the gasoline soot in the triple isotope diagram, indicating that there was some anthropogenic impact in the area since this period. Costa et al. (2016) also observed anthropogenic impacts around 1940 using a core collected in the same area.

The latter detected an increase in ∑PAHs from bottom to top of the core, as well as a change in total organic carbon at 1940 and Unresolved/Resolved ratios (UR/R), indicating the presence of waste associated to biodegraded oil in this region.

It is important to note that the development of Todos os Santos Bay is relatively recent (Figure S1). The man-made changes were initially driven by the production of the first Brazilian oil fields (1939-1950) and the construction of the RLAM in 1950, close to core CI5. The RLAM promoted a significant increase in the population growth (IBGE, 2016) and, from the 1960s, in the industrialization resulting in the construction of the largest petrochemical complex in the southern hemisphere. The inflection in Pb isotope profile for CI4 is coincident to the installation of the Aratu harbor that served the industrial complex, while the inflection in CI5 Pb isotope profile is contemporaneous to the start of the production in oil fields as well as the later operation of the RLAM. The construction of the refinery marked a time when the transport of goods and people stopped being exclusively maritime and was slowly substituted by road transport, which increased the use of gasoline that at this time was mainly imported from the USA.

Although coal burning has been present in the bay since previous centuries (Figure S1), Pb isotope ratios for coals (from Peru ^{206}Pb/^{207}Pb= 1.193-1.122; ^{208}Pb/^{206}Pb= 2.029–2.103 (Díaz-Somoano et al., 2009)), and diesel (^{206}Pb/^{207}Pb= 1.194-1.199; ^{206}Pb/^{204}Pb= 18.676-18.854 (Gioia et al., 2005)), alike, are very variable and overlap with background values. Besides, coal usage as the main energy resource in BTS happened since the 1600s in the sugarcane farms (Caroso et al., 2011), which makes it harder to identify the coal origin and its isotopic signature. Diesel has also been largely used in BTS as a ship fuel. However, the variability of diesel ratios and the lack of its signature for the region make difficult the identification of possible impacts of the usage of diesel and also coal in BTS using Pb isotopes as tracers.

Among the studied cores, $^{206}Pb/^{207}Pb$ data did not vary significantly with 1/Pb for CI1, at the mouth of the Paraguaçu River. This result implies that changes in Pb concentrations were not reflected in the Pb isotopic ratios, which indicated that the source of the Pb throughout CI1 was the same along the time, *i.e.,* mostly natural, and/or with only a minor contribution of anthropogenic source that could not be clearly identified. Another possibility is that a linear model cannot explain satisfactorily the variability in the dataset, that results from the existence of more than one anthropogenic source of Pb for the area, which is reinforced by the mixing line for CI1 data observed in the triple isotope diagrams.

Other possible sources that could have impacted Pb ratios of the CI1 area are the Pedra do Cavalo Dam and the São Roque do Paraguaçu shipyard, build in 1986 and 1976, respectively. However, the variations of Pb ratios over the time, together with Pb concentrations did not show any significant change after these events.

4.3. History and current status of metal contamination

The Paraguaçu River is considered relatively well preserved, especially when compared to other estuaries (de Souza et al., 2011; Hatje and Barros, 2012). The construction of the Pedra do Cavalo Dam and the São Roque do Paraguaçu shipyard are the major changes that happened in the Paraguaçu River basin in the past 60 years. Even so, no element has indicated a relationship with the dam, nor with the shipyard constructions and operations. The peaks in Cu, Zn, Pb, and V and the increase in Fe concentrations around 1950 cannot reflect these events. The high correlations ($r > 0.70$, $p < 0.05$) presented between Cu, Pb, Zn and Fe indicated they had the same origin. However, as Fe presents a very different profile in the last 60 years it is possible that its high correlation with these elements is derived from the period before 1950 when they showed similar

distributions through time. There are other few small industries and private marinas operating in the Paraguaçu river area, but it is unlike that they represent a major source of trace elements, except for the traditional handmade potteries and tanneries, many of which did not exist before 1950s. It is important to notice that the concentrations of Pb, Cu, Zn, Cr, and Mn throughout the core are low, especially when compared with the concentrations of superficial sediments along the course of the Paraguaçu River (Barros et al., 2008; Hatje and Barros, 2012). Cadmium presented low concentrations, and its highest value was still within the background range (0.09 ± 0.01 mg kg^{-1}) determined by Argollo (2001). These facts together with the isotopic signal of Pb suggest that diffuse sources are generating relatively low impacts in the Paraguaçu River area and that the Pedra do Cavalo Dam and the São Roque do Paraguaçu shipyard did not cause significative changes in the Pb isotopic ratios and trace elements concentrations in the area where core CI1 was collected.

The lead smelter, which operated in Santo Amaro until the 1990s producing $11–32 \times 10^6$ kg of Pb bars year^{-1}, was responsible for exposing people to high levels of toxic elements (Carvalho et al., 1984, 2003, 1989; Tavares et al., 1989). The smelter also caused the contamination of the Subaé estuary, causing a decrease in the abundance and richness of benthic macrofauna assemblages and impairing the ecological services promoted by this system (Hatje et al., 2006; Hatje and Barros, 2012). Nowadays, the Subaé estuary is known as one of the most contaminated areas of BTS mainly due to this lead smelter, which still is a source of contamination through atmospheric, runoff and groundwater dispersion of a large waste reservoir (Hatje et al., 2006; Hatje and Barros, 2012; Machado et al., 2012). According to de Andrade Lima and Bernardez (2010), the lead smelter dust was rich in Pb, Zn, Cd and As oxides. Core CI2, located near the mouth of the Subaé River, showed an increase in concentrations of Pb, Cd, and Zn during the period of

uncontrolled emissions of the smelter, followed by reductions of these values after 1980, when mitigation measures begun to be taken (Machado et al., 2012). The high correlations between Zn and Pb concentrations, together with the Pb isotope ratios, reinforce the hypothesis that these contaminants are from the smelter.

Lead, Zn, Cu, Fe, V and Cd concentrations in CI3 showed similar temporal patterns to CI2 and also high correlation between the cited elements, indicating these elements are from the same source, similarly to CI2. However, they did not present significant reductions after 1980, perhaps due to the surface mixing layer that comprised about 30 cm of this core. Comparing the CI2 and CI3 results with the composition of the lead smelter slag (Andrade Lima and Bernardez, 2010), it is noticeable that some of its main constituents (Fe, Pb, Zn) and also elements in relatively high (Cu) and very low (Cd) contents have presented increased concentrations since the start of the smelter operations, with pronounced a peak during a period of high production of the smelter, when no mitigation measures were in place.

The CIA is a multisectoral industrial complex, founded in 1967, which is served by the Port of Aratu. This port is one of the most relevant drains for the production the Aratu Industrial Complex and the Camaçari Industrial Center production nationwide. It was installed in 1975 and its structure allows operations with a variety of products, including ores, chemical and petrochemical products. The remarkable increases in concentrations of Cu, Pb, Zn and Cd in core CI4 since 1978, especially between 1985 and 1990, can be related to the beginning of the port of Aratu and the Petrochemical Complex of Camaçari (COPEC) operations. It is noteworthy that Cu concentrations increased by one order of magnitude in this period and stabilized around high values (>100 mg kg^{-1}) afterwards. In general, trace elements concentrations in the base of this core (1954) were already higher than in other cores. Vanadium concentrations, for

instance, were 2-fold higher in the base of this core than in the top. During this period, neither the CIA nor the Port of Aratu were operating, however, there was an oil field in Candeias that started production by the end of 1941. The port of Salvador was in operation and most of the transport was maritime at this time. As V is generally linked to petroleum exploration (Khalaf et al., 1982; Soldi et al., 1996), the general increase in concentrations of trace elements in cores might be related to the exploration of the Candeias Oil Field and the intense flux of vessels.

Since the start of the RLAM construction (Figure S1) many jobs were created promoting the economic growth and subsequently attracting more investments to the area. Nowadays, it produces 31 varieties of products daily, including diesel, gasoline, lubricant etc. (Petrobrás, 2016). The increase in concentrations of Cu, Zn, and Pb in core CI5 since mid-20th century, together with the strong correlations between Fe, Cu, Zn, and Pb, indicate that the exploration of the first Brazilian oil fields had an impact in the concentrations of these elements in the surrounding environment, corroborating with Costa et al. (2016). However the latter elements also show a higher increase in concentrations between 1944 and 1960, period that comprises the construction (1950) and an extension of RLAM activities (1959) together with the start of operations of TEMADRE (1957), the private harbour of RLAM. The stability in the concentrations of Pb, Cu, and Zn from 1975 onwards is possibly due to the presence of a surface mixing layer (SML) of about 20 cm in CI5. The presence of the SML in this core also prevented the observation of any environmental changes that management actions might have produced.

In all cores the calculated enrichment factor showed no enrichment in Cr, which, together with the high correlations this element showed with Al in cores CI1, CI2, CI3, and CI5, indicated that Cr is mainly associated to natural sources. The significative

anthropogenic enrichment in Pb concentrations that CI2 exhibited in the 80's is another indication of the impact the lead smelter had in this environment particularly when in operation. Copper, in CI4 was the element that presented the highest enrichment levels among the studied elements. In CI4, Cu EFs gradually increased from the bottom of the core, becoming highly enriched since 1990's. This period coincides with an expansion of Brazilian participation in the international market and also of the Camaçari Industrial Center (Bahia, 2013), which consequently increased the traffic of vessels at Port of Aratu. Antifouling paints of boats are considered one of the main sources of Cu in areas of intense boat activities (Dafforn et al., 2011). Although data for Aratu harbor operations is available only from 2000 (CODEBA, 2016b), the number of vessels that docked in Port of Aratu since then was significantly correlated to the concentrations of Cu (r=0.84, *p*<0.05), indicating that Cu originates primarily from the antifouling paints from vessels. Cindrić et al. (2015) also noted an increase in Cu concentrations in the Krka River estuary during periods of increased maritime traffic.

Cu concentrations in core CI4 exceeded the Threshold Effect Level (TEL= 35.70 mg kg^{-1} (Buchman, 2008)) from the 1990's up to date. All the other cores did not present concentrations above TEL values.

In general, trace metals showed some enrichment after 1950, showing that the northern part of BTS has been overall impacted by anthropogenic activities. Although some areas are more impacted than others, in general Pb, Cu, and Zn are the elements of concern, considering their toxicity and noticeable tendency to increase in concentrations over time. Comparing to highly industrialized and urban coastal systems such as Sepetiba (Wasserman et al., 2001) or Guanabara bay (de Carvalho Aguiar et al., 2016), Chesapeak bay, Spanish bays (Casado-Martínez et al., 2006), Tagus (Cobelo-García et al., 2011),

New South Wales estuaries (Birch et al., 2015), the levels of metals measured here indicated a much lower level of anthropogenic impacts.

5. Conclusion

Very distinct sedimentation rates were observed in different areas of Todos os Santos Bay. Unexpectedly high SR was observed in CI2, comparable to SRs observed in bays with a large input of sediments through fluvial transport.

The trace elements concentrations and Pb isotopes in the sediments of Todos os Santos bay are examples of the impact of anthropogenic activities characteristic of the Anthropocene. Although the colonization of the bay started in 1550s, the intense human activities in BTS basin only jumped in the mid 19th century. The exploration of oil, followed by the construction of the first industries (RLAM, CIA, Pb smelter and harbors) caused changes in the Pb isotopic signatures and trace metal concentrations.

The two main sources of anthropogenic Pb to Todos os Santos Bay through the years have been the Pb smelter that operated in Santo Amaro and the burning of fossil fuels (refinery, maritime and terrestrial traffic). The smelter was also associated to increase in concentrations of other elements such as Zn, Cu and Cd in the northeast area of the Bay, which presented the highest sedimentation rates.

Increases in concentrations of trace metals, especially after 1950, were associated to different anthropogenic activities: Pb smelting (CI2 and CI3), burning of fossil fuels (all cores at some extend), maritime traffic (CI4), petroleum related activities (CI5), and changes in land uses (CI1). Impacts of the damming of the Paraguaçu River were not observed in sediments, possibly due to the buffer effect caused by Iguape Bay, which was directly affected by hydrological and water chemistry modifications after damming.

Although many elements, in all cores, presented a substantial enrichment along time, all metals, except Cu at CI4, presented concentrations bellow TEL, indicating that contamination in the studied areas are not prone to cause adverse effects to biota. Moreover the concentration levels of contaminants are substantially lower than most industrialized and/or highly urbanized bays. The results of implementation of environmental policies to improve the waters of the bay could not be noted for the cores evaluated.

References

Aily, C., 2001. Caracterização isotópica de Pb na atmosfera: Um exemplo da cidade de São Paulo. Universidade de São Paulo.

Alonso-Hernández, C.M., Tolosa, I., Mesa-Albernas, M., Díaz-Asencio, M., Corcho-Alvarado, J.A., Sánchez-Cabeza, J.A., 2015. Historical trends of organochlorine pesticides in a sediment core from the Gulf of Bataban??, Cuba. Chemosphere 137, 95–100. doi:10.1016/j.chemosphere.2015.05.044

Álvarez-Iglesias, P., Quintana, B., Rubio, B., Pérez-Arlucea, M., 2007. Sedimentation rates and trace metal input history in intertidal sediments from San Simón Bay (Ría de Vigo, NW Spain) derived from 210Pb and 137Cs chronology. J. Environ. Radioact. 98, 229–250. doi:10.1016/j.jenvrad.2007.05.001

Appleby, P.G., Oldfield, F., 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported 210Pb to the sediment. Catena 5, 1–8.

doi:10.1016/S0341-8162(78)80002-2

Argollo, R.M., 2001. Usando, Cronologias de sedimentação recente e de deposição de metais pesados na Baía de Todos os Santos 210Pb e 137Cs. Universidade Federal da Bahia.

Bahia, 2013. Plano diretor do Polo Industrial de Camaçari.

Bai, J., Jia, J., Zhang, G., Zhao, Q., Lu, Q., Cui, B., Liu, X., 2016. Spatial and temporal dynamics of heavy metal pollution and source identification in sediment cores from the short-term flooding riparian wetlands in a Chinese delta. Environ. Pollut. 1–10. doi:10.1016/j.envpol.2016.05.016

Baker, J., Peate, D., Waight, T., Meyzen, C., 2004. Pb isotopic analysis of standards and samples using a 207Pb-204Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. Chem. Geol. 211, 275–303. doi:10.1016/j.chemgeo.2004.06.030

Barros, F., Hatje, V., Figueiredo, M.B., Magalhães, W.F., Dórea, H.S., Emídio, E.S., 2008. The structure of the benthic macrofaunal assemblages and sediments characteristics of the Paraguaçu estuarine system, NE, Brazil. Estuar. Coast. Shelf Sci. 78, 753–762. doi:10.1016/j.ecss.2008.02.016

Begy, R.C., Preoteasa, L., Timar-Gabor, A., Mihăiescu, R., Tănăselia, C., Kelemen, S., Simon, H., 2016. Sediment dynamics and heavy metal pollution history of the Cruhlig Lake (Danube Delta, Romania). J. Environ. Radioact. 153, 167–175. doi:10.1016/j.jenvrad.2015.12.020

Benninger, L., Aller, R., Cochran, J., Turekian, K., 1979. Effects of biological sediment mixing on the 210 Pb chronology and trace metal distribution in a Long Island Sound sediment core. Earth Planet. Sci. Lett. 43, 241–259. doi:10.1016/0012-821X(79)90208-5

Beretta, M., Britto, V., Tavares, T.M., da Silva, S.M.T., Pletsch, A.L., 2014. Occurrence of pharmaceutical and personal care products (PPCPs) in marine sediments in the Todos os Santos Bay and the north coast of Salvador, Bahia, Brazil. J. Soils Sediments 14, 1278–1286. doi:10.1007/s11368-014-0884-6

Birch, G.F., Chang, C.H., Lee, J.H., Churchill, L.J., 2013. The use of vintage surficial sediment data and sedimentary cores to determine past and future trends in estuarine metal contamination (Sydney estuary, Australia). Sci. Total Environ. 454–455, 542–561. doi:10.1016/j.scitotenv.2013.02.072

Birch, G.F., Gunns, T.J., Olmos, M., 2015. Sediment-bound metals as indicators of anthropogenic change in estuarine environments. Mar. Pollut. Bull. 101, 243–257. doi:10.1016/j.marpolbul.2015.09.056

Bird, G., 2011. Provenancing anthropogenic Pb within the fluvial environment: developments and challenges in the use of Pb isotopes. Environ. Int. 37, 802–19. doi:10.1016/j.envint.2011.02.007

Bollhöfer, A., Rosman, K.J.R., 2000. Isotopic source signatures for atmospheric lead: The Northern Hemisphere. Geochim. Cosmochim. Acta 65, 1727–1740. doi:10.1016/S0016-7037(00)00630-X

Borja, P.C., Dias, M.C., Álvares, M.L.P., Lordelo, M.S., Loureiro, A.L., Neto Dias, A.A., Cruz, C.S., Silva, R.M.L., Santana, R. de A., Cruz, F., Gomes, F.S., 2004. Avaliação Quali-quantitativa dos Serviços de Saneamento da Cidade do Salvador, in: 1º Caderno de Pesquisa Em Engenharia de Saúde Pública. FUNASA, Brasília, pp. 27–66.

Boyle, E., Lee, J.-M., Echegoyen, Y., Noble, A., Moos, S., Carrasco, G., Zhao, N., Kayser, R., Zhang, J., Gamo, T., Obata, H., Norisuye, K., 2014. Anthropogenic Lead Emissions in the Ocean: The Evolving Global Experiment. Oceanography 27, 69–75. doi:10.5670/oceanog.2014.10

Bruland, K.W., Bertine, K., Koide, M., Goldberg, E.D., 1974. History of metal pollution in southern California coastal zone. Environ. Sci. Technol. Sci. Technol. 8, 425–432. doi:10.1021/es60090a010

Bryan, G.W., Langston, W.J., 1992. Bioavailability, Accumulation and Effects of Heavy-Metals in Sediments with Special Reference to United-Kingdom Estuaries - a Review. Environ. Pollut. 76, 89–131. doi:Doi 10.1016/0269-7491(92)90099-V

Buchman, M.F., 2008. NOAA Screening Quick Reference Tables. Seattle WA.

Cantwell, M.G., Sullivan, J.C., Katz, D.R., Burgess, R.M., Bradford Hubeny, J., King, J., 2015. Source determination of benzotriazoles in sediment cores from two urban estuaries on the Atlantic Coast of the United States. Mar. Pollut. Bull. 101, 208–218. doi:10.1016/j.marpolbul.2015.10.075

Caroso, C., Tavares, F., Pereira, C., 2011. Baía de Todos os Santos: aspectos humanos. EDUFBA, Salvador.

Carvalho, F., Tavares, T.M., Souza, S.P., Linhares, P.S., 1984. Lead and cadmium concentrations in the hair of fishermen from the Subae River basin, Brazil. Environ. Res. 33, 300–306. doi:10.1016/0013-9351(84)90027-6

Carvalho, F.M., Silvany-Neto, A.M., Melo, A.M.C., Chaves, M.E.C., Brandão, A.M., Tavares, T.M., 1989. Cadmium in Hair of Children Living Near a Lead Smelter in Brazil. Sci. Total Environ. 84, 119–128.

Carvalho, F.M., Silvany Neto, A.M., Tavares, T.M., Costa, A.C.A., Chaves, C. d'El R., Nascimento, L.D., Reis, M.D.A., 2003. Chumbo no sangue de crianças e passivo ambiental de uma fundição de chumbo no Brasil. Rev. Panam. Salud Publica 13, 19–23.

Casado-Martínez, M.C., Buceta, J.L., Belzunce, M.J., DelValls, T.A., 2006. Using sediment quality guidelines for dredged material management in commercial ports from Spain. Environ. Int. 32, 388–396. doi:10.1016/j.envint.2005.09.003

Cheng, H., Hu, Y., 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review. Environ. Pollut. 158, 1134–1146. doi:10.1016/j.envpol.2009.12.028

Cindrić, A.M., Garnier, C., Oursel, B., Pižeta, I., Omanović, D., 2015. Evidencing the natural and anthropogenic processes controlling trace metals dynamic in a highly stratified estuary: The Krka River estuary (Adriatic, Croatia). Mar. Pollut. Bull. 94, 199–216. doi:10.1016/j.marpolbul.2015.02.029

Cirano, M., Lessa, G.C., 2007. Oceanographic Characteristics of Baía de Todos os Santos, Brazil. Rev. Bras. Geofísica 25, 363–387. doi:http://dx.doi.org/10.1590/S0102-261X2007000400002

Cobelo-García, A., Neira, P., Mil-Homens, M., Caetano, M., 2011. Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal). Mar. Pollut. Bull. 62, 646–650. doi:10.1016/j.marpolbul.2010.12.018

CODEBA, 2016a. Porto Aratu-Candeias [WWW Document]. Cia. das docas do estado da Bahia. URL http://www.codeba.com.br/eficiente/sites/portalcodeba/pt-br/porto_aratu.php (accessed 7.8.16).

CODEBA, 2016b. Movimentação de cargas porto de Salvador [WWW Document]. Cia. das docas do estado da Bahia. URL http://www.codeba.com.br/eficiente/sites/portalcodeba/pt-br/modulos/inc.movimentacoescargas.php?ano=2000&porto=A (accessed 3.8.16).

Combi, T., Miserocchi, S., Langone, L., Guerra, R., 2016. Polychlorinated biphenyls (PCBs) in sediments from the western Adriatic Sea: Sources, historical trends and

inventories. Sci. Total Environ. 562, 580–587. doi:10.1016/j.scitotenv.2016.04.086

Costa, A.B., de Souza, J.R.B., Zucchi, M.D.R., de Azevedo, A.E.G., de Argollo, R.M., 2016. Characterization of organic matter in a sediment Core near the Mataripe refinery, Bahia-Brazil. Mar. Pollut. Bull. 105, 411–5. doi:10.1016/j.marpolbul.2016.01.048

Crutzen, P.J., Stoermer, E.F., 2000. The Anthropocene. Glob. Chang. Newsl. 17–18.

Dafforn, K.A., Lewis, J.A., Johnston, E.L., 2011. Antifouling strategies: History and regulation, ecological impacts and mitigation. Mar. Pollut. Bull. 62, 453–465. doi:10.1016/j.marpolbul.2011.01.012

de Andrade Lima, L.R.P., Bernardez, L.A., 2010. Characterization of the heavy metal contamination due to a lead smelter in Bahia, Brazil, in: Siegmund, A., Centomo, L., Geenen, C., Piret, N., Richards, G., Stephens, R. (Eds.), Lead-Zinc 2010. John Wiley & Sons, Inc., Hoboken, New Jersey, pp. 917–927.

de Andrade Lima, L.R.P., Bernardez, L. a., 2011. Isotope Source Signatures for a Primary Lead Smelter Located Close to Todos os Santos Bay, Brazil. Soil Sediment Contam. An Int. J. 20, 672–687. doi:10.1080/15320383.2011.594109

de Carvalho Aguiar, V.M., de Lima, M.N., Abuchacra, R.C., Abuchacra, P.F.F., Neto, J.A.B., Borges, H.V., de Oliveira, V.C., 2016. Ecological risks of trace metals in Guanabara Bay, Rio de Janeiro, Brazil: An index analysis approach. Ecotoxicol. Environ. Saf. 133, 306–315. doi:10.1016/j.ecoenv.2016.07.012

Dean, J.R., Leng, M.J., Mackay, a. W., 2014. Is there an isotopic signature of the Anthropocene? Anthr. Rev. 1, 276–287. doi:10.1177/2053019614541631

de Souza, M.M., Windmöller, C.C., Hatje, V., 2011. Shellfish from Todos os Santos Bay, Bahia, Brazil: treat or threat? Mar. Pollut. Bull. 62, 2254–63. doi:10.1016/j.marpolbul.2011.07.010

Díaz-Somoano, M., Kylander, M.E., López-Antón, M.A., Suárez-Ruiz, I., Martínez-Tarazona, M.R., Ferrat, M., Kober, B., Weiss, D.J., 2009. Stable Lead Isotope Compositions In Selected Coals From Around The World And Implications For Present Day Aerosol Source Tracing. Environ. Sci. Technol. 43, 1078–1085.

Doe, B.R., 1970. Lead Isotopes. Springer, Berlin.

Ellam, R.M., 2010. The graphical presentation of lead isotope data for environmental source apportionment. Sci. Total Environ. 408, 3490–3492. doi:10.1016/j.scitotenv.2010.03.037

Ettler, V., 2015. Soil contamination near non-ferrous metal smelters: A review. Appl.

Geochemistry 64, 56–74. doi:10.1016/j.apgeochem.2015.09.020

Figueiredo, A.G., de Toledo, M.B., Cordeiro, R.C., Godoy, J.M.O., da Silva, F.T., Vasconcelos, S.C., dos Santos, R.A., 2014. Linked variations in sediment accumulation rates and sea-level in Guanabara Bay, Brazil, over the last 6000 years. Palaeogeogr. Palaeoclimatol. Palaeoecol. 415, 83–90. doi:10.1016/j.palaeo.2014.08.027

Foster, K.L., Stern, G.A., Carrie, J., Bailey, J.N.L., Outridge, P.M., Sanei, H., Macdonald, R.W., 2015. Spatial, temporal, and source variations of hydrocarbons in marine sediments from Baffin Bay, Eastern Canadian Arctic. Sci. Total Environ. 506–507, 430–443. doi:10.1016/j.scitotenv.2014.11.002

Garcia-Orellana, J., Cañas, L., Masqué, P., Obrador, B., Olid, C., Pretus, J., 2011. Chronological reconstruction of metal contamination in the Port of Ma?? (Minorca, Spain). Mar. Pollut. Bull. 62, 1632–1640. doi:10.1016/j.marpolbul.2011.06.013

Genz, F., 2006. Avaliação dos efeitos da Barragem Pedra do Cavalo sobre a circulação estuarina do Rio Paraguaçu e Baía de Iguape. Universidade Federal da Bahia.

Gioia, S.M.C.L., Babinski, M., Pimentel, M.M., 2005. Determination of Lead Isotopic compositions in fuels by thermal ionisation mass spectrometry (TIMS), in: XIV Semana de Geoquímica/VIII Congresso de Geoquímica Dos Países de Língua Portuguesa. Aveiro, pp. 737–740.

Gioia, S.M.C.L., Pimentel, M.M., Tessler, M., Dantas, E.L., Campos, J.E.G., Guimarães, E.M., Maruoka, M.T.S., Nascimento, E.L.C., 2006. Sources of anthropogenic lead in sediments from an artificial lake in Brasília-central Brazil. Sci. Total Environ. 356, 125–42. doi:10.1016/j.scitotenv.2005.02.041

Graney, J.R., Halliday, A.N., Keeler, G.J., Nriagu, J.O., Robbins, J.A., Norton, S.A., 1995. Isotopic record of lead pollution in lake sediments from the northeastern United States. Geochim. Cosmochim. Acta 59, 1715–1728. doi:10.1016/0016-7037(95)00077-D

Halpern, B.S., Walbridge, S., Selkoe, K. a, Kappel, C. V, Micheli, F., D'Agrosa, C., Bruno, J.F., Casey, K.S., Ebert, C., Fox, H.E., Fujita, R., Heinemann, D., Lenihan, H.S., Madin, E.M.P., Perry, M.T., Selig, E.R., Spalding, M., Steneck, R., Watson, R., 2008. A global map of human impact on marine ecosystems. Science 319, 948–52. doi:10.1126/science.1149345

Hatje, V., Barros, F., 2012. Overview of the 20th century impact of trace metal contamination in the estuaries of Todos os Santos Bay: past, present and future

scenarios. Mar. Pollut. Bull. 64, 2603–14. doi:10.1016/j.marpolbul.2012.07.009

Hatje, V., Barros, F., Figueiredo, D.G., Santos, V.L.C.S., Peso-Aguiar, M.C., 2006. Trace metal contamination and benthic assemblages in Subaé estuarine system, Brazil. Mar. Pollut. Bull. 52, 982–987. doi:10.1016/j.marpolbul.2006.04.016

IBGE, 2016. Dados demograficos de Salvador de 1940 até 2014 [WWW Document]. Inst. Bras. Geogr. e Estatística. URL http://www.ibge.gov.br/home/ (accessed 3.5.16).

Jennerjahn, T.C., 2012. Biogeochemical response of tropical coastal systems to present and past environmental change. Earth-Science Rev. 114, 19–41. doi:10.1016/j.earscirev.2012.04.005

Kaiser, D., Schulz-Bull, D.E., Waniek, J.J., 2016. Profiles and inventories of organic pollutants in sediments from the central Beibu Gulf and its coastal mangroves. Chemosphere 153, 39–47. doi:10.1016/j.chemosphere.2016.03.041

Khalaf, F., Literathy, V., Anderlini, V., 1982. Vanadium as a tracer of oil pollution in the sediments of Kuwait. Hydrobiologia 91–92, 147–154. doi:10.1007/BF00940104

Komárek, M., Ettler, V., Chrastný, V., Mihaljevic, M., 2008. Lead isotopes in environmental sciences: a review. Environ. Int. 34, 562–77. doi:10.1016/j.envint.2007.10.005

Krishnaswamy, S., Lal, D., Martin, J.M., Meybeck, M., 1971. Geochronology of lake sediments. Earth Planet. Sci. Lett. 11, 407–414. doi:10.1016/0012-821X(71)90202-0

Lessa, G., Dias, K., 2009. Distribuição espacial das litofácies de fundo da Baía de Todos os Santos. Quat. Environ. Geosci. 1, 84–97.

Lessa, G.C., Bittencourt, a. C.S.P., Brichta, a, Dominguez, J.M.L., 2000. A Reevaluation of the Late Quaternary Sedimentation\rin Todos os Santos Bay (BA), Brazil. An. Acad. Bras. Cienc. 72, 1–18. doi:http://dx.doi.org/10.1590/S0001-37652000000400008

Lessa, G.C., Dominguez, J.M.L., Bittencourt, A.C.S.P., Brichta, A., 2001. The Tides and Tidal Circulation of Todos os Santos Bay, Northeast Brazil : a general characterization. An. Acad. Bras. Cienc. 73.

Lima, G.M.P., Lessa, G.C., 2002. The fresh-water discharge in Todos os Santos Bay (BA) and its significance to the general water circulation. Pesqui. em Geociencias 28, 85–97.

Machado, S., Rabelo, T.S., Portella, R.B., Carvalho, M.D.F., Magna, G.A.M., 2012. A study of the routes of contamination by lead and cadmium in Santo Amaro, Brazil. Environ. Technol. 34, 559–71. doi:10.1080/09593330.2012.692717

Marques, A.N., Monna, F., da Silva Filho, E. V., Fernex, F.E., Fernando Lamego Simões Filho, F., 2006. Apparent discrepancy in contamination history of a sub-tropical estuary evaluated through 210Pb profile and chronostratigraphical markers. Mar. Pollut. Bull. 52, 532–539. doi:10.1016/j.marpolbul.2005.09.048

Martin, J., Meybeck, M., 1979. Sampling procedures An outline of sampling procedures is given in Table I . Whenever possible ,. Mar. Chem. 7, 173–206.

Martins, C.C., Doumer, M.E., Gallice, W.C., Dauner, A.L.L., Cabral, A.C., Cardoso, F.D., Dolci, N.N., Camargo, L.M., Ferreira, P.A.L., Figueira, R.C.L., Mangrich, A.S., 2015. Coupling spectroscopic and chromatographic techniques for evaluation of the depositional history of hydrocarbons in a subtropical estuary. Environ. Pollut. 205, 403–414. doi:10.1016/j.envpol.2015.07.016

Masqué, P., Sanchez-Cabeza, J.A., Bruach, J.M., Palacios, E., Canals, M., 2002. Balance and residence times of 210Pb and 210Po in surface waters of the northwestern Mediterranean Sea. Cont. Shelf Res. 22, 2127–2146. doi:10.1016/S0278-4343(02)00074-2

Meybeck, M., 2003. Global analysis of river systems: from Earth system controls to Anthropocene syndromes. Philos. Trans. R. Soc. Lond. B. Biol. Sci. 358, 1935–55. doi:10.1098/rstb.2003.1379

Milliman, J., Farnsworth, K., 2013. River discharge to the coastal ocean: a global synthesis 24, 392. doi:10.1017/CBO9780511781247

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134–139.

Oulhote, Y., Bot, B. Le, Deguen, S., Glorennec, P., 2011. Using and interpreting isotope data for source identification. Trends Anal. Chem. 30, 302–312. doi:10.1016/j.trac.2010.10.015

Peng, X., Wang, Z., Yu, Y., Tang, C., Lu, H., Xu, S., Chen, F., Mai, B., Chen, S., Li, K., Yang, C., 2008. Temporal trends of hydrocarbons in sediment cores from the Pearl River Estuary and the northern South China Sea. Environ. Pollut. 156, 442–448. doi:10.1016/j.envpol.2008.01.037

Petrobrás, 2016. Refinaria Landulpho Alves (RLAM) [WWW Document]. URL http://www.petrobras.com.br/pt/nossas-atividades/principais-operacoes/refinarias/refinaria-landulpho-alves-rlam.htm (accessed 5.3.16).

Reuer, M.K., Boyle, E.A., Grant, B.C., 2003. Lead isotope analysis of marine carbonates

and seawater by multiple collector ICP-MS. Chem. Geol. 200, 137–153. doi:10.1016/S0009-2541(03)00186-4

Ribeiro, L.F., Eça, G.F., Barros, F., Hatje, V., 2016. Impacts of shrimp farming cultivation cycles on macrobenthic assemblages and chemistry of sediments. Environ. Pollut. 211, 307–15. doi:10.1016/j.envpol.2015.12.031

Ruiz-Fernández, A.C., Sprovieri, M., Piazza, R., Frignani, M., Sanchez-Cabeza, J.A., Feo, M.L., Bellucci, L.G., Vecchiato, M., Pérez-Bernal, L.H., Páez-Osuna, F., 2012. 210Pb-derived history of PAH and PCB accumulation in sediments of a tropical inner lagoon (Las Matas, Gulf of Mexico) near a major oil refinery. Geochim. Cosmochim. Acta 82, 136–153. doi:10.1016/j.gca.2011.02.041

Sanchez-Cabeza, J. a, Masque, P., Ani-Ragolta, I., 1998. Lead-210 and polonium-210 analysis in sediments and soils by microwave acid digestion. J. Radioanal. Nucl. Chem. 227, 19–22. doi:10.1007/BF02386425

Shotyk, W., Rausch, N., Outridge, P.M., Krachler, M., 2016. Isotopic evolution of atmospheric Pb from metallurgical processing in Flin Flon, Manitoba: Retrospective analysis using peat cores from bogs. Environ. Pollut. 218, 338–348. doi:10.1016/j.envpol.2016.07.009

Soldi, T., Riolo, C., Alberti, G., Gallorini, M., Peloso, G.F., 1996. Environmental vanadium distribution from an industrial settlement. Sci. Total … 181, 45–50.

Tavares, T.M., Brandão, A.M., Carvalho Chaves, M.E., Silvany Neto, A.M., Carvalho, F.M., 1989. Lead in Hair of Children Exposed to Gross Environmental Pollution. Int. J. Environ. Anal. Chem. 36, 221–230. doi:10.1080/03067318908026875

Viers, J., Dupré, B., Gaillardet, J., 2009. Chemical composition of suspended sediments in World Rivers: New insights from a new database. Sci. Total Environ. 407, 853–868. doi:10.1016/j.scitotenv.2008.09.053

Wang, F., Wang, H., Li, J., Pei, Y., Fan, C., Tian, L., Shang, Z., Song, M., Geng, Y., 2008. 210Pb and 137Cs measurements in the Circum Bohai Sea coastal region: Sedimentation rates and implications. Front. Earth Sci. China 2, 276–282. doi:10.1007/s11707-008-0046-5

Wang, S., Wang, Y., Zhang, R., Wang, W., Xu, D., Guo, J., Li, P., Yu, K., 2015. Historical levels of heavy metals reconstructed from sedimentary record in the Hejiang River, located in a typical mining region of Southern China. Sci. Total Environ. 532, 645–654. doi:10.1016/j.scitotenv.2015.06.035

Wasserman, J.C., Figueiredo, A.M.G., Pellegatti, F., Silva-Filho, E. V., 2001. Elemental composition of sediment cores from a mangrove environment using neutron activation analysis. J. Geochemical Explor. 72, 129–146. doi:10.1016/S0375-6742(01)00158-3

Waters, C.N., Zalasiewicz, J.A., Williams, M., Ellis, M.A., Snelling, A.M., 2014. A stratigraphical basis for the Anthropocene? Geol. Soc. London, Spec. Publ. 395. doi:10.1144/SP395.18

Waters, C.N., Zalasiewicz, J., Summerhayes, C., Barnosky, A.D., Poirier, C., Ga, A., Cearreta, A., Edgeworth, M., Ellis, E.C., Ellis, M., Jeandel, C., Leinfelder, R., Mcneill, J.R., Richter, D., Steffen, W., Syvitski, J., Vidas, D., Wagreich, M., Williams, M., Zhisheng, A., Grinevald, J., Odada, E., Oreskes, N., Wolfe, A.P., 2016. The Anthropocene is functionally and stratigraphically distinct from the Holocene. Science (80-.). 351, aad2622-1-aad2622-10. doi:10.1126/science.aad2622

Yang, C., Rose, N.L., Turner, S.D., Yang, H., Goldsmith, B., Losada, S., Barber, J.L., Harrad, S., 2016. Hexabromocyclododecanes, polybrominated diphenyl ethers, and polychlorinated biphenyls in radiometrically dated sediment cores from English lakes, ~1950-present. Sci. Total Environ. 541, 721–728. doi:10.1016/j.scitotenv.2015.09.102

Yu, R., Zhang, W., Hu, G., Lin, C., Yang, Q., 2016. Heavy metal pollution and Pb isotopic tracing in the intertidal surface sediments of Quanzhou Bay, southeast coast of China. Mar. Pollut. Bull. 105, 416–21. doi:10.1016/j.marpolbul.2016.01.047

Zhang, F., Zhang, R., Guan, M., Shu, Y., Shen, L., Chen, X., Li, T., 2016. Polycyclic aromatic hydrocarbons (PAHs) and Pb isotopic ratios in a sediment core from Shilianghe Reservoir, eastern China: Implying pollution sources. Appl. Geochemistry 66, 140–148. doi:10.1016/j.apgeochem.2015.12.010

Zimmerman, A.R., Canuel, E.A., 2002. Sediment Geochemical Records of Eutrophication in the Mesohaline Chesapeake Bay. Limnol. Oceanogr. 47, 1084–1093. doi:10.2307/3069027
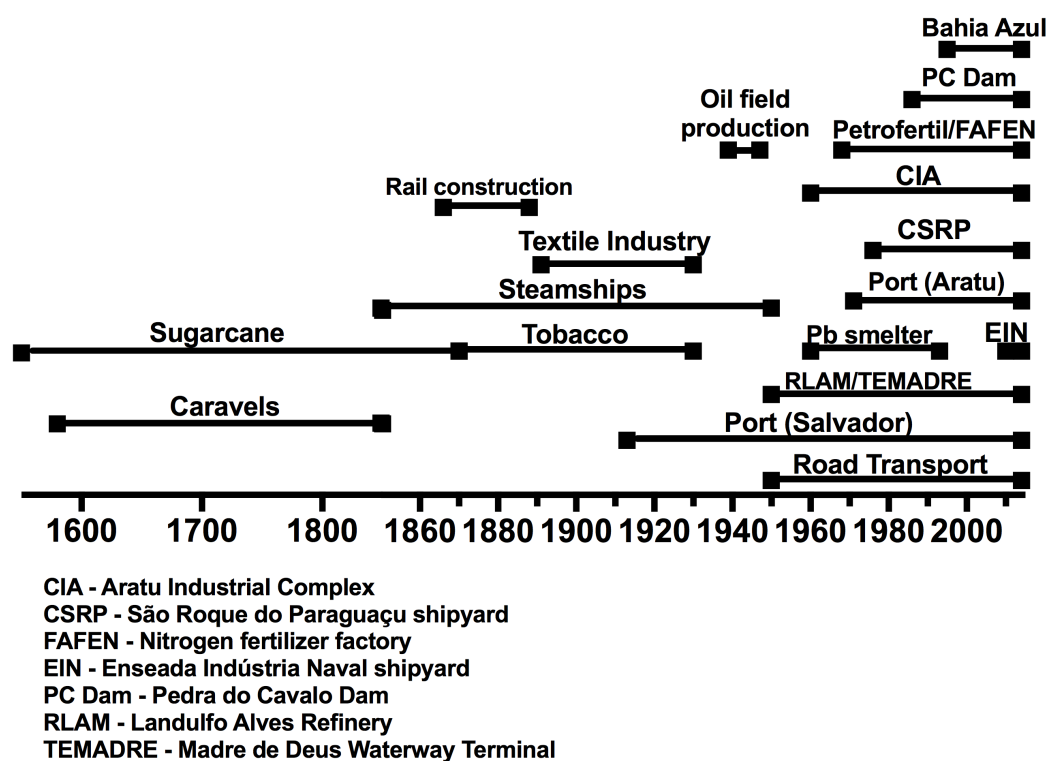
Figure S1 – Timeline of main anthropogenic sources of contamination to Todos os Santos Bay, Bahia.