NIELSON MACHADO DOS SANTOS

REFERENCE VALUES, ISOTOPIC SIGNATURE OF Pb AND HEAVY METAL ENRICHMENT FACTORS IN SOILS SURROUNDING AN ENVIRONMENTALLY-IMPACTED BAY IN BRAZIL

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Soil Science) at the Federal Rural University of Pernambuco.

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Title "**REFERENCE VALUES, ISOTOPIC SIGNATURE OF Pb AND HEAVY METAL ENRICHMENT FACTORS IN SOILS SURROUNDING AN ENVIRONMENTALLY-IMPACTED BAY IN BRAZIL"**, a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Soil Science) at the Federal Rural University of Pernambuco, and approved on July 06, 2015

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“Os homens de ciência e de espirito, segundo o mundo, têm geralmente tão alta consideração de si mesmo e de sua superioridade, que olham as coisas Divinas como indignas de sua atenção; seus olhares, concentrados sobre sua pessoa, não podem se elevar até Deus. Essa tendência a se crer acima de tudo não os leva se não, muito frequentemente, a negar o que, estando-lhes acima poderia rebaixá-los e a negar mesmo a Divindade; ou se consentem em admiti-la, contestam-lhe um dos seus mais belos atributos: sua ação providencial sobre as coisas deste mundo, persuadidos de que só eles bastam para bem governá-lo. Tomando sua inteligência por medida da inteligência universal, e se julgando aptos a tudo compreender, não podem crer na possibilidade daquilo que não compreendem; quando pronunciaram seu julgamento, têm-no por inapelável”

(Evangelho segundo o espiritismo)

“To be humble to superiors is a duty, to equals courtesy, to inferiors nobleness.”

Benjamin Franklin

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ABSTRACT

Nielson Machado dos Santos, D. Sc. Federal Rural University of Pernambuco, Recife, July, 2015. Reference values, isotopic signature of Pb and heavy metal enrichment factors in soils surrounding an environmentally-impacted bay in Brazil. . Adviser: Clistenes Williams Araújo do Nascimento.

This work was carried out to investigate the possible influence of human activities on heavy metal concentrations, by enrichment factor and isotopic signature of Pb and determine the natural levels of heavy metals in the vicinity Todos os Santos Bay-BA (BTS). For this, two sampling design of the soil around the BTS were realized. The first sampling 114 topsoil samples (0.0 - 0.2 m depth) were collected from 38 samplings sites and the concentrations of Pb, Zn, As, Cd, and Hg were determined by ICP-OES or AA-FIAS after microwave sample digestion. Results showed that mean values for heavy metal concentrations in soils (mg kg^{-1}) followed the order Pb (39.45) > Zn (12.52) > As (1.95) > Cd (0.23) > Hg (0.09). The mean natural concentrations of heavy metals found in the soils of an important economic region of Brazil's were generally lower than those reported in the national and international literature, with exception Pb concentration that was higher than all compared soils.The quality reference values (QRvs) calculated for the TSB based on the 75th percentile, were as follows (mg kg^{-1}): Pb (54.37); Cr (36.55); Zn (10.40); Cu (7.10); Ni (4.05); Co (0.38); Cd (0.30). The second sampling six soil profiles were collected, the samples were collected from different horizons, totaling 44 samples. Soil pits were dug until 2 m or until the parent material (C horizon) was reached.The soil samples were microwave digested in the mixture of HNO_3, H_2O_2 using the method described by Sah and Miller (1992). Concentrations of Pb and the isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb were measured on an inductively coupled plasma (quadrupole) mass spectrometry. Pb concentrations varied from 3.2 to 44.1 mg kg^{-1} with an average concentration of 13.65 mg kg^{-1}. In general the samples feature a wide range of Pb isotope ratios, ranging from 36.71 to 47.38 for $^{208}Pb/^{204}Pb$, 16.86 to 20.59 for $^{206}Pb/^{204}Pb$, 1.10 to 1.31 for $^{206}Pb/^{207}Pb$ and a ranged slightly from 15.00 to 15.65 for $^{207}Pb/^{204}Pb$. The PCA

performed identified that Pb, Zn, and Cd were associated with the same factor (F1) and had chiefly anthropogenic origin whereas Pb and Zn have also contributions from both sources (natural, lithogenic and anthropogenic). The As and Hg concentrations (F2) were related to the natural component; the parent material underlying the soils (igneous-metamorphic rocks) seemingly confirm this hypothesis. The natural concentrations of heavy metals in soils of TSB had the following decreasing order: Pb > Cr > Zn > Cu > Ni > Co > Cd. Pb concentration in all soil profiles not seem have been influenced by the abandoned lead smelter plant located in the municipality of Santo Amaro da Purificação-BA. The distinct Pb isotopic compositions were clearly related to the different exposure of the sampling sites in relation to atmospheric deposition and geological parent material.

GENERAL INTRODUCTION

Todos os Santos Bay is located at the edge of the third largest city in Brazil, Salvador, capital of Bahia state, being the largest tropical bay of Brazil, with an area of 1112 km^2 and approximate maximum width and length of 32 km and 50 km, respectively (Hatje and Barros, 2012). It has 15 municipalities along its 185 km coastline perimeter and an urban population over 3 million people (Wagener et al., 2010). The bay is an important economic area of the country with a gross domestic product (GDP) of approximately US$ 23 billion which represents 1.74% of country's GDP (IBGE, 2010).

Besides the increasing problem of pollution in coastal metropolitan areas caused by discharge of industrial and domestic wastes, Todos os Santos Bay area is known for one of the most important cases of urban lead (Pb) contamination in the world which aroused from slag disposal, atmospheric deposition and the overflow of tailings from an abandoned lead smelter plant located in the municipality of Santo Amaro da Purificação. The Pb smelter plant produced up to 32 x 10^6 kg of Pb bars/year. Until 1980 the smelter dross (up to 3% Pb) was freely given to the population for paving yards as well as used extensively by the local council for paving streets and public places, including local schools (Hatje et al., 2006). As a result, high Pb and Cd concentrations have been found in humans living in nearby towns, especially children (Carvalho et al., 1986; 1995; Tavares et al., 1989; Silvany-Neto et al., 1989, 1996), marine organisms (Amado-Filho et al., 2008; Souza et al., 2011; Barros et al., 2012), soils (Santos et al., 2014; Niemeyer et al., 2012), and sediments (Celino et al., 2008; Hatje et al., 2010; Costa et al., 2011). Nevertheless, studies on the spatial extent and sources of contamination by heavy metals in soils surrounding the BTS are still very scarce.

The concentration and distribution of heavy metals in soils are dependent on soil parent material (lithogenic source) and anthropogenic sources (Alloway, 2013) the difference between these two sources has been widely investigated (Li et al., 2009; Uría et al., 2009; Zhong et al., 2014; Luo et al., 2015). This difference is fundamental for establishing a soil protection legislation in connection with a real condition of the local

environment, avoiding inappropriate interventions that can cause financial and social damage. The evaluation of the source of heavy metals in soil is necessary, especially in areas with high economic development, such as TSB.

Quality reference values of soil reflect the natural concentration of heavy metals in soils that are free of anthropogenic activities (Teng et al. 2009). Reference values estimation is crucial for establishing soil environmental quality standards, besides being indispensable to building environmental legislation.

Geostatistical methods have been widely used for spatial interpolation of heavy metals in soils and evaluation of contaminated sites (Zhao et al., 2010; Xie et al., 2011; Sun et al., 2013; Dragovic et al., 2014) while multivariate analysis are useful to assist the interpretation of environmental data (Li and Fang, 2011; Gu et al., 2014). The combination of these statistical tools can be used to assess the distribution of heavy metals in soils and to distinguish between natural and anthropogenic sources (Lu et al., 2012).

The Pb isotopic composition is another tool that has been used to identify sources of heavy metals in soil. The element has four natural stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) being the latter three products of the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, respectively (Komárek et al., 2008). The isotopic composition of Pb is commonly expressed by ^{206}Pb/^{207}Pb, ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{206}Pb/^{204}Pb ratios (Cheng et al., 2010). The ^{206}Pb/^{207}Pb is the most commonly used ratio in environmental studies (Komárek et al., 2008). The variations in ^{206}Pb/^{207}Pb in different lithogenic and anthropogenic sources are produced because this ratio decreases with the age of the source and increases with its U/Pb ratio (Tyszka et al., 2012).

Enrichment factors (EF) have also been widely used to identifying contamination of heavy metals in soils (Bourennane et al., 2010; Zhang et al., 2014; Enamorado-Báez et al., 2015). EF considers the abundance of the element of interest relative to the abundance of a conservative, lithogenic element with no significant anthropogenic source. This ratio is normalized to the corresponding ratio in the sample at the lowest soil depth (Blaser et al. 2000).

This work was carried out to assess the possible influence of human activities on heavy metal concentrations in soils surrounding Todos os Santos Bay, from the use of the enrichment factor and Pb isotopic signature and determine the natural levels of heavy metals in the vicinity the bay.

LITERATURE REVIEW

Natural levels and reference values for heavy metals in soil

The natural levels of heavy metals in soil are result from parent material and pedogenic processes, together with the geomorphological and climatic conditions that make the metal levels in each soil specific. Therefore, to follow soil values obtained in other countries is a misguided strategy (Biondi et al., 2011). Current Brazilian law contemplates three guideline values: soil quality reference values (QRV), soil prevention reference values, and soil research reference values (CONAMA 2009). These guideline values are known by a variety of other names in other countries, but all of them establish ranges of values that indicate the natural concentrations of metals in soils (Santos and Alleoni, 2013).

Evaluation of soil contamination for the heavy metals, it is necessary to determine the natural background or geochemical baselines. These values are the amount of naturally occurring substances in the environment, exclusive of that from anthropogenic sources (NREPC, 2004). Geochemical baselines or natural background concentrations of elements are needed to provide guidelines and quality standards for environmental legislation and political decision-making especially in the assessment of contaminated soil (Salminen and Tarvainen, 1997).

The contaminated area is considered that the concentrations of elements or substances of interest are above the set point value, which indicates potential for deleterious effects on human health. In this case, there is need for immediate intervention in the area and emergency measures, such as, detailed research and restricting access of people to the area, should be taken into account (CETESB, 2001).

Therefore, taking into account the socio-economic importance of the Todos os Santos Bay, it is necessary to determine the reference values local, in order that they can reflect the true concentration of heavy metals in the soils of the region.

Geology of the Todos os Santos Bay

Todos os Santos Bay (TSB) is located at the edge of the third largest city in Brazil, Salvador, capital of Bahia state, being the largest tropical bay of Brazil, with an area of 1112 km^2 and approximate maximum width and length of 32 km and 50 km, respectively (Hatje and Barros, 2012).

The TSB has its origin related to Lower Cretaceous fault lines that formed the Recôncavo Basin (Medeiros and Ponte 1981) (Figure 1). The surroundings of the bay are composed of Jurassic and Cretaceous sedimentary rocks excepting for a small area, in the city of Salvador, where the pre-Cambrian basement outcrops along the Salvador Fault (Figure 2). Along the northern and eastern coast, as well as in the various islands inside the bay, Lower Cretaceous shale, siltstone and sandstone (Santo Amaro Group) are the most prominent rocks. At the south-western margin and along the Paraguaçu channel, Upper Jurassic red sandstone intercalated with shale (Sergi Formation) predominate until Iguape Bay, where Cretaceous shale and siltstone (Santo Amaro Group) appears in sharp contact with the Pre- Cambrian basement along the Maragojipe fault. Quaternary deposits, including alluvial fan, marine terraces and mangrove occur along the margins, especially at the western half of the bay (Figures 1). Quaternary alluvial fan deposits are restricted to the vicinity of the hills dominated by the Jurassic sandstone (Figure 1) (Lessa et al., 2000).

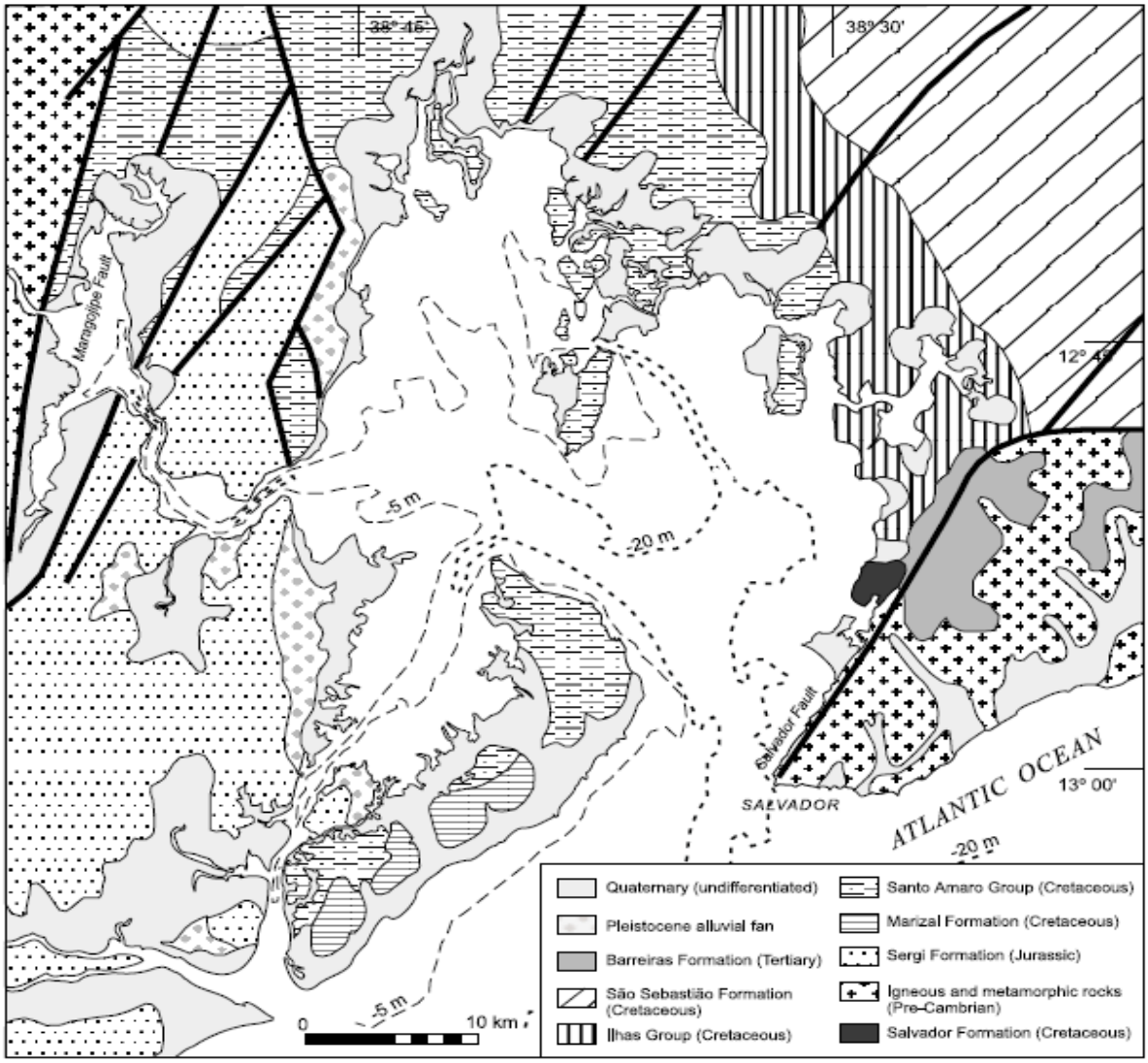

Figure 1. Geologic map of the surroundings of Todos os Santos Bay (Lessa et al., 2000*).*

Economy of Municipalities around the Todos os Santos Bay

Todos os Santos Bay has in its surrounding 15 municipalities: Salvador, Simões Filho, Candeias, São Francisco do Conde, Madre de Deus, Santo Amaro da Purificação, Saubara, Cachoeira, São Félix, Maragogipe, Salinas da Margarida, Nazaré, Jaguaripe, Vera Cruz and Itaparica. According to the IBGE data of 2010, the number of habitant, taking into account all municipalities is 3.2 million with a GDP of approximately US$23 billion.

From the discovery of oil in Lobato, railroad suburb of Salvador in 1939, began the petroleum activities on the BTS, being drilled over 5000 wells in the basin, resulting in the

discovery of about 80 oil and gas fields (Magnavita et al., 2005). In the bay area lies the largest petrochemical complex of southern hemisphere and several chemical, petrochemical, metallurgical and food industries (Souza et al., 2011). Several anthropogenic activities, including influx of domestic effluents and solid wastes, as well as agriculture, industry (chemicals, petrochemicals, smelters, etc.), harbor and mining activities influence the environmental system's quality local (Hatje et al., 2010).

Scientific basis for assessment of contaminated sites

In environmental science, to assess the origin heavy metals in soil, if litogênica or anthropogenic, has been widely used geochemical normalization. Geochemical normalization or Enrichment Factor (EF) defined as a mathematical correlation between the concentration of the metal under study and the concentration of a reference element in the source material. The reference element should be litogênica origin, and its concentration should not be significantly influenced by anthropogenic input (Loring, 1990). For FE is assumed that values close to 1 is indicative of litogênica origin and values greater than 1 are considered to be non-natural (Galuszka and Migaszewski, 2011). The reference elements most widely used are Al, Fe, Li, Sc, Ti and Zr (Reimann and Caritat, 2000).

Although enrichment factor has been widely used to identifying contamination of heavy metals in soils, it has been criticized (Reimann and Caritat 2000; 2005; Sucharovà et al., 2012). According to the authors the EF use isolated for investigations concerning anthropogenic contribution to concentration of metals in soil is flawed, because the soil profile is not a closed system, there is exchange of elements between the layers, the rocks have a variable composition (assembly mineralogical heterogeneous). Therefore, a comparison of the concentration of the element in the surface layer with the average concentration of the element in the Earth's crust, value generally used in formula FE, is inappropriate.

Stable lead isotope ratios for assessment of soil contamination

Knowing only the total concentrations and chemical/mineralogical position of Pb is not sufficient for a precise evaluation of contamination sources. Lead isotopes have thus been introduced as “fingerprints” of environmental pollution and therefore, can be used to distinguish sources the heavy metals in soils (anthropogenic or natural) (Komarek et al., 2008). Lead ores display a characteristic isotopic composition (signature), which does not change during the physical or physicochemical processes associated with smelting, refining and manufacturing. Thus, stable Pb isotopes represent a powerful tool for tracing the origin of contamination, such as coal or gasoline combustion and ore smelting (Ettler et al., 2004). Isotopic measurement is superior to using concentrations alone in tracing pollutant sources because isotope ratios are significantly more sensitive tracers than elemental concentrations or ratios (Cheng e Hu, 2010).

Lead is present in the environment as four main isotopes: ^{208}Pb (52%), ^{206}Pb (24%), ^{207}Pb (23%) and ^{204}Pb (1%). While radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb are products of radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively, ^{204}Pb is the only primordial stable isotope with a constant abundance on Earth in time (Komarek et al., 2008). While the abundances of ^{207}Pb, ^{206}Pb, and ^{208}Pb co-vary strongly and depend on when the ore was formed. As a result, the isotopic compositions characteristic of different types of Pb-containing minerals are caused by the interplay of a number of processes, including radioactive decay of U and Th to Pb, the relative proportion of U–Th–Pb in the system, and mixing of Pb from different sources (Cheng e Hu, 2010).

In environmental sciences, the isotopic composition of Pb is commonly expressed as ratios ^{206}Pb/^{204}Pb, ^{206}Pb/^{207}Pb, ^{208}Pb/^{206}Pb with ^{206}Pb/^{207}Pb being the most preferred because it can be determined precisely analytically and the abundances of these isotopes are relatively important (Komarek et al., 2008).

Incident of contamination of the Santo Amaro da Purificação town

The contamination had larger proportions reaching the urban area as a result of improper use the slag for paving roads, school yards and sidewalks (Machado et al., 2003). Thereby, as consequence of exposure to contamination has emerged various

health problems among the population and former employees of the plant, such as cancers and birth defects.

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CHAPTER I:

REFERENCE VALUES AND CONTAMINATION INDICES IN SOILS FROM TODOS OS SANTOS BAY AREA

Reference values and contamination indices in soils from Todos os Santos Bay area

Abstract

Todos os Santos Bay is one of the most important waterways in Brazil. An abandoned Pb smelter plant located in one of the Bay towns (Santo Amaro da Purificação) left tones of slag rich in Pb, Cd and Zn untreated. The main objectives of this research were to establish the quality reference values and to assess the pollution status for the heavy metals Cd, Co, Cr, Cu, Ni, Pb, and Zn in soils from Todos os Santos Bay using geo-accumulation (I_{geo}) and pollution (PI) indices. A total of 114 topsoil samples (0.0 - 0.2 m depth) were collected from 38 samplings sites with minimal human activity around the Bay. Concentrations of Pb, Cr, Zn, Cu, Ni, Cd and Co in extracts were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). For assessing the pollution status of heavy metals in soils, geo-accumulation and pollution index for every metal in each sample was estimated. The natural concentrations of heavy metals in soils followed the order Pb > Cr > Zn > Cu > Ni > Co > Cd. Quality reference values established from the 75th percentile (upper quartile) for the studied soils were lower than the values established for foreign soils, except for Pb values, seems to be from anthropogenic influence. It was observed that the study area is not contaminated with Cr and Cd; however, some of the sampling locations showed moderate soil contamination by Pb, Ni, Zn and Cu and high soil contamination by Co. Pollution index for Cd, Co, Cr, Cu, Ni, Pb, and Zn are found ranging 0.0 - 4.3; 0.0 - 73.6; 0.01 - 1.8; 0.04 - 6.0; 0.11 - 7.15; 0.1 - 2.1 and 0.0 - 4.43 respectively. Reference values (mg kg^{-1}) calculated for the Todos os Santos Bay soils were as follows: Pb (37.47), Cr (27.16), Zn (7.48), Cu (5.29), Ni (3.22), Co (0.36) and Cd (0.22). The mean natural concentrations of heavy metals found in soils of this economically important region of Brazil were generally lower than those reported in the national and international literature, with exception for Pb concentration, seems to be controlled by past atmospheric deposition from abandoned lead smelter plant.

Key words: Soil pollution; soil quality; geo-accumulation; pollution index

Introduction

Todos os Santos Bay is one of the most important waterways in Brazil, covering an area of 1,100 km^2 (Soares et al., 2011) that holds a major urban center of Northeastern Brazil with 15 cities and 3.2 million inhabitants (IBGE 2010). The Bay area is located at the vicinity of Salvador, capital of Bahia state and the third largest city in the country. An abandoned Pb smelter plant located in one of the Bay towns (Santo Amaro da Purificação) left tones of slag rich in Pb, Cd and Zn untreated. As a result, high Pb and Cd concentrations have been found in humans living nearby, especially children (Carvalho et al., 1995; Silvany-Neto et al., 1996).

In order to assess the level of soil contamination the region it is essential to establish soil guidance values in order to protect human and ecosystems health. Quality reference values of soil reflect the natural concentration of heavy metals in soils that are free of anthropogenic activities (Teng et al. 2009). Reference values estimation is crucial for establishing soil environmental quality standards, besides being indispensable to building environmental legislation. After all, wrongly identifying a soil as contaminated can have serious financial and social implications (Horckmans et al., 2005).

Background concentrations of elements in soil are highly dependent on the mineralogical composition of the parent material and on the weathering processes that led to its formation (Tack et al., 1997; Temmerman et al., 2003). Consequently, the natural concentration of elements in soil varies widely making inappropriate to use universal background levels for assessing the extent and risks of trace metal contamination in a specific soil type (Horckmans et al., 2005).

Urban and industrial expansion in coastal metropolitan areas increases the input and mobilization of heavy metals, which may affect biodiversity and health human. In the bay area lies the largest petrochemical complex of southern hemisphere and several chemical, petrochemical, metallurgical and food industries (Souza et al., 2011). Several anthropogenic activities, including influx of domestic effluents and solid wastes, as well as agriculture, industry (chemicals, petrochemicals, smelters, etc.), harbor and mining activities influence the environmental system's quality local (Hatje et al., 2010). As result, several studies have been conducted with marine ecosystems (Soares et al., 2011;

Amado Filho et al., 2008) and in sediments (Felizzola et al., 2008; Hatje et al., 2012; Costa et al., 2011). Nevertheless, published information about the metal contamination status in soils surrounding the bay are still very scarce and there is no article, up to date, in the scientific literature reporting these reference values.

The main objectives of this research were to establish the quality reference values and to assess the pollution status for the heavy metals Cd, Co, Cr, Cu, Ni, Pb, and Zn in soils from Todos os Santos Bay using geo-accumulation (I_{geo}) and pollution (PI) indices. The results of this study can be used to establish regional soil guidance values for the monitoring of heavy metal contamination.

Materials and methods

Study area and soils

The average rainfall in Todos os Santos Bay ranges from 1400 to 2600 mm with maximum, minimum and average temperatures of 28.2°C; 22.7°C and 25.2°C, respectively. The climate is classified as humid tropical according to Köppen classification. The relative air humidity is high throughout the year, with average indexes ranging from 77% to 85%. January is the driest month while the April-July period exceeds 85% humidity. The bay area is composed predominantly of secondary vegetation (Atlantic Forest) but highly degraded areas and agricultural activities are also common (Guedes and Santos, 1997).

Soils have been originated to Lower Cretaceous fault lines that formed the Recôncavo Basin. The surroundings of the bay are composed of Jurassic and Cretaceous sedimentary rocks excepting for a small area, in Salvador city, where the pre-Cambrian basement outcrops along the Salvador Fault (Lessa et al., 2000). Vertisols, Ultisols, Oxisols and Entisol were the soils orders found surrounding bay area.

Soil sampling and chemical analysis

Were collected 114 topsoil samples (0.0 - 0.2 m depth) from 38 samplings sites with minimal human activity around the bay (Figure 1). At each sampling site three composite samples were formed from four individual samples. The sampling design was based on the representativeness of different geologic materials and soil orders throughout the bay area. For soil analysis, approximately 1.0 kg of each soil sample was taken and mixed thoroughly. The soil samples were air-dried and passed through a 2.0 mm-sieve. Portions of 50 g were ground in an agate grinder and sieved through a 0.3 mm sieve.

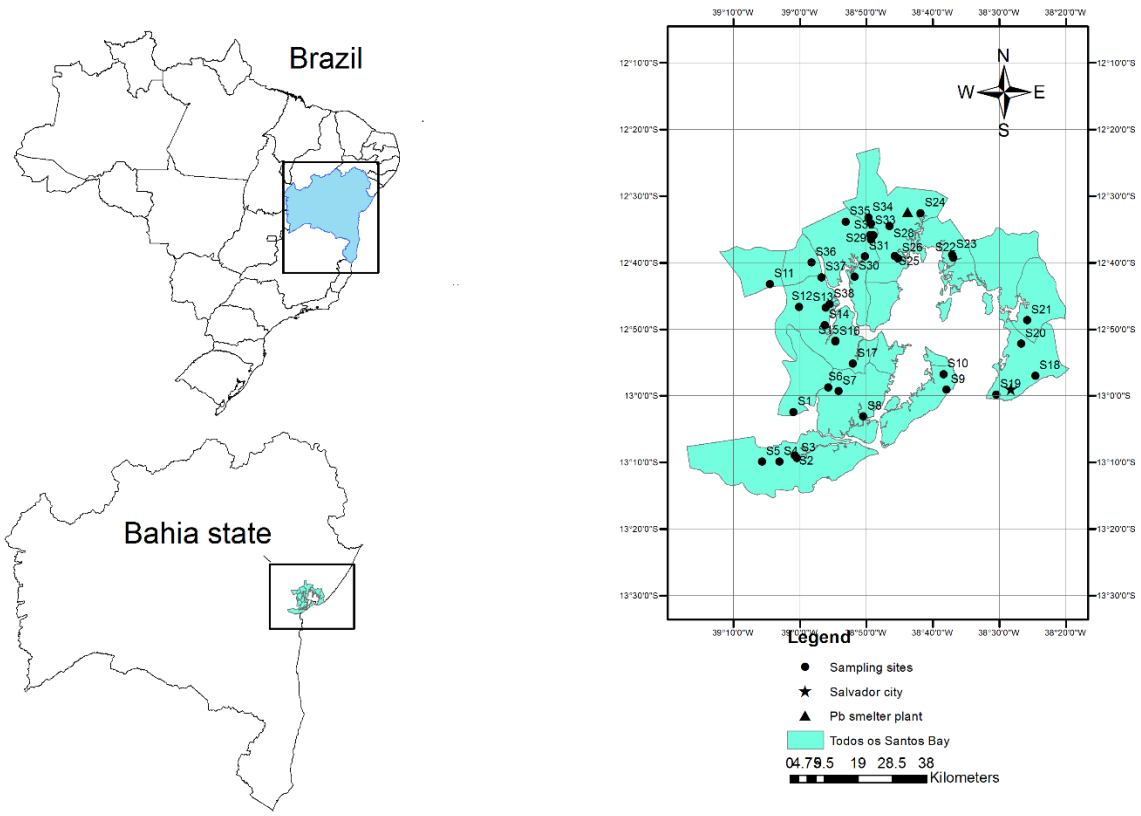

Figure 1. Map of the study area showing the sampling sites.

Soil samples were digested in a mixture of HNO_3, HCl using Method 3051A based on microwave digestion (USEPA, 2007). Concentrations of Pb, Cr, Zn, Cu, Ni, Cd and Co in extracts were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). All the chemicals used were guaranteed reagent grade. Standard reference materials certified for elements content SRM 2709 - San Joaquin Soil from National

Institute of Standards and Technology (NIST) was analyzed as part of quality assurance and quality control procedures.

Statistical and data analyses

The quality reference value for each metal was calculated based on the 75th percentile the frequency distribution of data, with the anomalies being previously withdrawn through a boxplot. Average, minimum and maximum values as well as the standard deviation for all elements analyzed were calculated.

For assessing the pollution status of heavy metals in soils, geo-accumulation (I_{geo}) and pollution index (PI) for every metal in each sample was estimated. I_{geo} was calculated as:

$$I_{geo} = \log_2 \left(\frac{Cn}{1.5Bn} \right) \quad (1)$$

where C_n is the concentration of heavy metal in soil and B_n is the reference value of the same metal in the soil calculated from 75th percentile. The geo-accumulation index (I_{geo}) was distinguished into seven classes by Müller (Buccolieri et al., 2006): $I_{geo} \leq 0$, class 0, unpolluted; $0 < I_{geo} \leq 1$, class 1, from unpolluted to moderately polluted; $1 < I_{geo} \leq 2$, class 2, moderately polluted; $2 < I_{geo} \leq 3$, class 3, from moderately to strongly polluted; $3 < I_{geo} \leq 4$, class 4, strongly polluted; $4 < I_{geo} \leq 5$, class 5, from strongly to extremely polluted; and $I_{geo} > 5$, class 6, extremely polluted.

Single factor pollution index (PI) and the pollution load index (PLI) were calculated for every sample to investigate the level of pollution of the soils surrounding Todos os Santos Bay.

$$PI = \frac{Cn}{Bn} \quad (2)$$

where C_n is a metal's/pollutant's concentration and B_n is the reference value of the same metal in the soil.

$$PLI = \sqrt[n]{PI1 x PI2 x PI3 x ... PIn} \quad (3)$$

where n is the number of metals assessed (i.e., 7) and PI is the single factor pollution index of each metal.

Results and discussion

Heavy metal concentrations

The natural concentrations of heavy metals in soils followed the order Pb > Cr > Zn > Cu > Ni > Co > Cd. Comparing these results with Brazilian and International soils (Table 1) is observed that natural concentration of heavy metals not were equivalent. These results are a reflection the geochemistry specificity each metal in soil, being arising from different parent materials, pedogenic processes and anthropogenic influence.

Table 1. Average natural concentrations of heavy metals in Todos os Santos Bay soils (TSB) compared with data compiled from the international literature

Heavy metals (mg kg^{-1})	Brazilian soils						International soils				World average soil[j]
	TSB	MG[a]	ES[b]	PE[c]	RN[d]	RO and MT[e]	China[f]	Cuba[g]	Finland[h]	USA[i]	
Cd	0.22	0.5	<LD	0.62	0.07	<LD	0.07	1.2	0.2	1.6	1.1
Co	0.36	16.5	8.64	3.54	11.28	20.3	11	31.4	8.4	6.7	6.9
Cr	27.16	100.1	41	27.14	26.55	39.4	54	463.2	37	37	42
Cu	5.29	30.9	5.5	7.15	10.63	16.5	20	83.7	19.15	17	14
Ni	3.22	30.1	6.6	6.0	14.78	1.3	23	294.2	12.45	13	18
Pb	37.47	3.9	8.8	11.18	11.5	8.1	24	34.6	20	16	25
Zn	7.48	13.1	22.6	22.52	21.67	6.8	67	90.7	72.5	48	62

<LD below the detection limit; [a] Caires (2009); [b] Paye et al. (2010); [c] Biondi (2011); [d] Preston et al. (2014); [e] Santos and Alleoni (2013); [f] Su and Yang (2008); [g] Alfaro et al. (2015); [h] Salonen and Korkka-Niemi (2007); [i] Chen et al. (1991); [j] Alloway (2013)

In general, the average soil concentrations found were lower than reported the literature for other countries and other Brazilian states (Table 1), with exception Pb concentration that was higher than all compared soils. Despite in the bay area there representative areas with Vertisols and Ultisols, these soils were formed from shale of lower Cretaceous (mudstone and siltstone). Among common sedimentary rocks shales have higher Pb abundance (Alloway, 2013). The elevated lead concentration seems to be controlled by past atmospheric deposition from abandoned lead smelter plant.

The different heavy metal concentrations found between soils under study and those documented in soils of other Brazilian states and in other countries highlight the importance of establishing QRVs for each region. Taking into account each region's specific pedological and geological conditions, it is necessary a more detailed assessment in areas of high economic importance.

Quality reference values for heavy metals

The QRVs established from the 75th percentile (upper quartile) for the studied soils (Table 2) were lower than the values established for English soils (McGrath and Zhao 2006), Asian soils (Su and Yang 2008), African soils (Pinto et al. 2015), Cuban soils (Alfaro et al., 2015) and Serbian soils (Mrvić et al., 2011), except for Pb values, what seemingly reinforces the hypothesis of the anthropogenic influence. They were also lower than those obtained to Brazilian soils, such as Espírito Santo (Paye et al. 2010), Pernambuco (Biondi et al. 2010), southwestern Amazonia (Santos and Alleoni 2013), and Rio Grande do Norte (Preston et al., 2014), except for Pb values. These quality reference values were then used for the pollution assessment of selected heavy metals in soils.

Table 2. Quality reference values (QRV), average, minimum, and maximum values, and standard deviation for heavy metals in soils Todos os Santos Bay.

Heavy metals (mg Kg^{-1})	Valid N	N[a]	QRV	Average	Minimum	Maximum	Standard deviation
Cd	113	1	0.30	0.22	0.00	2.50	0.25
Co	96	18	0.38	0.36	0.00	2.45	0.67
Cr	111	3	36.55	27.16	0.75	81.35	21.85
Cu	102	12	7.10	5.29	0.30	18.70	4.57
Ni	102	12	4.05	3.22	0.40	9.80	2.24
Pb	111	3	54.37	37.47	8.95	78.30	18.85
Zn	96	18	10.40	7.48	0.00	28.30	6.25

[a] Samples total excluded like anomalies to from the boxplot

Geo-accumulation index and pollution index

Geo-accumulation index results for Cd, Co, Cr, Cu, Pb, Ni and Zn are presented in Figure 2. It was observed that the study area is not contaminated with Cr and Cd;

however, some of the sampling locations showed moderate soil contamination by Pb, Ni, Zn and Cu and high soil contamination by Co.

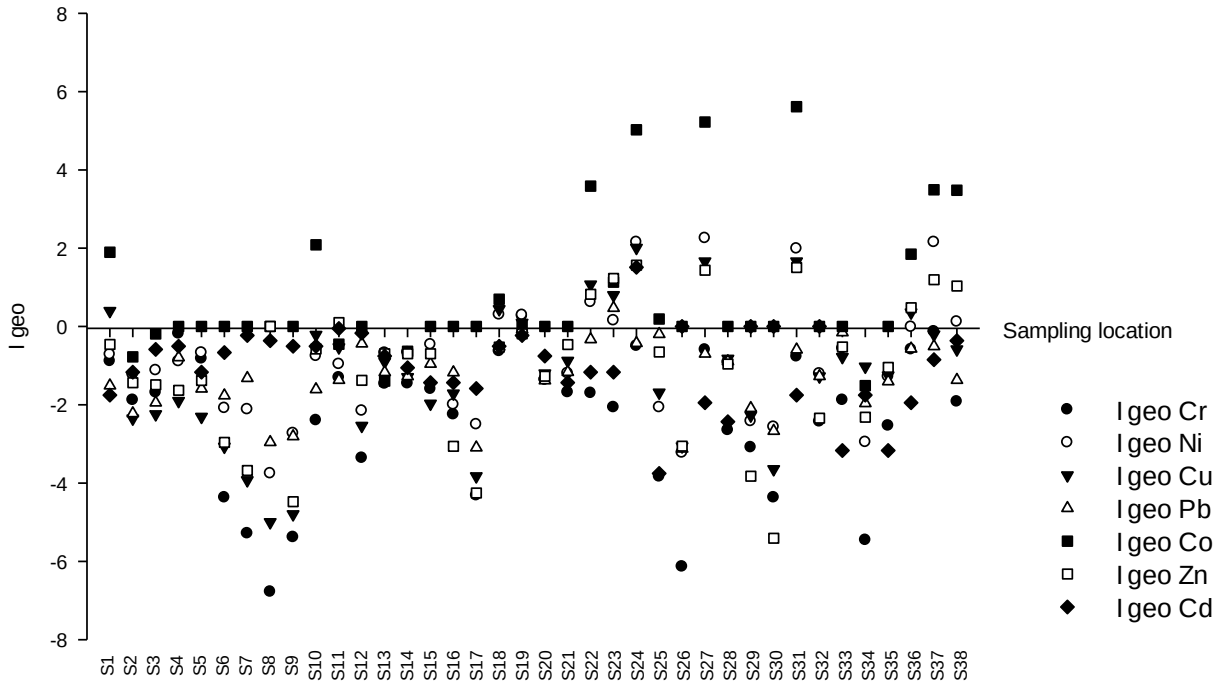

Figure 2. Igeo values of heavy metals at different sampling locations.

Although, the high I_{geo} by Co for S1; S10; S22; S23; S27; S31; S37 and S38, these high indices seems to be originated from a natural source, once these sites showed Fe concentration (32760; 9895; 13170; 12287; 33000; 38195; 24352; 20327 mg kg^{-1} soil, respectively) and all these sites were taken from soils formed from metamorphic rock and sedimentary rocks (shales). Cobalt tends to be most abundant as a substitute ion in ferromagnesian minerals, and therefore has relatively high concentrations in mafic and ultramafic rocks. Higher concentrations of Co may be associated with finer textured sediments (shales) (McLaren, 2005).

The sampling location S24 was classified as unpolluted by Pb and Cr, moderately polluted by Zn and Cd, moderately to strongly polluted by Ni and Cu and extremely polluted by Co. This sample was taken close to the chimney of the Pb smelter plant

demonstrating anthropogenic influence from past atmospheric deposition. The composition of Pb, Zn, Co, Cu, Cr and Cd in the slag abandoned at the Pb smelter plant as determined by X-ray fluorescence in wt% is (3.8), (7.7), (0.04), (0.04) and (0.09), respectively. The Cd content of the slag is (25 mg kg^{-1}) (Machado, 2002). Supposedly, Pb Igeo was low, due high background value that was resulted from high Pb concentration in some soils under anthropogenic influence.

Spatial distribution maps of the PI and IPL for each selected heavy metal in 38 soil samples are summarized in Figure 3. PI for Cd, Co, Cr, Cu, Ni, Pb, and Zn are found ranging 0.0-4.3; 0.0-73.6; 0.01-1.8; 0.04-6.0; 0.11-7.15; 0.1-2.1 and 0.0-4.43 respectively. High PI values for all metals in the North part the bay area demonstrate that those soils are influenced by both anthropogenic and lithogenic source of heavy metals, since that the sampling localized in the North bay, have been taken in Vertisols and Ultisols these soils were formed from shale of lower Cretaceous (mudstone and siltstone) and one site (S24) seems have been influenced by past atmospheric emission from chimney of Pb smelter plant. The spatial distribution maps of the PI for Pb and Cr shown other hotspots in the part East under investigated area closely Salvador city. Atmospheric inputs of Pb and Cr are derived mainly from anthropogenic sources, e.g. vehicular exhaust (Wong et al., 2003; Kuzmanoski et al., 2014).

Pollution load index is a simple comparative means for assessing the level of heavy metal pollution. PLI = 0 background concentration; $0 < PLI \leq 1$ unpolluted; $1 < PLI \leq 2$ moderately to unpolluted; $2 < PLI \leq 3$ moderately polluted; $3 < PLI \leq 4$ moderately to highly polluted; $4 < PLI \leq 5$ highly polluted; $PLI > 5$ very highly polluted (Zhang et al., 2011). In this study, PLI values varied from 0 to 4.60. Most sites sampled, had PLI either zero or close of one except four locations which have PLI higher than two. The difference in PLI indices is due to the enrichment of the heavy metals, being the bay area receive both natural and anthropogenic load. The higher PLI value was found in site closer Pb smelter plant (S24), demonstrating a clear anthropogenic influence, being narrowly controlled by past atmospheric contamination from chimney Pb smelter plant.

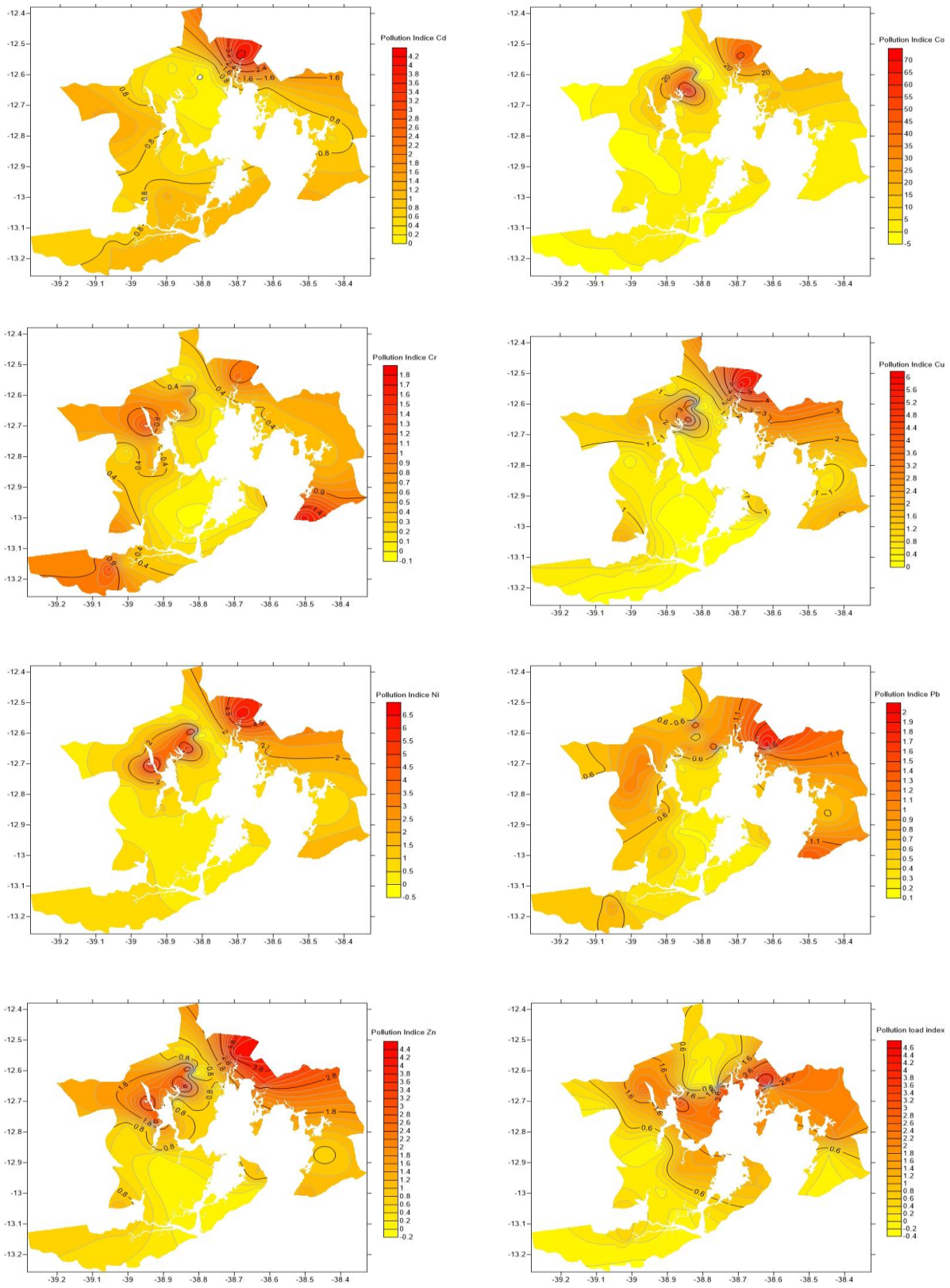

Figure 3. Spatial distribution maps of the PI and PLI of Cd, Co, Cr, Cu, Ni, Pb, and Zn in soils around Todos os Santos Bay-Brazil.

Conclusions

Quality reference values (mg kg^{-1}) calculated for the Todos os Santos Bay soils were as follows: Pb (54.37), Cr (36.55), Zn (10.40), Cu (7.10), Ni (4.05), Co (0.38) and Cd (0.30). The mean natural concentrations of heavy metals found in soils of this economically important region of Brazil were generally lower than those reported in the national and international literature, with exception for Pb concentration, seems to be controlled by past atmospheric deposition from abandoned lead smelter plant.

Geo-accumulation index results indicated that the area is not contaminated with Cr or Cd; however, some locations presented moderate soil contamination by Pb, Ni, Zn and Cu and high soil contamination by Co. PI variation for metals were 0.0-4.3 (Cd); 0.0´-73.6 (Co); 0.01-1.8 (Cr); 0.04-6.0 (Cu); 0.11-7.15 (Ni); 0.1-2.1(Pb), and 0.0-4.43 (Zn). High PI values for all metals in the north area of the Bay demonstrate that soils were influenced by both anthropogenic and lithogenic sources of heavy metals. PLI values varied from 0 to 4.60. The difference in PLI indices is due to the enrichment of the heavy metals, bay area have received both natural and anthropogenic loads.

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CHAPTER II:

ASSESSING SPATIAL DISTRIBUTION AND SOURCES OF METALS IN SOILS OF AN ENVIRONMENTALLY-IMPACTED BAY IN BRAZIL BY MULTIVARIATE AND GEOSTATISTICAL ANALYSES

Assessing spatial distribution and sources of metals in soils of an environmentally-impacted bay in Brazil by multivariate and geostatistical analyses

Abstract

Todos os Santos Bay area is known for one of the most important cases of urban lead contamination in the world. The primary objective of this research was to assess the spatial distribution of Pb, Zn, As, Cd, and Hg in soils of this environmentally impacted bay area using a combination of geostatistical and multivariate analysis in order to distinguish between natural and anthropogenic sources of metals in soils. Were collected 114 topsoil samples (0.0 - 0.2 m depth) from 38 samplings sites and the concentrations of Pb, Zn, As, Cd, and Hg were determined by ICP-OES or AA-FIAS after microwave sample digestion. Results showed that mean values for heavy metal concentrations in soils (mg kg^{-1}) followed the order Pb (39.45) > Zn (12.52) > As (1.95) > Cd (0.23) > Hg (0.09). The PCA performed identified that Pb, Zn, and Cd were associated with the same factor (F1) and had chiefly anthropogenic origin whereas Pb and Zn have also contributions from both sources (natural, lithogenic and anthropogenic). The As and Hg concentrations (F2) were related to the natural component; the parent material underlying the soils (igneous-metamorphic rocks) seemingly confirm this hypothesis. The heterogeneity of sources and the complexity of the spatial distribution of metals in such large areas as Todos os Santos Bay warrant the importance of multivariate and geostatistical analyses in the interpretation of environmental data.

Key words: Soil pollution; soil quality; trace elements; lead; arsenic.

Introduction

Todos os Santos Bay is located at the edge of the third largest city in Brazil, Salvador, capital of Bahia state, being the largest tropical bay of Brazil, with an area of 1112 km^2 and approximate maximum width and length of 32 km and 50 km, respectively (Hatje and Barros, 2012). It has 15 municipalities along its 185 km coastline perimeter

and an urban population over 3 million people (Wagener et al., 2010). The bay is an important economic area of the country with a gross domestic product (GDP) of approximately US$ 23 billion which represents 1.74% of country's GDP (IBGE, 2010).

Besides the increasing problem of pollution in coastal metropolitan areas caused by discharge of industrial and domestic wastes, Todos os Santos Bay area is known for one of the most important cases of urban lead (Pb) contamination in the world which aroused from slag disposal, atmospheric deposition and the overflow of tailings from an abandoned lead smelter plant located in the municipality of Santo Amaro da Purificação. The Pb smelter plant produced up to 32 x 10^6 kg of Pb bars/year. Until 1980 the smelter dross (up to 3% Pb) was freely given to the population for paving yards as well as used extensively by the local council for paving streets and public places, including local schools (Hatje et al., 2006). An epidemiological survey with 396 children living nearby indicates persistently high blood Pb levels in 96% of sampled children (Carvalho et al., 1986). Besides Pb, Cd, Zn, As and Hg are also present in dross and slags (Machado, 2002; Guo et al., 2007; Dung et al., 2014). This serious environmental threat to human health gave rise to several works dealing with marine and sediments pollution (Souza et. al., 2011; Paixão et al., 2011; Costa et. al., 2011; Brito et al., 2012; Krull at al., 2014) but studies on soil contamination in areas surrounding the bay are still very scarce (Santos et al., 2014; Niemeyer et al., 2012).

From a soil protection legislation perspective, it is essential to distinguish between natural and anthropogenic inputs in order to investigate a case of a presumed contamination. The concentration and distribution of heavy metals in soils are dependent on soil parent material (lithogenic source) and anthropogenic sources (Alloway, 2013). These elements are found in minerals of igneous rocks at the time they crystallize and their concentration in soil is also associated with the variability of soil physicochemical properties (Nanos and Martín, 2012). Anthropogenic inputs such as mining, industrial emissions, disposal or leakage of industrial wastes contribute to increase the concentration of heavy metals in soils. Geostatistical methods have been widely used for spatial interpolation of heavy metals in soils and evaluation of contaminated sites (Zhao et al., 2010; Xie et al., 2011; Sun et al., 2013; Dragovic et al., 2014) while multivariate

analysis are useful to assist the interpretation of environmental data (Li and Feng, 2012; Gu et al., 2014). The combination of these statistical tools can be used to assess the distribution of heavy metals in soils and to distinguish between natural and anthropogenic sources (Lu et al., 2012). The knowledge of the natural heavy metal contents in soils and anthropogenic inputs are essential to establish metal soil guidelines that protect environment and human health.

The present study was carried out to assess the spatial distribution and sources of Pb, Zn, As, Cd, and Hg in soils surrounding the Todos os Santos Bay by geostatistical and multivariate analysis. This is fundamental to understand both the natural variability of elements concentration in the environment and the contamination spread across the bay. The results of this study can be useful not only to establish a regional soil background for the studied metals but also to evaluate the potential risks to human health and environment in an economically important and environmentally impacted bay.

Material and methods

Study area

The average rainfall in Todos os Santos Bay ranges from 1400 to 2600 mm with maximum, minimum and average temperatures of 28.2°C; 22.7°C and 25.2°C, respectively. The climate is classified as humid tropical according to Köppen classification. The relative air humidity is high throughout the year, with average indexes ranging from 77% to 85%. January is the driest month while the April-July period exceeds 85% humidity. The bay area is composed predominantly of secondary vegetation (Atlantic Forest) but highly degraded areas and agricultural activities are also common (Guedes and Santos, 1997). In the bay area lies the largest petrochemical complex of southern hemisphere and several chemical, petrochemical, metallurgical and food industries (Souza et al., 2011).

Soil sampling and chemical analyses

Were collected 114 topsoil samples (0.0 - 0.2 m depth) from 38 samplings sites with minimal human activity around the bay (Fig. 1). At each sampling site three composite samples were formed from four individual samples. The sampling design was based on the representativeness of different geologic materials and soil orders throughout the bay area. For soil analysis, approximately 1.0 kg of each soil sample was taken and mixed thoroughly. The soil samples were air-dried and passed through a 2.0 mm-sieve. Portions of 50 g were ground in an agate grinder and sieved through a 0.3 mm sieve.

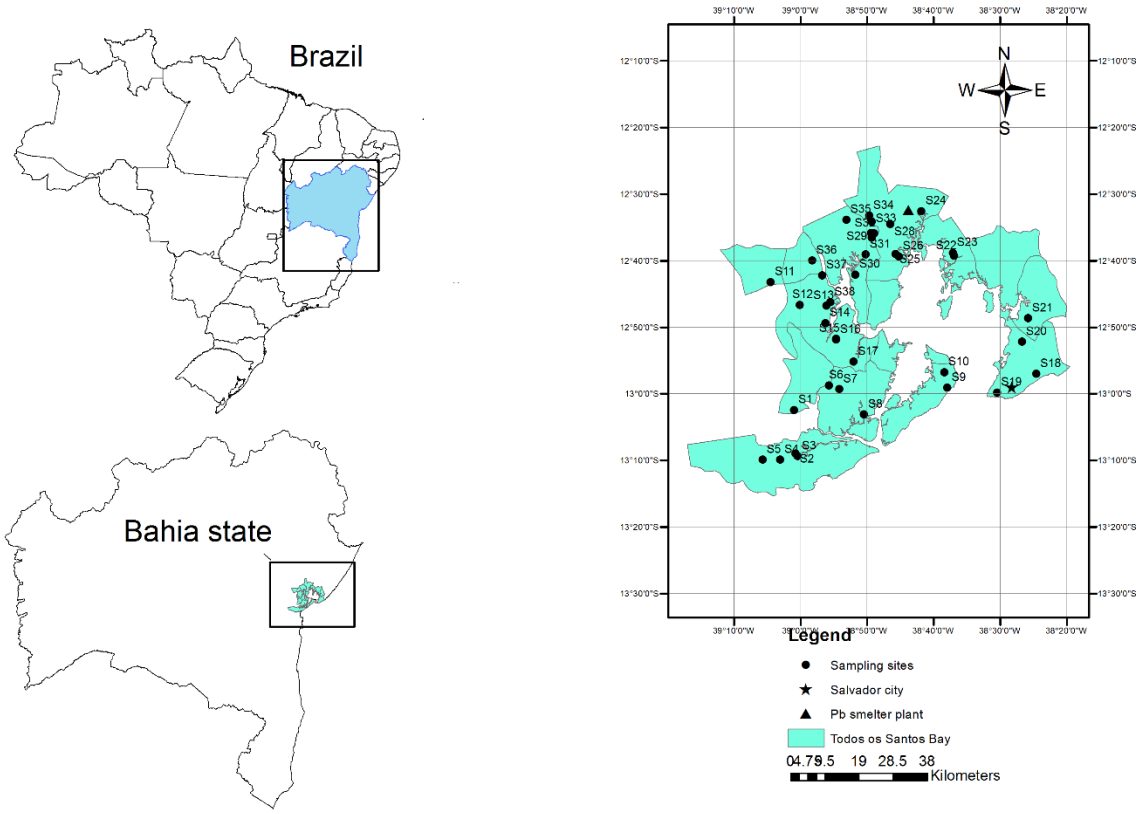

Figure 1. Map of the study area showing the sampling sites.

The soil samples were digested in the mixture of HNO_3, HCl using Method 3051A based on microwave digestion (USEPA, 2007). Concentrations of Pb, Zn and Cd in extracts were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) while concentrations of As and Hg were determined by atomic absorption spectrophotometer coupled hydride generation (AA-FIAS). All the chemicals used were guaranteed reagent grade. Standard reference materials certified for elements content SRM 2709 - San Joaquin Soil from National Institute of Standards and Technology (NIST) was analyzed as part of quality assurance and quality control procedures.

In order to correlate soil characteristics with metal contents in soil, soil pH was measured in a soil:water 1:2.5 ratio, soil organic carbon (SOC) content was determined by modified Walkley-Black method (Nelson and Sommers, 1996) and soil particle-size distribution was determined using Bouyoucos hydrometer method.

Statistical analyses and spatial distribution maps

Basic statistical parameters for soil data were established and the Kolmogorov–Smirnov test was used for data normality assessment. A *p* value higher than 0.05 was used to agree with the hypothesis of the data set belonging to a normal distribution. Geostatistical analysis was performed and spatial distribution maps were made by Kriging interpolation method. Principal component analysis (PCA) was carried out to cluster metals that behaved similarly in order to identify natural and anthropogenic sources. Using factor analysis, factors with eigenvalues greater than 1.0 were extracted by PCA, and factor axes were rotated using the method Varimax normalized. The value of 0.7 for significant factor loadings was established for this study. Varimax rotation was applied because orthogonal rotation minimizes the number of variables with a high loading on each component and facilitates the interpretation of results. Pearson correlation analysis was done to relate concentrations among the various metals as well as to relate such concentrations with soil properties.

Results and discussion

Descriptive statistics and correlation matrix

Descriptive statistics of soil properties and heavy metal concentrations in soils are presented in Table 1. The Kolmogorov-Smirnov test confirmed that soil properties were non-normally distributed ($P< 0.05$), as also inferred by high Skewness values, with exception of soil organic matter (SOM) and sand. Soil pH ranged from 3.9 to 7.3. SOM showed a wide range 7 to 60 g kg^{-1} with a mean value of 29 g kg^{-1}. Soils are texturally classified as sand, sandy loam, loam, clay loam and clay.

Table 1. Descriptive statistics of soil properties and heavy metal concentrations in soils around Todos os Santos Bay, Bahia, Brazil.

	Mean	Min	Max	S.D.[a]	C.V.[b]	Skewness	Kurtosis
pH	4.88	3.9	7.3	0.64	13.06	1.23	1.99
				g kg^{-1}			
SOM	29	7.0	60.0	10.9	37.8	0.24	-0.04
Sand	575.6	40.0	959.0	230.0	39.9	-0.31	-0.27
Silt	157.1	8.0	568.0	115.4	73.5	1.3	1.07
Clay	267.3	10.0	664.0	171.9	64.3	0.31	-1.02
				mg kg^{-1}			
Pb	39.45	8.95	116.25	22.12	56.26	1.02	1.34
Zn	12.52	0.0	46.25	13.18	105.26	1.37	0.69
As	1.95	0.001	12.76	2.19	112.21	2.16	6.39
Cd	0.23	0.0	2.50	0.26	113.23	6.03	51.42
Hg	0.09	0.01	0.29	0.06	68.08	0.98	0.31

[a] Standard deviation
[b] Coefficients of variation (%)

The mean values for heavy metal concentrations in soils (mg kg^{-1}) followed the order Pb (39.45) > Zn (12.52) > As (1.95) > Cd (0.23) > Hg (0.09) (Table 1). The K–S test confirmed that heavy metal concentrations in soils were non-normally distributed. This can be attributed to the presence of disturbed soils associated with some specific human practices (Sun et al., 2013). It is unlikely that natural concentrations of Pb in soils are higher than Zn (Chen et al., 1991; Salonem and Korkka-Niemi, 2007; Preston et al., 2014; Alfaro et al., 2015). Therefore the high Pb concentration found in soils from Todos os Santos Bay is probably due to human activities. Conversely, concentrations of Cd, As and Hg are lower or similar to soil background concentrations commonly reported in Brazil (Biondi, 2010; Preston et al., 2014).

Significantly high correlation coefficients ($P < 0.01$) were found between Pb and Zn and As and Hg (Table 2). Positive correlations between elements may indicate that they have similar sources (Lv et al., 2014). For example, Pb and Zn presented the highest concentrations in both the slag of the smelter plant and the soils of the area. On the other hand, the low concentrations of As and Hg in soils along with the high correlation between them suggest that both elements are derived mainly from the soil parent material. Organic matter showed no correlation with Pb, Zn, and Cd and it was poorly correlated with As and Hg. This is probably due to the low contents of SOM in soil from the study area (Table 1). Pb, Zn, As and Hg showed significant correlation with clay contents, suggesting that clay adsorption may be the main pool retaining metals in soil, despite the low clay content; this result also corroborates the lower metal concentration normally found in sandy soils.

Table 2. Correlations matrix among heavy metal concentrations and some soil properties.

Variables	Pb	Zn	Cd	As	Hg	Sand	Silt	Clay	SOM	Fe
Zn	0.60**									
Cd	0.16	0.36*								
As	0.36*	0.15	0.18							
Hg	0.27	-0.13	-0.12	0.58**						
Sand	0.46**	0.73**	-0.34*	-0.33*	-0.32*					
Silt	0.26	0.69**	0.23	-0.04	-0.20	0.69**				
Clay	0.45**	0.52**	0.30	0.47**	0.57**	0.88**	0.26			
SOM	0.24	0.24	0.19	0.37*	0.52**	0.61**	0.24	0.65**		
Fe	0.42**	0.59**	0.36*	0.55**	0.32	0.78**	0.45**	0.74**	0.52**	
pH	0.67**	0.82**	0.34*	0.40*	0.04	0.60**	0.43**	0.52**	0.22	0.55**

*, **Significant at $P < 0.05$ and $P < 0.01$, respectively.

Factor Analysis - Principal Component Analysis (PCA)

PCA was used to identify the source of heavy metals in soils. The eigenvalues of the first two extracted factors were all greater than 1.0 (Table 3). Therefore the metals can be grouped into a two-component model that accounts for 68.9% of all the data variation. The spatial representation of the two rotated components is shown in Figure 2. The component matrix showed that Pb and Zn were associated with the first factor (F1) whereas the second factor (F2) included As and Hg. Cd was the only metal not demonstrating a clear association with either the first or the second component using a load value of 0.7 as a limite, but loading plots were observed for F1 (0.59) (Table 3).

Table 3. Total variance explained and component matrixes (two principal components selected) for heavy metals in soil.

Component	Eigenvalue	Total Variance (%)	Cumulative Eigenvalue	Cumulative (%)
1	2.000172	40.00344	2.000172	40.0034
2	1.444775	28.89550	3.444947	68.8989
3	0.879889	17.59778	4.324836	86.4967
4	0.404541	8.09082	4.729377	94.5875
5	0.270623	5.41247	5.000000	100.0000

Rotated component matrix

Element	Factor 1	Factor 2
As	0.191560	0.833938
Cd	0.597814	-0.081097
Hg	-0.174589	0.901111
Pb	0.703490	0.455642
Zn	0.896570	0.003585

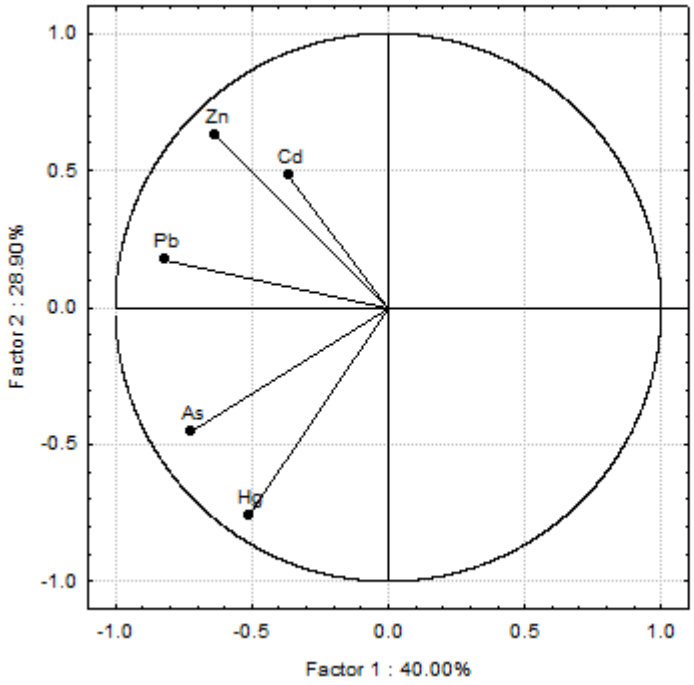

Figure 2. Graphical display of the first two factors of the PCA of heavy metals in soils around Todos os Santos Bay, Bahia, Brazil.

F1 component explained 40% of the total variance of data which is likely to be a mixed source with both anthropogenic and lithogenic origin. This is corroborated by the fact that the point closest to the plant (S24) presents high concentrations of three metals present in the slag (Pb, Zn, and Cd), whereas a point more far away the plant (S28) showed only high Pb concentration, seemly from a lithogenic source.

The component F2 including As and Hg explained 28.89% of the total variance. In such a case, both elements in soils seem to be originated mainly from the underlying parent material. The variability of As and Hg can be controlled by parent material (Wu and Zhang, 2010; Schroeder and Munthe, 1998). Concentrations of As was significantly positive correlation with concentrations of Fe (Table 2), suggesting that As can have been originated from parent material weathering. Zarcinas et al. (2004) using PCA suggested that As and Hg were strongly correlated with Fe, i.e., background variations were mainly due to changes in soil mineralogy.

Spatial distribution of heavy metals

The sites presenting the highest concentrations of Pb, Zn and Cd in soils are found near Santo Amaro da Purificaçao town, where the Pb smelter plant was located. The total concentration of these metals in the abandoned slag is Pb (3%), Zn (12%) and Cd (25 mg kg^{-1}) (Machado, 2002). Machado et al. (2013) reported Pb and Cd soil concentrations higher than 1000 and 10 mg kg^{-1}, respectively, in soil samples collected at 1 km from the smelter plant while soil samples taken 5 km away from the plant presented only 15 and 3 mg kg^{-1} of Pb and Cd respectively. Thus, past atmospheric deposition of dusts coming from the chimney was an important source of Pb, Zn and Cd for the soils near the Pb smelter plant.

These results demonstrate an anthropogenic influence narrowly controlled by past atmospheric deposition from the chimney plant. Cd, Pb and Zn can be transported long distance by air (Lee et al., 2007). Wind direction probably played an important role in spreading contamination from chimney. Taking in account two points close to the plant chimney (S24 and S28, Figure 1), only the one located northeast (S24) presents Cd, Pb, and Zn high concentrations. The preferred direction of the winds in this sector of the Brazilian coast is not surprisingly east-northeast (Lessa et al., 2009).

The spatial distribution maps of Pb and As shown hotspots in Salvador (S19), one of the biggest cities in the country (Figure 3). Atmospheric inputs of Pb are derived mainly from anthropogenic sources, e.g. vehicular emissions (Wong, et al., 2003). On the other hand, there is no remarkable increase in Zn, Cd, and Hg soil concentrations across these urban soils. Pb concentration in surface soils is more linked to atmosphere deposition from vehicles emissions than Cd, Cu, and Zn (Hu et al., 2013).

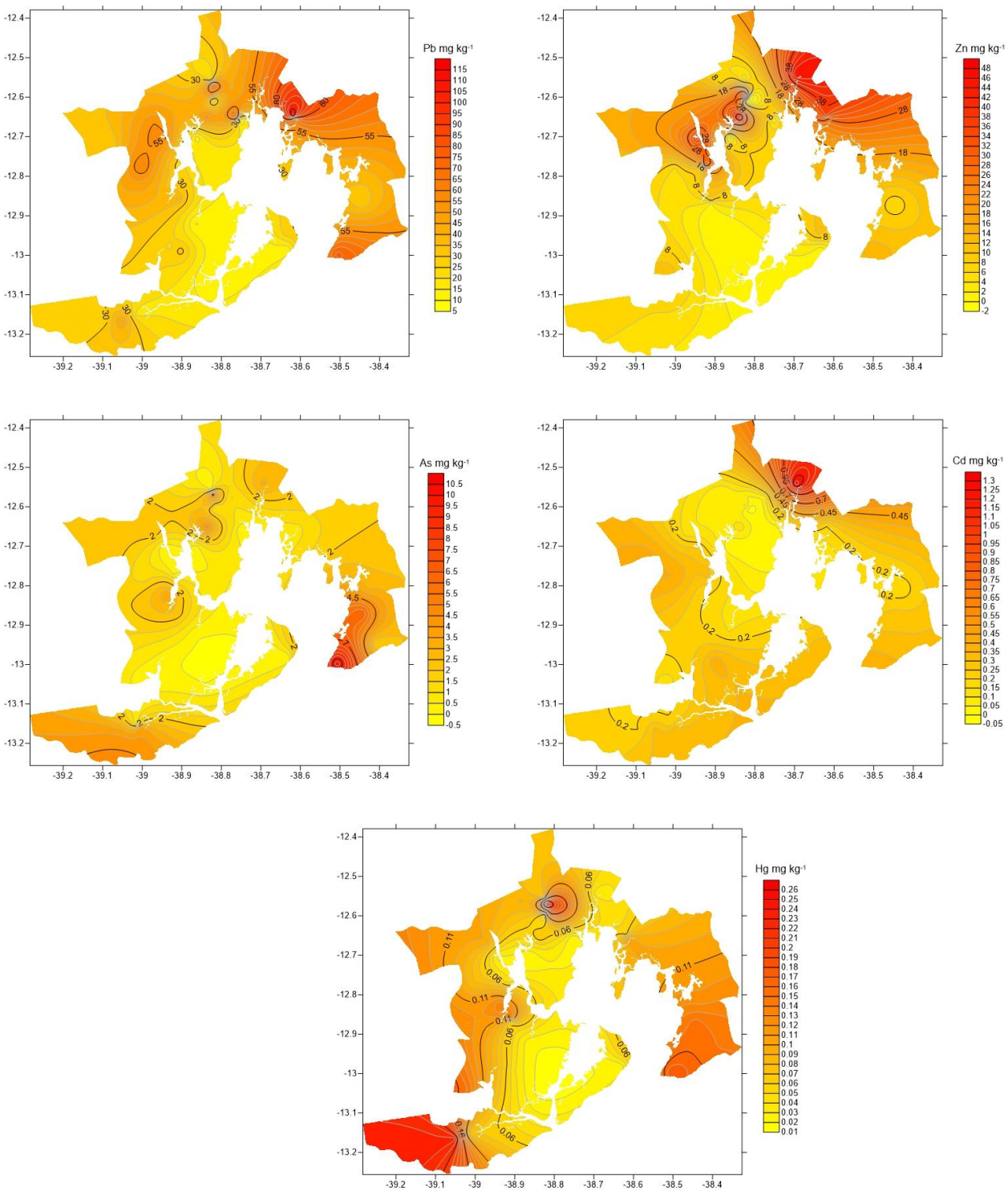

Figure 3. Spatial distribution maps of Pb, Zn, As, Cd, and Hg in the soils around Todos os Santos Bay-Brazil.

The highest As concentrations are found in the east part of the bay (Salvador city, S19) where soils are probably derived from igneous-metamorphic rocks (Figure 4).

Comparing two near samples taken in Salvador (S18 and S19) with distinct soil parent material (sedimentary rock and igneous-metamorphic rock, respectively), only the sample S19 showed high As concentration; thus As concentration can be narrowly controlled by the parent material.

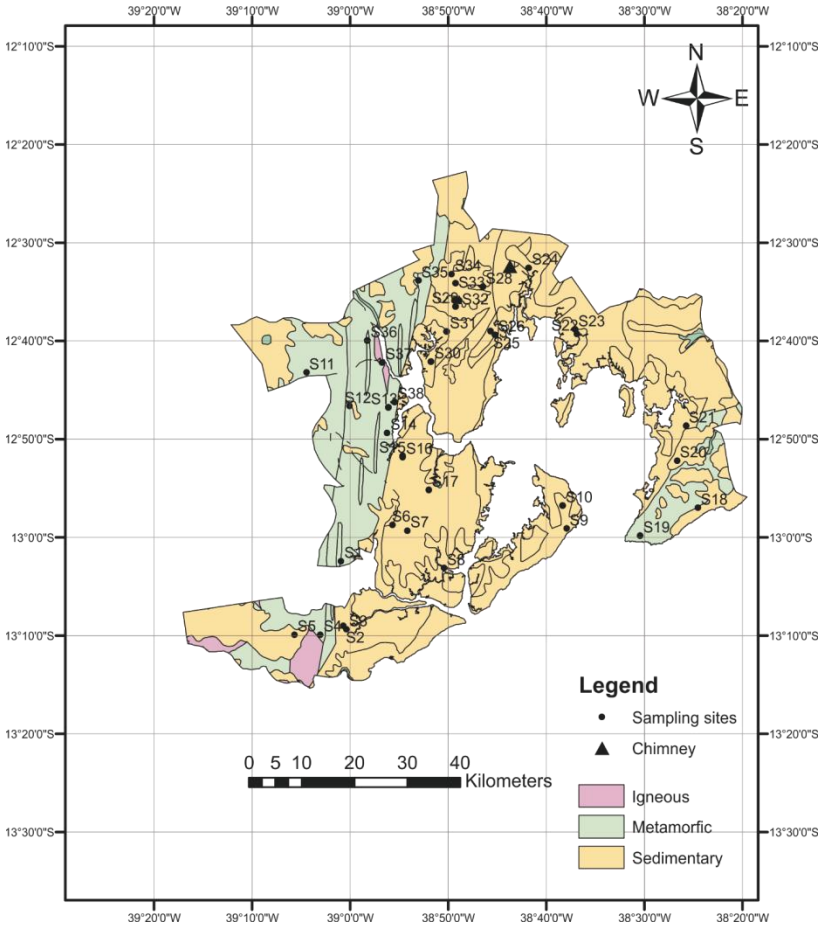

Figure 4. Geologic map of the study area showing the sampling sites.

Sites containing high Hg concentrations are samples of soils derived from sedimentary rocks or black shales (Figure 4). Sedimentary rocks are substantially richer in Hg than igneous rocks (Yudovich and Ketris, 2005). Several works found a distinct decreasing trend in Hg concentration from the city center to the suburban areas (Lu et al., 2010; Fang et al., 2011; Lu et al., 2012; Lv et al., 2014). Our study, on the other hand, shows that Hg had a widespread concentration through all Todos os Santos Bay area,

suggesting that atmospheric Hg deposition did not play an important role in increasing Hg concentration in the urban soils studied.

Conclusions

The results obtained in this work increase our knowledge regarding heavy metal concentrations and their natural or anthropogenic sources in soils of an environmentally impacted, economically important and densely populated bay in Brazil. The PCA performed identified that Pb, Zn, and Cd were associated with the same component (F1) and had chiefly anthropogenic origin whereas Pb and Zn have also contributions from both sources (natural, lithogenic and anthropogenic). The As and Hg concentrations (F2) were related to the natural component; the parent material underlying the soils (igneous-metamorphic rocks) seemingly confirm this hypothesis. Therefore, Pb, Zn, and in lower extent Cd were very likely originated from many years of uncontrolled plant seem emissions that increased the background content of these metals in the soils. Indeed, some sampling sites in the bay area present concentrations of Pb and Cd above the regulatory value (Prevention Value) that can pose an unacceptable risk to human and ecological receptors. Pb and Zn in soils farthest from the abandoned plant smelter hys to be mainly originated from parent material. Geostatistical analysis demonstrates that increased soil Pb concentration in the vicinity of the largest bay city (Salvador) is probably owing to vehicular emission. The heterogeneity of sources and the complexity of the spatial distribution of metals in such large areas as Todos os Santos Bay denote the importance of multivariate and geostatistical analyses in the interpretation of environmental data.

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CHAPTER III:

SOURCES AND CONCENTRATIONS OF LEAD IN SOIL PROFILES OF TODOS OS SANTOS BAY AS RELATED TO Pb ISOTOPES AND ENRICHMENT FACTORS

Sources and concentrations of lead in soil profiles of Todos os Santos Bay as related to Pb isotopes and enrichment factors

Abstract

Todos os Santos Bay area is known for one of the most important cases of lead contamination in the world, with tragic consequences regarding human health and social affairs. The work was carried out to assess the concentration and sources of Pb based on lead isotopes and enrichment factor of soil profiles surrounding Todos os Santos Bay. Forty-four samples of the six soil profiles selected were collected from different horizons. Concentrations of Pb and the isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb were determined on an inductively coupled plasma (quadrupole) mass spectrometry (ICP-MS). The enrichment factor was calculated considering Al and Fe as index elements. Average Pb concentration (15.87 mg kg^{-1}) in uppermost horizons (all six soil profiles under study) of TSB is highest than soil background concentrations commonly reported in Brazil. Pb concentration in all horizons of soil profiles, under study, did not exceed the concentration limit (Prevention Value) according to the soil environmental quality standard of Brazil. Samples feature a wide range of Pb isotope ratios, ranging from 36.71 to 47.38 for $^{208}Pb/^{204}Pb$, 16.86 to 20.59 for $^{206}Pb/^{204}Pb$, 1.10 to 1.31 for $^{206}Pb/^{207}Pb$ and a ranged slightly from 15.00 to 15.65 for $^{207}Pb/^{204}Pb$. The highest EF Fe values are found in profile 1, particularly in the first two horizons (3.74 and 3.01). EF values for others horizons not exceeded the upper limit considered to be in the range of natural variability. Pb concentration in all soil profiles were not influenced by the abandoned lead smelter plant located in the municipality of Santo Amaro da Purificação-BA. The distinct Pb isotopic compositions were clearly related to the different exposure of the sampling sites in relation to atmospheric deposition, and geological parent material.

Key words: Soil pollution; soil quality; lead isotope signature

Introduction

Todos os Santos Bay (TSB) area is known for one of the most important cases of lead contamination in the world, with tragic consequences regarding human health and social affairs. This situation took place after a Pb smelter plant located in the municipality of Santo Amaro da Purificação, Bahia state, Brazil, being abandoned leaving behind tones of a slag rich in Pb, Cd and Zn. As a result, high Pb and Cd concentrations have been found in humans living in nearby towns, especially children (Carvalho et al., 1986; 1995; Tavares et al., 1989; Silvany-Neto et al. 1989, 1996), marine organisms (Amado-Filho et al., 2008; Souza et al., 2011; Barros et al., 2012), soils (Santos et al., 2014; Niemeyer et al., 2012), and sediments (Celino et al., 2008; Hatje et al., 2010; Costa et al., 2011). TSB is located in the vicinity of Salvador, capital of Bahia state and third biggest metropolitan region in the country; surrounding the bay lies the largest petrochemical complex of the southern hemisphere and several chemical, petrochemical, metallurgical and food industries (Souza et al., 2011).

The concentration of Pb in soils depends on soil parent material and anthropogenic inputs (Tyszka et al., 2012; Walraven et al., 2013; Walraven et al., 2014). Distinguishing these two sources is fundamental to both establish soil protection regulations and avoid inappropriate interventions that implies in financial and social unnecessary costs (Horckmans et al., 2005). Thus, assessing concentration and sources of Pb in soils of regions environmentally impacted and economically developed such as Todos os Santos Bay is the paramount importance. Several techniques have been developed in order to differentiate sources of Pb driving topsoil concentrations driving topsoil concentrations and to understand the distribution of the element in soil profiles. Among them, Pb isotopes analyses (Luo et al., 2011; Galušková et al., 2014; Gutiérrez-Caminero et al., 2015) and enrichment factors (Bourennane et al., 2010; Cesari et al., 2012; Zhang et al., 2014) have been extensively used.

Lead isotope ratios are fingerprints for different Pb sources in various environmental compartments such as marine (Zillén et al., 2012; Zaborska et al., 2014) and lake sediments (Zhang et al., 2008b; Sun et al., 2011; Tan et al., 2014), atmosphere

(Kylander et al., 2010; Tomasevic et al., 2013), and soils (Walraven et al., 2014; Wen et al., 2015). The element has four natural stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) being the latter three products of the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, respectively (Komárek et al., 2008). The isotopic composition of Pb is commonly expressed by $^{206}Pb/^{207}Pb$, $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ ratios (Cheng et al., 2010). The $^{206}Pb/^{207}Pb$ is the most commonly used ratio in environmental studies (Komárek et al., 2008). The variations in $^{206}Pb/^{207}Pb$ in different lithogenic and anthropogenic sources are produced because this ratio decreases with the age of the source and increases with its U/Pb ratio (Tyszka et al., 2012). Although Pb isotopes have been routinely used as environmental tracers worldwide their use in studies on soil contamination in Brazil are still scarce (Gioia et al., 2006; Schucknecht et al., 2011).

Although criticized (Reimann and Caritat 2000; 2005; Sucharovà et al., 2012), enrichment factors (EF) have also been widely used to identifying contamination of heavy metals in soils (Bourennane et al., 2010; Zhang et al., 2014; Enamorado-Báez et al., 2015). EF considers the abundance of the element of interest relative to the abundance of a conservative, lithogenic element with no significant anthropogenic source. This ratio is then normalized to the corresponding ratio in the sample at the lowest soil depth (Blaser et al. 2000). A range of normalizing conservative elements (Al, Fe, Ti, Sc) have been employed to calculate EF (Shotyk et al., 2000, 2001; Zhang et al., 2008a; Yao et al., 2013). The conservative elements are mainly derived from aluminum silicate of source material, and are thus less affected by human activities (Xu et al., 2014).

Taking into account the need for environmental studies on largely populated, economically important and environmentally impacted areas in order to protect human health and ecosystems, the work was carried out to assess the concentration and sources of Pb based on lead isotopes and enrichment factor of soil profiles surrounding Todos os Santos Bay. The results of this study can be used to aid on the establishment of Pb regulatory standards to the region as well as to screen out soils that had Pb levels increased by anthropogenic inputs.

Material and methods

Study area

The study area lies within the largest tropical bay of Brazil, with an area of 1112 km^2 and approximate maximum width and length of 32 km and 50 km, respectively (Hatje and Barros, 2012). It has 15 municipalities along its 185 km coastline perimeter and an urban population over 3 million people (Wagener et al., 2010). The average rainfall ranges from 1400 to 2600 mm with maximum, minimum and average temperatures of 28.2°C; 22.7°C and 25.2°C, respectively. The climate is classified as humid tropical according to Köppen classification. The relative air humidity is high throughout the year, with average indexes ranging from 77% to 85%. January is the driest month while the April-July period exceeds 85% humidity. The bay area is composed predominantly of secondary vegetation (Atlantic Forest) but highly degraded areas and agricultural activities are also common (Guedes and Santos, 1997).

Soil sampling and soil profiles

The sampling was designed to represent the different geologic materials and soil orders throughout the bay area (Figure 1; Table 1). Forty-four samples of the six soil profiles selected were collected from different horizons. Soil profiles were open up to 2 m deep or until the parent material (C horizon) was reached. For soil analysis, approximately 1.0 kg of each soil sample was taken and mixed thoroughly. Soil samples were then air-dried and passed through a 2.0 mm-sieve. Portions of 50 g were ground in an agate grinder and sieved through a 0.3 mm sieve.

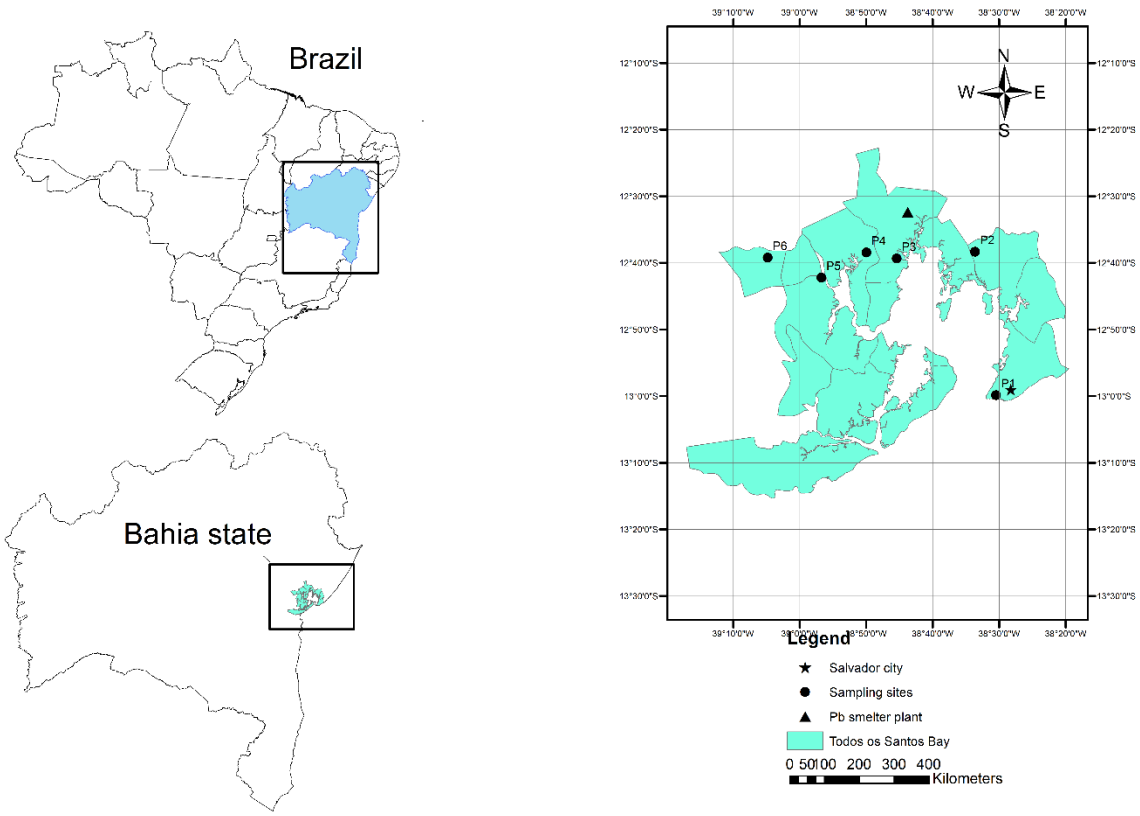

Figure 1. Map of the study area showing sampling sites, abandoned lead smelter plant, and Salvador city.

Table 1. Soil classification and geological materials of samples collected in Todos os Santos Bay, Bahia, Brazil.

Profiles	Soil	Geology/Lithology
1	Typic Hapludults	Metamorphic- granulite
2	Oxyaquic Hapludents	Sedimentary- Sandstone, shale and mudstone
3	Oxyaquic Ultic Haplonthods	Sedimentary- Sandstone and mudstone sandy
4	Oxyaquic Hapludents	Sedimentary- Sandstone and shale
5	Lithic Uderthents	Ígneous- Dacite and rhyodacite
6	Xanthic Hapludox	Sedimentary- Sandstone and mudstone

Soil routine analyses

Selected soil characteristics were measured and correlated with Pb concentrations in soil. Soil pH was measured in a soil:water 1:2.5 ratio, soil organic matter (SOM) content was determined by modified Walkley-Black method (Nelson and Sommers, 1996) and soil particle-size distribution was determined using Bouyoucos hydrometer method.

Lead concentration and isotope analyses

In order to measure Pb concentrations and isotopes, soil samples were microwave digested in a mixture of HNO_3, H_2O_2 using the method described by Sah and Miller (1992). Concentrations of Pb and the isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb were determined on an inductively coupled plasma (quadrupole) mass spectrometry (ICP-MS; Agilent 7500CE, Agilent Technologies, Palo Alto, CA) at the Interdisciplinary Center for Plasma Mass Spectrometry of the University of California in Davis. All the chemicals used were guaranteed reagent grade. Standard reference materials certified for elements content SRM 1640a - Trace Elements in Natural Water from National Institute of Standards and Technology (NIST) and NIST 981 (Common Lead Isotopic Standard) were analyzed as part of quality assurance and quality control procedures for Pb concentration and Pb isotope ratio measurements, respectively. The recovery rate for Pb in the standard reference materials 1640a and 981 (using $^{208}Pb/^{206}Pb$) were 99% and 98.8%, respectively. Along with quality control standards, two points of the standard curve e one sample were analyzed in duplicate every 10 samples as quality controls.

Enrichment factor calculations

Lead sources in the soils of bay area were estimated by the Pb signature and enrichment factor (EF). The EF was calculated considering Al and Fe as index elements according to the following equations (Blaser et al., 2000).

$$\mathrm{EF_{Al}} = \frac{\left(\frac{\mathrm{Pb}}{\mathrm{Al}}\right)\ \mathrm{sample}}{\left(\frac{\mathrm{Pb}}{\mathrm{Al}}\right)\ \mathrm{lowest\ horizon}} \quad (1)$$

$$\mathrm{EF_{Fe}} = \frac{\left(\frac{\mathrm{Pb}}{\mathrm{Fe}}\right)\ \mathrm{sample}}{\left(\frac{\mathrm{Pb}}{\mathrm{Fe}}\right)\ \mathrm{lowest\ horizon}} \quad (2)$$

Where (Pb/ Al and Fe) $_{sample}$ is these metals concentration in the soil horizons. (Pb/Al and Fe)$_{lowest\ horizon}$ is the concentration these elements in the sample collected from the lowest horizon (Br/C or C).

Statistical analysis

Basic statistical parameters (minimum value, maximum value, mean, median and standard deviation) for soil data were established.

Results and discussion

Results of descriptive statistics for soil properties and concentrations of Pb, Al and Fe as well as Pb isotopes ratios are presented in Table 2. Soil pH ranged widely from 4.2 to 8.8. Soil organic matter also showed a wide variation from 3.3 to 67 g kg^{-1} with a mean value of 13.3 g kg^{-1}. Regarding textural classes, soils are sandy loam, loamy sand, sandy clay and clay. The highest concentrations of Al and Fe are typical of tropical highly weathered soils.

Table 2. Descriptive statistics of soil properties, Pb isotopes and Pb, Al and Fe concentrations, average of all horizons of six soil profiles surrounding Todos os Santos Bay, Bahia, Brazil.

	Mean	Min	Max	S.D.[a]
pH	5.6	4.2	8.8	1.16
$^{208}Pb/^{204}Pb$	38.68	36.71	47.38	2.53
$^{207}Pb/^{204}Pb$	15.28	15.00	15.65	0.12
$^{206}Pb/^{204}Pb$	17.98	16.86	20.59	0.86
$^{206}Pb/^{207}Pb$	1.17	1.10	1.31	0.05
		g kg^{-1}		
SOM	13.3	3.3	67.0	12.0
Sand	398.8	14.5	932.4	306.5
Silt	216.1	16.0	535.5	157.4
Clay	385.2	30.0	750.0	205.1
Al	24.8	1.8	53.4	14396.3
Fe	35.9	1.3	82.0	23636.6
		mg kg^{-1}		
Pb	13.65	3.2	44.1	7.8

[a] Standard deviation

Concentration of Pb in soil profiles

Average Pb concentration (15.87 mg kg^{-1}) in uppermost horizons (all six soil profiles under study) of TSB is highest than soil background concentrations commonly reported in Brazil (Biondi, 2010; Preston et al., 2014). Pb concentration in all horizons of soil profiles, under study, did not exceed the concentration limit (Prevention Value) according to the soil environmental quality standard of Brazil.

The differences of lead concentration in six soil profiles were related to the different exposure of the sampling sites in relation to atmospheric deposition, and geological parent material.

The soil profiles 2, 3 and 4 are derived from the same parent material, having a similar Pb concentration in the bottom (Figure 2). These soil profiles (Vertisols and Entisol) were formed from shale of lower Cretaceous (mudstone and siltstone). Among common sedimentary rocks shales have higher Pb abundance (Alloway, 2013). The profile 6 seemingly confirm this hypothesis, although it is also originated from sedimentary rock has less Pb concentration in the bottom than profiles 2, 3 and 4. The Pb concentration in the bottom of profiles 1 and 5 are resembling the values reported in the literature for metamorphic and igneous rock (15 - 20 and 2 - 30 mg kg^{-1}, respectively) (Han, 2007).

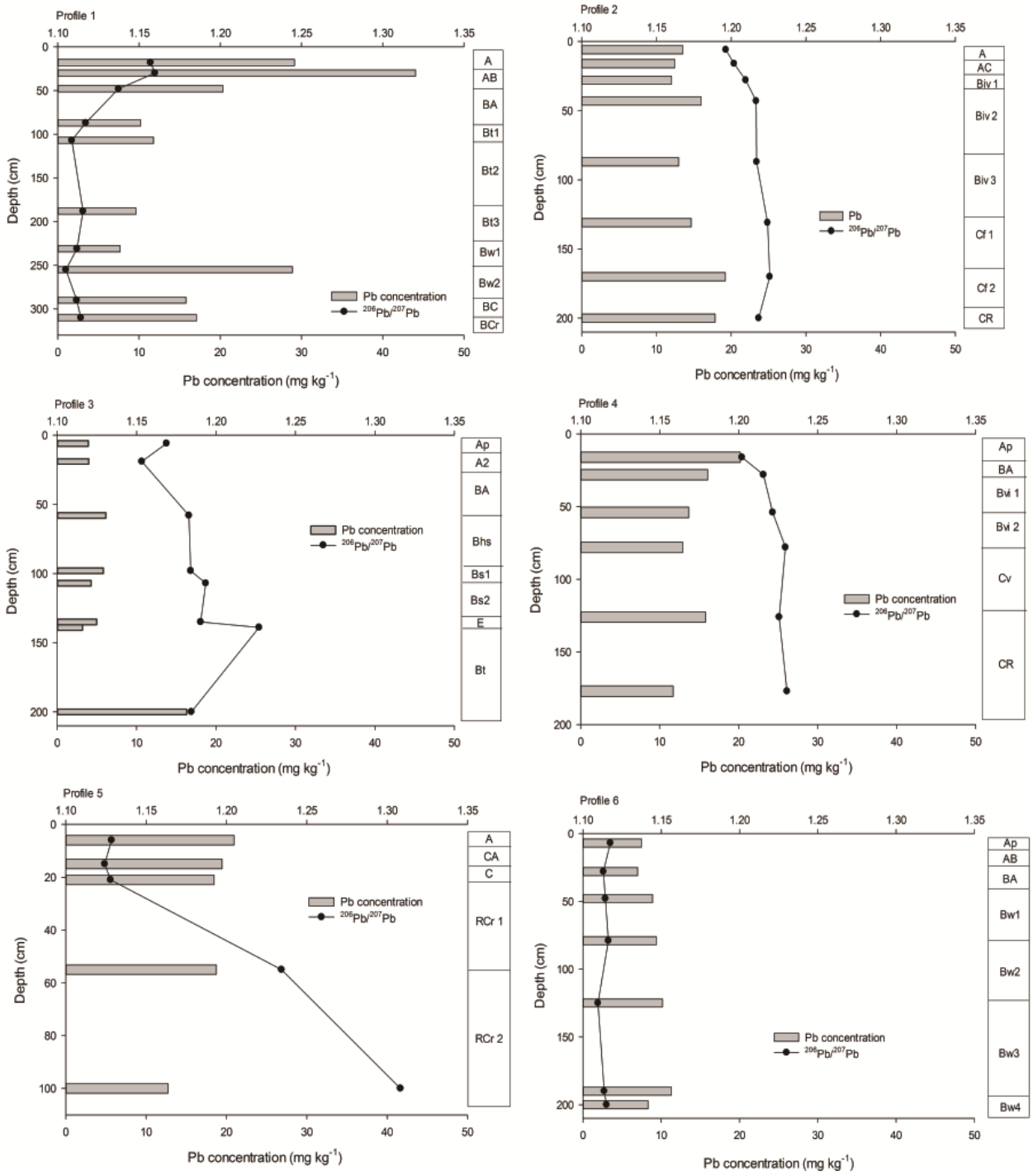

Figure 2. Pb concentration and isotopic ratio ($^{206}Pb/^{207}Pb$) in soil profiles surrounding Todos os Santos Bay - BA- Brazil.

Unlike reported in literature, where the surface horizon has a higher concentration of Pb due to the enrichment in organic matter (Ettler et al., 2011; Tyszka et al., 2012) the

profile 1 showed a highest Pb concentration in the underlying horizon (Figure 2). This phenomenon might be related to the low clay content in uppermost horizon which facilitates downward migration of Pb. Kaste et al. (2005) suggest that inorganic phases play an important role in determining Pb mobility even in surface soils dominated by organic matter.

The profile 6 was classified as Oxisol and its high weathering process seems develop a key role in an even distribution of Pb throughout the profile. The Pb concentration varied slightly from 6.97 to 11.29 mg kg^{-1}.

The horizon Cv of profile 4 showed in increase Pb concentration from bottom (Figure 2), likely due carbonate concentration (it was confirmed by field test using HCl). The primary cause of Pb mobilization in soils appears to be dissolution and oxidation of metallic Pb to form Pb carbonates or sulfate compounds (Cao et al., 2003).

The Pb concentration tended to increase with depth only in the soil profiles 2 and 3, ranging from 13.5 to 17.8 and 3.9 to 16.3 mg kg^{-1}, respectively. This might be attributed to clay distribution within the soil horizons, which increased with depth ranging from 250 and 30 g kg^{-1} uppermost horizon to 600 and 270 g kg^{-1} in the bottom of soil profiles 2 and 3, respectively. Heavy metals form strong bonds with clay minerals (Adriano, 2001). The increased Pb concentration with soil profile depth may also be attributed the distribution of the oxides of Al and Fe down the profile. Al and Fe oxides have a strong affinity for heavy metals (Eze et al., 2010).

Pb-isotopic ratios

In general, samples feature a wide range of Pb isotope ratios, ranging from 36.71 to 47.38 for $^{208}Pb/^{204}Pb$, 16.86 to 20.59 for $^{206}Pb/^{204}Pb$, 1.10 to 1.31 for $^{206}Pb/^{207}Pb$ and a ranged slightly from 15.00 to 15.65 for $^{207}Pb/^{204}Pb$ (table 2). The $^{206}Pb/^{207}Pb$ ratio is lowest than mean values reported in soils of northeastern Brazil of 1.19 (range: 1.08 to 1.39) (Schucknecht et al., 2011). The $^{206}Pb/^{207}Pb$ ratio that is most commonly used in environmental studies because it can be determined precisely analytically and the abundances of these isotopes are relatively important (Komárek et al., 2008). The isotope

ratio $^{206}Pb/^{207}Pb$ revealed a different behavior between soil profiles at each sampling site (Figure 2).

Regardless Pb sources (lithogenic or anthropogenic) the average all horizons of each soil profiles for $^{206}Pb/^{207}Pb$ ratio followed the order soil profile 4 (1.22) > profile 2 (1.21) > profile 3 (1.185) > profile 5 (1.184) > profile 1 (1.12) > profile 6 (1.11).

The topsoil horizons A and AB (profile 1) showed the $^{206}Pb/^{207}Pb$ value of 1.157 and 1.159, respectively. This might be attributed the atmospheric contamination from vehicle emissions. Leaded petrol combustion is a major source of atmospheric Pb; the atmospheric isotopic composition of large cities in Brazil is around 1.16 for $^{206}Pb/^{207}Pb$ (Bollhofer and Rosman, 2000).

The soil profile 5 was localized near of a state highway and has lower $^{206}Pb/^{207}Pb$ values in the uppermost horizons than in the lower part of the horizon (Figure 2). The $^{206}Pb/^{207}Pb$ value of 1.12 demonstrate an anthropogenic influence narrowly controlled by leaded gasoline in the past. When comparing the soil profiles 1 and 5, both have been influenced by atmospheric deposition; however, traffic density and hence vehicle emission seems to be a key factor for the observed pattern of Pb signature values in large and small cities. The isotopic composition ($^{206}Pb/^{207}Pb$) in aerosols of some Brazilian cities, decreasing in area, followed the order Sao Paulo 1.17 > Rio de Janeiro 1.16 > Belem 1.15 > Recife 1.14 > Rio Grande - RS 1.13 (Mirlean et al., 2005; Bollhofer and Rosman, 2000).

The Pb isotopic composition in soil profile 6 showed more stable behavior (Figure 2). This phenomenon seems to be attributed to the high weathering process and the absence of contamination in this soil profile. The relatively constant $^{206}Pb/^{207}Pb$ values show a good agreement with Pb concentration data (Figure 2). The $^{206}Pb/^{207}Pb$ values varied slightly from 1.109 to 1.117.

The abandoned lead smelter plant located in the municipality of Santo Amaro da Purificação-BA used in its processing a galena from the flotation plant of Boquira ore deposit. Each Pb source has its own specific isotopic composition and it is not significantly affected by physico-chemical fractionation (Komárek et al., 2008). Therefore, it could be

possible compare the signature of galena from Boquira ore deposit ($^{206}Pb/^{204}Pb$ 14.74) (Carvalho et al., 1997) with Pb isotope ratios found in soil the profiles studied (Figure 3). All soil profiles have a different Pb isotopic composition of galena from Boquira ore; therefore, association with the atmospheric contamination originated of the chimney Pb plant smelter has not been clearly demonstrated.

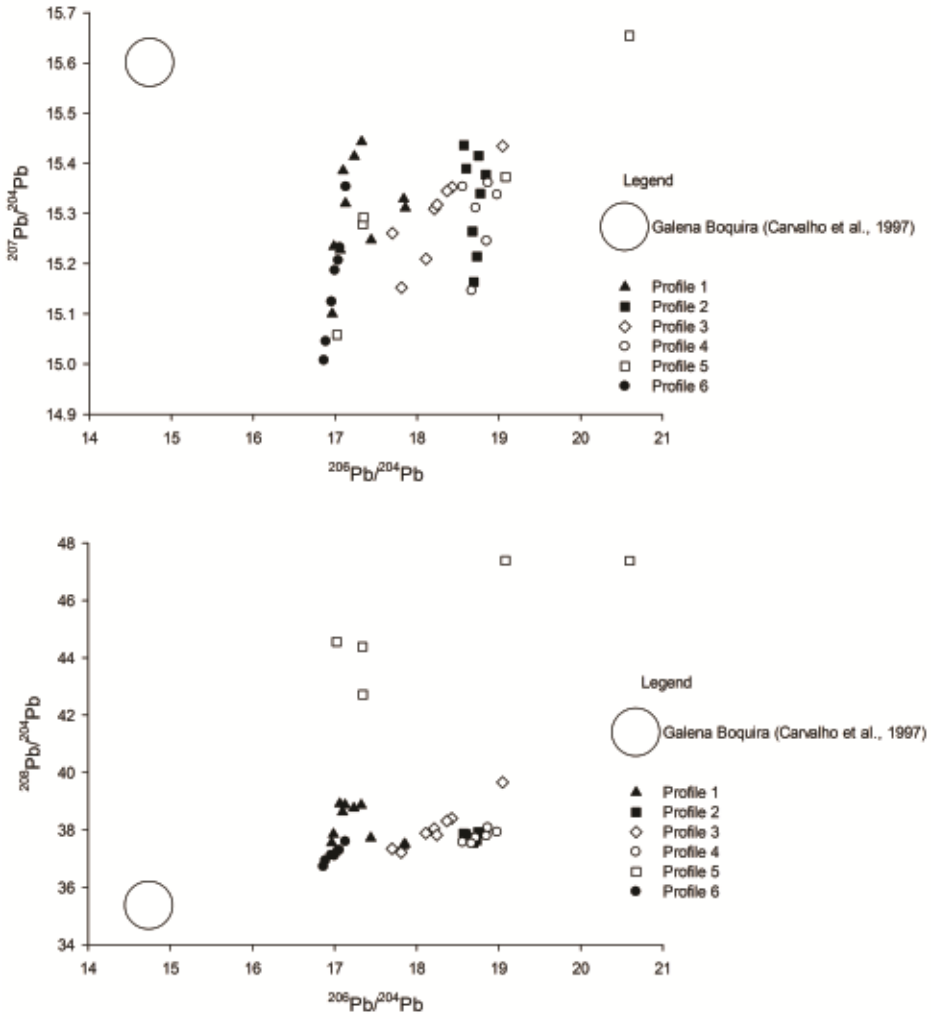

Figure 3. Isotope plot ($^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$) and ($^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$) showing the isotopic compositions of galbena from Boquira ore deposit in different soil profiles surround Todos os Santos Bay-BA-Brazil.

The isotopic composition of Pb in all soil profiles were more radiogenic than galena from Boquira ore (Figure 3). These results demonstrate Pb isotopic ratios were derived mainly from weathered parent material (except the uppermost horizons of soil profiles 1

and 5). The more radiogenic $^{206}Pb/^{204}Pb$ ratio in soil is due the majority Pb is derived from weathered bedrocks and the isotopic composition of Pb is mostly influenced by the decay of ^{238}U to ^{206}Pb (Komarek 2008). In the $^{208}Pb/^{204}Pb$ ratio versus $^{206}Pb/^{204}Pb$ ratio (Figure 3), may be observed a slight clustering between soil profiles 1 and 6, both are the most weathering soils under study (with average all horizons of each soil profile $^{208}Pb/^{204}Pb$ 38.20 and 37.14; $^{206}Pb/^{204}Pb$ 17.29 and 16.99, respectively). A clustering may be also noticed between soil profiles 2 and 4 (with average all horizons of each soil profile $^{208}Pb/^{204}Pb$ 37.79 and 37.76; $^{206}Pb/^{204}Pb$ 18.70 and 18.77, respectively) both have the same parent material (shale of lower Cretaceous mudstone and siltstone). The most radiogenic $^{208}Pb/^{204}Pb$ ratio (45.28) between all soil profiles taking into account the average all horizons of each profile were observed in profile 5, probably originated by the high Th concentration in the parent material. Acid plutonic rocks eg. syenites, have high Th concentration (NRPA, 2000).

The bottom horizons of profile 1 were classified in BC and BCr and both showed a low isotopic composition ($^{206}Pb/^{204}Pb$ = 17.12 and 17.06, respectively Figura 3) likely do not be a signature originated from parent material. This soil profile was developed on the Precambrian crystalline basement rock along the Salvador Fault (Lessa 2000). Highly radiogenic Pb isotope compositions ($^{206}Pb/^{204}Pb$ >19), have been reported above crystalline Precambrian basement (Vikre et al., 2011).

Enrichment factors

Enrichment factors (EF) were calculated in order to assess the enrichment or depletion of Pb in a given soil horizon. The graphics on Figure 4 show the EF regional distribution of those Al and Fe commonly used reference elements in EF normalizations. The resulting distribution patterns are clearly different. For instance, EF Al (Figure 4) shows higher values in profiles 2, 3 and 4 while EF Fe (Figure 4) exhibits higher values in profiles 1, 5 and 6. Therefore, depending on what reference element is adopted the contamination can be differently assessed.

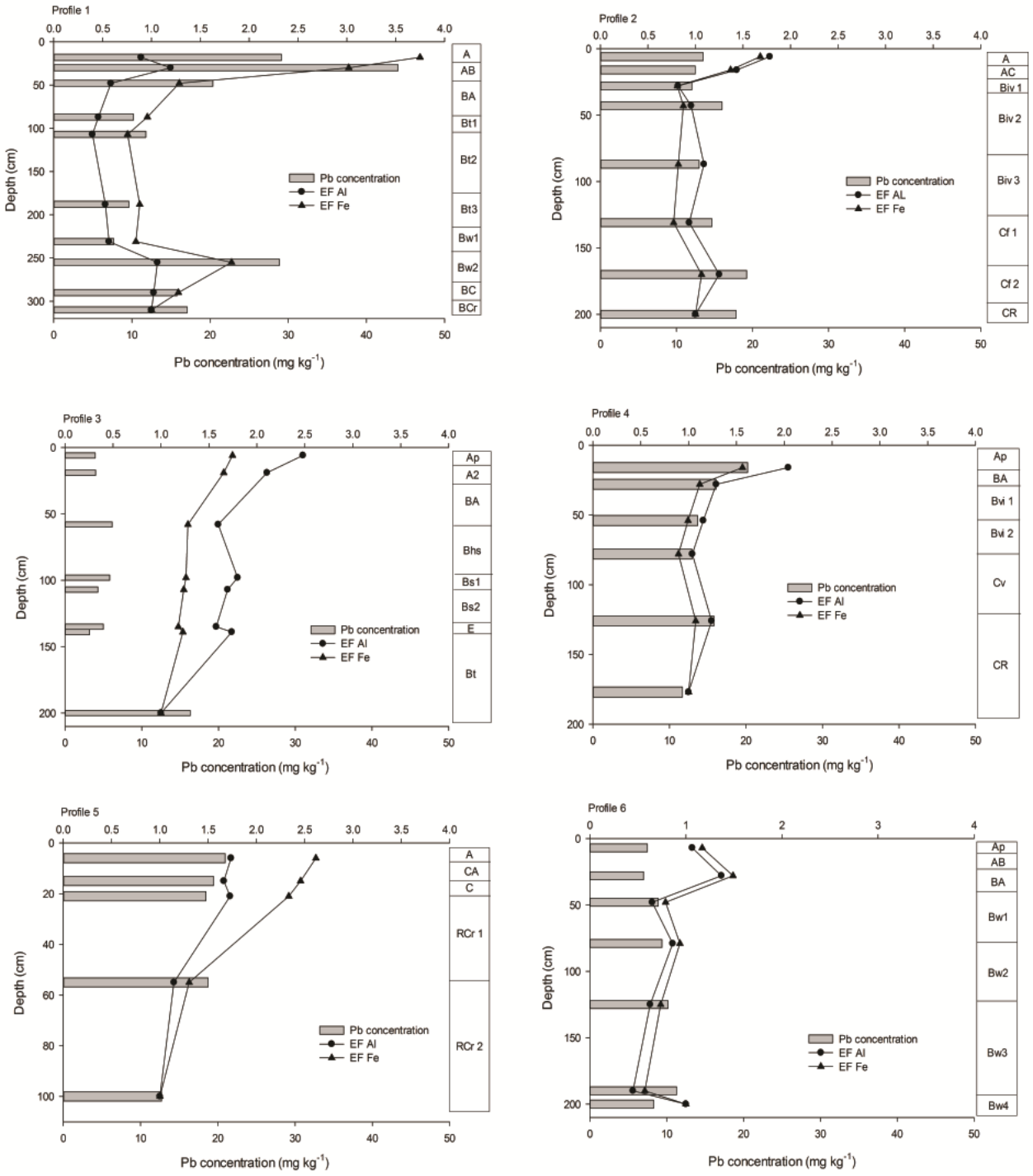

Figure 4. Pb concentration and enrichment factor using Al and Fe as reference elements in soil profiles surrounding Todos os Santos Bay- BA.

When comparing the EF results obtained by normalization with the two different reference elements, a very close behavior is found in all soil profiles studied, with

exception of profile 1 (Figure 4). As different reference elements can be chosen to calculate EF, they should show similar regional distribution patterns; however, different distribution model have been reported (Reimann and Caritat, 2005; Sucharovà et al., 2012). The large difference between EF Al and EF Fe in profile 1 is likely due to the increment in Al concentration in the first three horizons in relation the Al concentration in the lowest horizon.

The highest EF Fe values are found in profile 1, particularly in the first two horizons (3.74 and 3.01) (Figure 4). EF values for others horizons not exceeded the upper limit considered to be in the range of natural variability. EF values ranging between 0.5 and 2 can be attributed natural variability (Hernandez et al., 2003). The Pb anomaly was noticed by the EF calculated relative to the Pb/Fe ratio and confirms the atmospheric deposition from anthropogenic sources.

The profile 5 showed the EF Fe in first horizons (A; CA and C) just slightly exceeding the upper limit attributed to a natural source (2.61; 2.45 and 2.33, respectively) (Figure 4). As discussed for isotopic ratio, this profile is probably contaminated by atmospheric deposition coming from anthropogenic sources.

Conclusions

Pb concentration in all soil profiles were not influenced by the abandoned lead smelter plant located in the municipality of Santo Amaro da Purificação-BA. The distinct Pb isotopic compositions were clearly related to the different exposure of the sampling sites in relation to atmospheric deposition, and geological parent material. Although the average Pb concentration in uppermost horizons (all six soil profiles under study) is highest than soil background concentrations commonly reported in Brazil, Pb concentration in all horizons of soil profiles, under study, did not exceed the concentration limit (Prevention Value) according to the soil environmental quality standard of Brazil.

Both Pb isotopic composition and EF were useful tools to identify the anthropogenic influence in the studied soils. Regarding the use of reference elements in EF normalization, only Fe demonstrated a good agreement with Pb isotopic ratios.

The uppermost horizons that seem to have suffered anthropogenic impacts showed a lower radiogenic $^{206}Pb/^{207}Pb$ ratios (1.15; 1.12 soil profile 1 and 5, respectively) than soil profiles have shown a lithogenic influence (1.19; 1.16; 1.20 soil profile 2, 3 and 4, respectively) with exception the soil profile 6 (1.11).

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