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ARTICLE

Distribution and isotopic composition of lead in bottom sediments from the hydrographic system of Belém, Pará (western margin of Guajará Bay and Carnapijó River)

Distribuição e composição isotópica do chumbo em sedimentos de fundo do sistema hidrográfico de Belém, Pará (margem oeste da Baía do Guajará e Rio Carnapijó)

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ABSTRACT: This study first aimed to evaluate the effect of human activities on the distribution of lead within the estuarine system of Belém, Pará. This was achieved by studying the concentration and isotopic signature of Pb in bottom sediments from the western margin of Guajará Bay and from Carnapijó River, an area removed from the influence of the city of Belém. Secondly, the contribution of suspended matter in the transportation of anthropogenic Pb in Guajará Bay was evaluated. Third, the content and background isotopic signature of Pb in the hydrographic system of Belém was determined. Isotopic signatures of sediments from the western margin of Guajará Bay confirm an anthropogenic contribution of Pb throughout the entire bay. The Pb accumulation process has become more efficient over the last 10 years, and this can be attributed to the rapid population growth of Belém city. Sediments in Carnapijó River are not affected by human activities, and the average concentration values (Pb = 19.6 ± 3.7 mg kg^{-1}) and isotopic signatures ($^{206}Pb/^{207}Pb$ = 1.196 ± 0.004) confirm the background Pb values previously proposed for the river system in the Belém region. The isotopic signatures of suspended matter on the eastern ($^{206}Pb/^{207}Pb$ = 1.188) and western ($^{206}Pb/^{207}Pb$ = 1.174) margins of Guajará Bay show that suspended matter is an efficient Pb transportation mechanism of domestic and industrial wastewater from Belém to the western margin of the Bay due to tidal effects at the confluence with Guamá River.

KEYWORDS: Lead isotopes; Bottom sediments; Belém estuarine system.

RESUMO: *Este trabalho teve como objetivos: (1) avaliar a extensão da ação antrópica sobre a distribuição do chumbo no sistema estuarino da região de Belém, Pará, por meio do estudo da concentração e assinatura isotópica de Pb em sedimentos de fundo da margem oeste da baía do Guajará e do rio Carnapijó, localizado em uma área mais afastada da influência da cidade de Belém; (2) avaliar a contribuição do material em suspensão como meio de transporte de Pb antropogênico na baía do Guajará; e (3) conferir os teores e assinatura isotópica de background de Pb no sistema hidrográfico de Belém. As assinaturas isotópicas dos sedimentos da margem oeste da baía do Guajará confirmam uma contribuição antropogênica para o Pb na escala de toda a baía. O processo de acumulação de Pb se tornou mais eficiente nos últimos 10 anos e deve estar ligado ao crescimento populacional acelerado da cidade de Belém. Os sedimentos do rio Carnapijó ainda não foram afetados pela ação antrópica e os valores médios de concentração (Pb = 19,6 ± 3,7 mg kg^{-1}) e assinatura isotópica ($^{206}Pb/^{207}Pb$ = 1,196 ± 0,004) confirmam os valores de background de Pb anteriormente propostos para o sistema hidrográfico da região de Belém. As assinaturas isotópicas do material em suspensão nas margens oriental ($^{206}Pb/^{207}Pb$ = 1,188) e ocidental ($^{206}Pb/^{207}Pb$ = 1,174) da baía do Guajará mostram que o material em suspensão é um mecanismo eficiente de transporte do chumbo proveniente dos efluentes domésticos e industriais da cidade de Belém para a margem oeste da baía; em razão dos efeitos de maré na confluência com o rio Guamá.*

PALAVRAS-CHAVE: *Isótopos de Pb, Sedimentos de fundo, Sistema estuarino de Belém.*

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INTRODUCTION

The geochemistry of sediments from rivers, estuaries, and coasts provides important information about sediment origin and environmental changes due to both natural and anthropogenic influences. Therefore, chemical composition of river sediments can generally depict a high degree of spatial variation in relation to provenance, river transport, and depositional environment (Roig *et al*. 2005). In addition to geochemical studies of trace elements, the application of radiogenic isotopes is widely employed in hydrological, geological and atmospheric studies, due to their capability to characterize natural and anthropogenic sources (Banner 2004). Lead, in particular, has acquired great importance in environmental studies as it has been demonstrated that, unlike other heavy metals, the isotopic signatures of Pb from anthropogenic and geogenic sources are distinct and can, therefore, be used as tracers of contamination sources for this element (Komarék *et al*. 2008, Kylander *et al*. 2010, Bird 2011).

In recent years, urban growth has occurred in a disorganized manner in the metropolitan area of Belém, and this is directly reflected in the quality of water and sediments in Guamá River and Guajará Bay, which constitute the main hydrological elements from the Belém's estuary system. Guajará Bay is suffering from environmental degradation, and this is gradually increasing due to the accelerated population and industrial growth of the city of Belém, and the related dumping of domestic and industrial wastewater without prior treatment, that causes damage to organisms and sediments (IDESP 1990). In contrast, the Guajará estuary has intense hydrodynamics and therefore a large capacity for pollutant dilution.

Guajará Bay is formed at the confluence of Acará and Guamá Rivers, west of the city of Belém, and extends almost to the island of Mosqueiro. At this point it meets the Bay of Marajó, which with Pará River forms the southern-most estuary system at the mouth of Amazon River. Numerous channels and islands, the largest island of which is the Onças Island, make up the left margin of Guajará Bay and separate the bay from the Pará River. The interaction between the river currents, tides, and waves results in an environment with high-energy hydrodynamic conditions. In this respect, the water dynamics and extreme seasonal variations are important factors influencing the concentration of suspended matter and the complexity of the sedimentation processes (Gregório & Mendes 2009).

The study area is located on the western margin of Guajará Bay between 01° 10'- 01° 33' S and 48°38'- 48°15'W, and includes the islands of Onças, Jararaca, Jararaquinha, Mirim, Paquetá Açu, and Carnapijó River, which is located west of the islands (Fig. 1). The regional climate is hot and humid, with average annual humidity about 87%. Rain occurs frequently in the afternoon and evening, especially from January to April. The area is characterized by geological units of the Neogene and Quaternary periods, which include Miocene sediments of Barreiras formation and post-Barreiras Quaternary and recent sediments. The Barreiras deposits consist of continental siliciclastic sediments including claystones, sandstones, and conglomerates with poorly consolidated ferruginous sandstones (Rossetti 2001). The eastern margin consists of topographically lower area, and the low clay content in sediments shows that Guajará Bay presents a higher-energy hydrodynamic regime (Gregório & Mendes 2009).

Several studies involving Pb concentration and isotopes have been previously conducted in the metropolitan area of Belém. Bollhöfer and Rosman (2000) found an isotope ratio $^{206}Pb/^{207}Pb$ of 1.15 in aerosols in the Icoaraci district, an industrial district located in the northern sector of Belém. This result was considered an indication of anthropogenic contributions. In addition, Moura *et al*. (2004) determined $^{206}Pb/^{207}Pb$ ratios of bottom sediments and soil in three different areas (Fig. 1). Their results showed that in the Maguari Channel, located in the Icoaraci district, the bottom sediments had values between 1.162 and 1.199. In Água Preta Lake, one of the most important potable water supply of Belém, $^{206}Pb/^{207}Pb$ ratios of 1.166 to 1.176 and between 1.192 and 1.194 were obtained, respectively, in bottom sediments near the urban area and from a non-urbanized area. In between, intermediate $^{206}Pb/^{207}Pb$ values of 1.187 to 1.188 were determined. In the Aurá landfill area, which is the main waste disposal site of Belém and surrounding areas, the bottom sediments and soil were found to have a low $^{206}Pb/^{207}Pb$ ratio of 1.145 to 1.174. Moura *et al*. (2004) suggested that high isotopic ratios close to 1.20 reflect the isotopic Pb signature of the natural environment, and that lower isotope ratios indicate anthropogenic contributions related to industrial and urban settlement activity.

Oliveira *et al*. (2013) found Pb concentrations of 3 and 5 mg kg^{-1}, and $^{206}Pb/^{207}Pb$ values from 1.183 to 1.189 in *oligochaete* and *polychaete* organisms in sediments from the eastern margin of Guajará Bay, along the Belém waterfront. Bottom sediments sampled at the mouth of the Una Channel in the Bay (also from the eastern margin of the Bay) had a $^{206}Pb/^{207}Pb$ ratio of 1.167, revealing the contribution from domestic sewage that was discharged by the channel. At the Miramar petrochemical terminal, also on the Belém waterfront, a $^{206}Pb/^{207}Pb$ ratio of 1.188 was obtained; a value possibly related to some incipient impact of the byproducts of oil spreading anthropogenic Pb throughout the environment. At the mouth of the Tucunduba Channel, which empties into Guamá River (southern sector of the city of Belém), bottom sediments showed a $^{206}Pb/^{207}Pb$ ratio of 1.193 (Fig. 1).

Furthermore, Santos *et al.* (2012) obtained $^{206}Pb/^{207}Pb$ ratios in bottom sediments of Guamá River between 1.193 and 1.20 and 1.194 and 1.197, on the left and right margins, respectively. They considered that these geogenic values are not influenced by anthropogenic components. The authors additionally proposed a Pb background value of 18 mg kg^{-1} and a $^{206}Pb/^{207}Pb$ ratio of 1.196 as a natural reference in the hydrographic system of Belém. Locally, on the right margin of this river, $^{206}Pb/^{207}Pb$ ratios between 1.186 and 1.192 were observed and pointed to a specific anthropogenic contribution of Pb from a channel draining the Aurá landfill. On the western margin of Guajará Bay, Pb levels are higher than 28 mg kg^{-1}, and $^{206}Pb/^{207}$ ratios between 1.173 and 1.188 indicate an even higher contribution of anthropogenic sources. The only sample analyzed from the Belém waterfront, on the eastern margin of the Bay, provided the lowest $^{206}Pb/^{207}$ ratio value of 1.172, and contained 37 mg kg^{-1} of Pb. It is noteworthy that this sample came from the mouth of the Val de Cans Channel (Fig. 1), which also discharges untreated urban wastewater in the bay.

The purpose of this study was to evaluate the effect of human activities on the Pb trace metal distribution in the estuarine system of the Belém region, by studying the concentration and isotopic signature of Pb in bottom sediments in two areas: the western margin of Guajará Bay and the Carnapijó River, an area far removed from the influence of Belém metropolitan area. In addition, the study aimed to assess the contribution of suspended matter as means of transporting anthropogenic-related Pb in Guajará Bay, and to ascertain whether the contents and isotopic composition of Pb previously proposed as geogenic Pb (Santos *et al.* 2012) can be considered as a background for the whole river system of Belém.

MATERIALS AND METHODS

A total number of 13 bottom sediment samples were collected using a Russian Peat Borer-type core drill (Souza *et al.* 2008), and 1 sample (sample B5) was collected using a Petersen dredge. These 2 types of samples corresponded respectively to 10 and 5 cm of the surface layer of bottom sediments. Seven points were sampled on the western margin of Guajará Bay (samples 1A-7A), 6 in Carnapijó River (samples B2-B10) and 1 sample (sample B1) at the confluence of Acará River, Carnapijó River and Guajará Bay. These samples were initially stored in a Ziploc bag, before being dried at 50°C and then disaggregated in an agate mortar. A thin fraction (silt + clay) was separated from the samples by classical wet sieving method using a stainless steel sieve of 63 μm (250 mesh).

Two samples of suspended matter were collected in a 100 L container from Guajará Bay, one from the margin of the Belém waterfront (sample MS4) and the other from the western side of the Bay (sample MS3), and allowed to stand for a few days. The water was then filtered using 45 μm cellulose filter paper to determine the presence of suspended matter. The material deposited on the bottom of the container (approximately 0.3 and 0.5 g for MS3 and MS4, respectively) was transferred to a Teflon container and dried in a plate heater at 40°C. Only the isotopic composition of Pb was determined from these samples.

To calculate the percentage of organic matter in the sediments, organic carbon (OC) was determined by oxidizing 300 mg of the sample with 1N potassium dichromate ($K_2Cr_2O_7$) in an acid media (H_2SO_4 + H_3PO_4) at 100°C and, subsequently, performing titration with ferrous ammonium sulfate, using the method proposed by Loring & Rantala (1992).

The total concentrations of Pb, Al and Fe in the fine fraction of bottom sediments were then determined in a commercial laboratory. The standard procedure used was to fully dissolve 0.25 g of a sample using a combination of concentrated acids HF-HNO_3-$HClO_4$-HCl, for subsequent analysis by ICP-MS mass spectrometry. The concentration of exchangeable Pb in the fine fraction of bottom sediments was also determined in the same laboratory, using a standard procedure in which 0.5 g of a sample was leached with a combination of acid at a ratio of 1:3 HNO_3 – HCl (Aqua Regia), and subsequently analyzed with ICP-MS mass spectrometry. During chemical analysis, the analytical quality control procedure used within the laboratory included the analysis of samples in duplicate and against STD OREAS 24P and STD OREAS 45PA reference materials (in-house standard). Details on the procedures are available online on the laboratory's website (www.acmelab.com).

The isotopic compositions were then determined in the Isotope Geology Laboratory (Pará-Iso) at the Geosciences Institute of the Universidade Federal do Pará, according to the experimental procedure described by Lafon *et al.* (1993) and Santos *et al.* (2012). One gram of each sediment sample was leached with 3 mL of HNO_3 5N and stirred during 24 hours, and then leached using HBr 8N. Chromatographic separation of Pb was performed in Teflon micro columns filled with BioRad Dowex AG1-X8 resin, using a 200 – 400 mesh, in HBr 0.5N medium. The same procedure was used for the samples of suspended matter.

The isotopic composition of Pb in some of the samples was determined using mass spectrometry with thermal ionization (TIMS), and for others it was determined using mass spectrometry with Inductively Coupled Plasma (ICP-MS). For the TIMS analysis, purified Pb was concentrated with H_3PO_4 and deposited with silica gel on a rhenium filament. Isotopic analyses were performed in a static mode using a Finnigan MAT 262 model mass spectrometer equipped with multicollectors. $^{206}Pb/^{207}Pb$ ratios were corrected by a discrimination factor of 0.12 ± 0.03% per atomic mass unit, determined from repeated analysis of the reference material NBS 982 (equal atoms). For ICP-MS analysis, the purified Pb was dissolved in 2 mL of HNO_3 3% + Tl (thallium) 50 ppb. Isotopic analysis was then performed using a Thermo-Finnigan Neptune model mass spectrometer with multicollectors. In this mass spectrometer, the $^{205}Tl/^{203}Tl$ ratio was used to correct the isotopic ratios of Pb, from mass fractionation effects according to the exponential law (Platzner *et al.* 2001). Accuracy control of the analyses was performed with repeated analysis of NBS 981 reference material (common lead), and the multi-element Tune-up Reference Solution for Neptune furnished by Thermo Fisher Scientific. The total blanks used to estimate the level of contamination introduced during analytical procedures were always less than 0.1% of the Pb amount of the samples and were therefore negligible.

RESULTS

Detailed information relating to the particle size characterization with Shepard (1954) and Pejrup (1988) diagrams and the mineralogical composition of the clay fraction can be found in Oliveira *et al.* (in press).

The bottom sediments samples are composed mainly of sand and silty-sand, indicating high hydrodynamics depositional conditions. The mineralogical composition of the clay fraction of the bottom sediments showed a predominance of kaolinite, smectite, and illite clayminerals, similar to the composition described in previous studies (Santos *et al.* 2012).

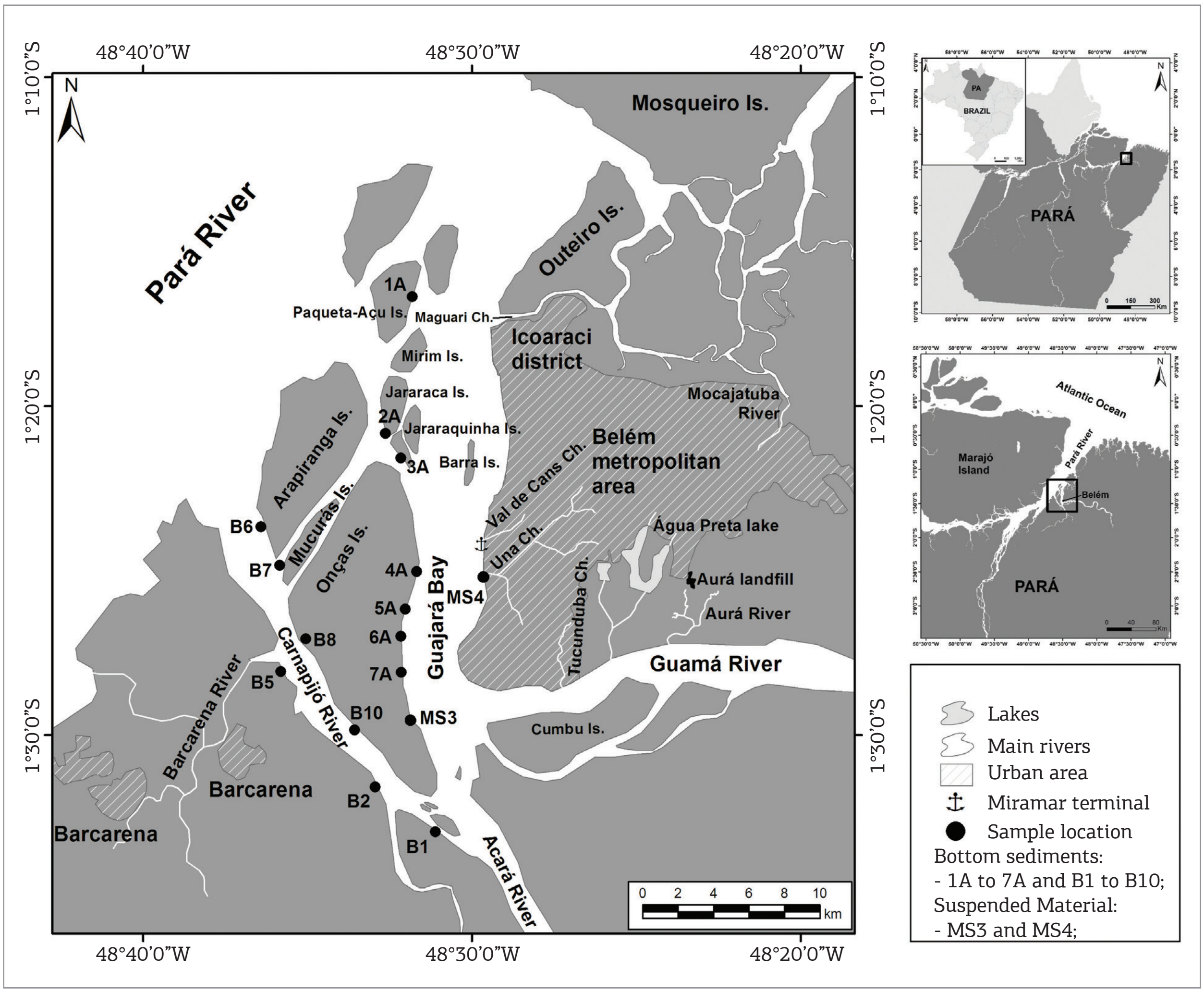


Figure 1. Map of the study area showing the sample location (modified from Pinheiro 1987).

Pb, Al, Fe and organic matter content in the sediments

The total concentration of Pb in samples from the western margin of Guajará Bay ranged from 17.1 to 32.4 mg kg^{-1}, with higher concentrations in the samples taken from the Paquetá Açu island (1A) and Onças island (4A and 6A) (Tab. 1). Concentrations in the sediments of Carnapijó River were slightly more homogeneous, ranging from 14.3 to 23.6 mg kg^{-1}, which overlap the range of the samples obtained from the Bay, but with lower values. The sample from the confluence of Acará River (B1) had a Pb content of 26 mg kg^{-1}, a value that was within the range of samples from the western margin of the Bay (Fig. 2).

Table 1. Total concentrations and exchangeable Pb (mg kg^{-1}), total abundances (weight %) of Al, Fe, and organic matter, determined in the fine fraction of bottom sediments from the western margin of Guajará Bay and Carnapijó River.

Sample	$Pb_{tot.}$	$Pb_{ex.}$	Al	Fe	OM
Western bank of Guajará Bay					
1A (Paquetá Açu Island)	27.3	21.4	5.0	3.6	3.0
2A (Jararaca Island)	25.6	n.d.	4.4	3.2	5.2
3A (Jararaquinha Island)	19.1	11.9	3.6	2.1	2.3
4A (Onças Island)	29.4	16.6	7.0	3.4	5.0
5A (Onças Island)	26.2	18.1	4.8	3.5	1.8
6A (Onças Island)	32.4	18.5	6.8	4.0	5.1
7A (Onças Island)	17.1	9.9	2.9	1.7	4.5
Mean	25.3	16.1	4.9	3.1	3.9
Standard deviation	5.4	4.3	1.5	0.8	1.4
Carnapijó River					
B6 (Arapiranga Island)	15.6	11.0	3.8	2.8	0.9
B7 (Mucurás Island)	22.0	16.3	4.9	3.5	1.3
B8 (Onças Island)	23.6	16.8	6.2	4.2	1.0
B5 (Confluence of river Barcarena)	14.3	9.2	3.0	2.3	0.8
B10 (Onças Island)	19.9	12.8	4.4	3.1	0.9
B2 (Western bank)	22.2	14.9	3.6	3.4	1.2
Mean	19.3	13.5	4.3	3.2	1.0
Standard deviation	3.7	3.0	1.1	0.6	0.2
B1 (Confluence of river Acará)	26.1	19.7	7.1	6.0	1.5

tot.: total concentrations; ex.: exchangeable; OM: organic matter.

The Pb contents determined in the exchangeable fraction of samples from the western margin of Guajará Bay varied from 9.9 to 21.4 mg kg^{-1}, while samples from Carnapijó River also varied from 9.2 to 16.3 mg kg^{-1} (Tab. 1). Again, the sample at the confluence of Acará River (B1) had a Pb content of 19.7 mg kg^{-1}, a value within the range from samples from the western margin of the bay (Fig. 2). Overall, proportionality between the total and exchangeable Pb concentrations was observed ($1.3 < Pb_{total}/Pb_{exchangeable} < 1.8$).

The samples from the western margin of Guajará Bay had a high organic matter (OM) content, with values of 1.8% for the sample on the Onças island (5A) and 5.2% for the sample on Jararaquinha island (2A). The samples from Carnapijó River and those taken at the confluence of Acará River showed lower levels, from 0.8–1.3 and 1.5%, respectively. There were no significant differences in the Al and Fe contents between the two sectors studied, with respective mean values of 4.9 and 3.1% for samples from the western

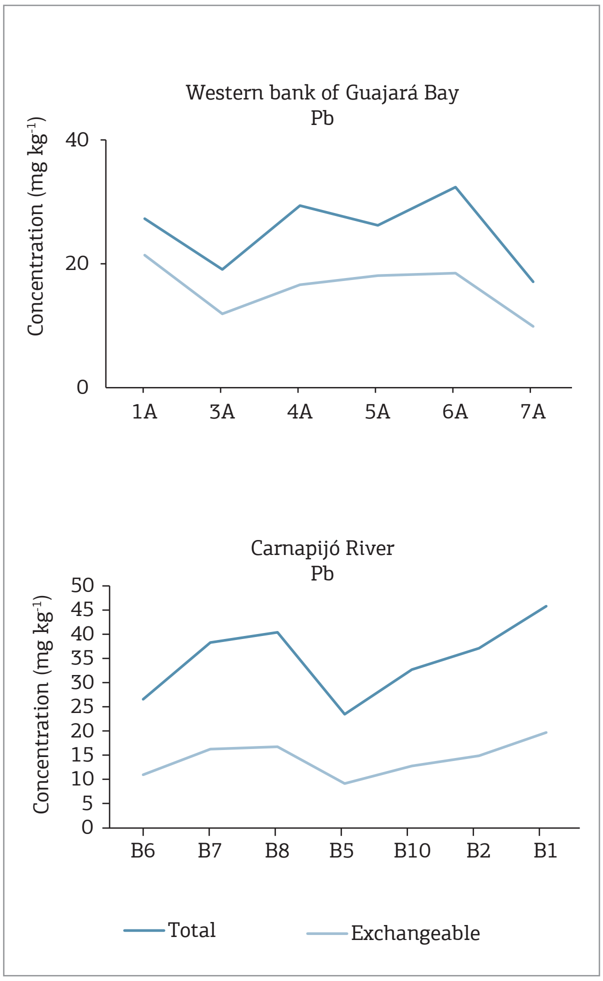


Figure 2. Diagram of the distribution of the total and exchangeable Pb content in bottom sediments. (A) Western margin of Guajará Bay, and (B) Carnapijó River.

margin of Guajará Bay, and 4.3 and 3.2% for sediments from Carnapijó River. The sample from the confluence of Acará River showed the highest values of all samples, at 7.1 and 6.0%, respectively.

The correlation coefficients between the Pb content and the Al, Fe and OM contents were determined using the Estatistica® program. On the western margin of Guajará Bay, Pb showed an excellent correlation with Al and Fe; however, no correlation was observed with OM (Tab. 2). The Carnapijó River samples, showed a very strong correlation with Al and Fe and a good correlation with OM (Tab. 3). When the B1 sample was excluded from the calculation, the correlation with Fe became even greater (Tab. 3).

Table 2. Correlation matrix between the total Pb and Al, Fe, and organic matter (OM) in sediments from the western margin of Guajará Bay. Values in bold type emphasize strong correlation (correlation coefficient > 0.80).

	Pb	Al	Fe	OM
Pb	1.00			
Al	**0.93**	1.00		
Fe	**0.97**	**0.83**	1.00	
OM	0.31	0.38	0.14	1.00

OM: organic matter.

Pb isotopic data of bottom sediments and suspended matter

Analyses of the Pb isotopic compositions from the samples of bottom sediments and two samples of suspended matter are displayed in Table 4.

Table 3. Correlation matrix between the total Pb and Al, Fe, and OM in sediments from Carnapijó River. The values in parentheses show the correlation coefficient excluding the B1 sample obtained from the confluence of Carnapijó River and Guajará Bay. Values in bold type emphasize strong correlation (correlation coefficient > 0.80).

	Pb	Al	Fe	OM
Pb	1.00			
Al	**0.84** (0.75)	1.00		
Fe	**0.88 (0.94)**	**0.93 (0.90)**	1.00	
OM	**0.82** (0.72)	0.66 (0.31)	**0.82** (0.57)	1.00

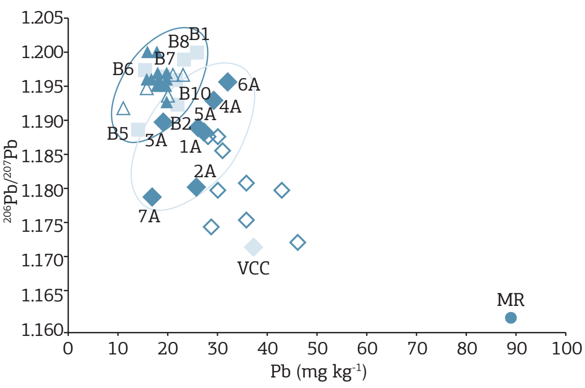
OM: organic matter.

Table 4. Pb isotopic ratios determined by leaching of the fine fraction of sediments from the western margin of Guajará Bay and Carnapijó River, and in suspended matter from Guajará Bay.

Sample	$Pb_{tot.}$	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$	2s
Western bank of Guajará Bay (Bottom sediments)										
1A	27.3	18.607	0.015	15.654	0.019	38.567	0.062	2.073	1.189	0.00001
2A	25.6	18.515	0.015	15.684	0.019	38.500	0.061	2.079	1.181	0.00002
3A	19.1	18.649	0.015	15.674	0.019	38.693	0.062	2.075	1.190	0.00005
4A	29.4	18.728	0.015	15.695	0.019	38.832	0.063	2.074	1.193	0.00002
5A	26.2	18.653	0.016	15.685	0.019	38.696	0.062	2.075	1.189	0.00003
6A	32.4	18.835	0.016	15.752	0.019	39.093	0.064	2.076	1.196	0.00003
7A	17.1	18.465	0.015	15.654	0.019	38.479	0.062	2.084	1.180	0.00004
Suspended matter (Guajará bay)										
MS3	--	18.404	0.0003	15.678	0.0003	38.390	0.001	2.086	1.174	0.00001
MS4	--	18.589	0.0006	15.649	0.0005	38.599	0.0001	2.076	1.188	0.00002
Carnapijó river (Bottom sediments)										
B6	15.6	18.755	0.023	15.662	0.028	38.792	0.093	2.068	1.197	0.00072
B7	22.0	18.683	0.003	15.620	0.003	38.705	0.007	2.072	1.196	0.00001
B8	23.6	18.777	0.001	15.662	0.001	38.834	0.004	2.068	1.199	0.00002
B5	14.3	18.629	0.022	15.668	0.028	38.700	0.093	2.077	1.189	0.00072
B10	19.9	18.726	0.003	15.652	0.003	38.761	0.006	2.070	1.196	0.00003
B2	22.2	18.687	0.022	15.672	0.028	38.748	0.093	2.074	1.192	0.00072
B1	26.1	18.825	0.030	15.688	0.032	38.900	0.102	2.066	1.200	0.00073

The $^{206}Pb/^{207}Pb$ isotopic ratios of bottom sediments from the western margin of Guajará Bay varied from 1.180 to 1.196, and the highest values were found in two samples taken from the Onças island (4A and 6A), with ratios of 1.193 and 1.196 and high Pb concentrations. However, the values of $^{206}Pb/^{207}Pb$ ratios observed in samples from the Paquetá Açu (1A), Jararaca (2A), Jararaquinha (3A) and Onças (5A and 7A) islands were significantly lower, with low concentrations of Pb. In Carnapijó River, $^{206}Pb/^{207}Pb$ ratios of 1.189 to 1.200 were obtained, with low concentrations of Pb. In addition, sample B5 had the lowest Pb isotope ratio. The suspended matter samples from margin of the Onças island (MS3) and from the mouth of the Una Canal (MS4) had $^{206}Pb/^{207}Pb$ ratios of 1.174 and 1.188, respectively.

In the diagram showing $^{206}Pb/^{207}Pb$ ratios versus the total concentrations of Pb (Fig. 3), including the data by Santos *et al.* (2012), and a sample from Mocajatuba River, which represents sediments with the lowest isotope ratio and highest Pb content in the Belém river system ($^{206}Pb/^{207}Pb$ = 1.162; [Pb] = 89 mg kg^{-1}; Moura *et al.* 2004), the Carnapijó River bottom sediments define a relatively homogeneous area. In addition, they have high isotopic ratios that overlap with the field of samples from Guamá River obtained by Santos *et al.* (2012). The bottom sediments from the western margin of Guajará Bay are more dispersed and define a wider field, with lower $^{206}Pb/^{207}Pb$ ratios and higher or equal Pb contents than those of the previous field samples and partially overlap that defined by the bottom sediment samples of Santos *et al.* (2012). However, unlike the samples analyzed by Santos *et al.* (2012), the points do not show a decreasing trend in the isotope ratios, with an increase in the Pb content (Fig. 3).



(◆, ⬭) western margin of Guajará Bay (this study), (■, ⬭) Carnapijó River (this study), (▲) left margin of Guamá River (Santos *et al.* 2012), (△) right margin of the Guamá River (Santos *et al.* 2012), (◇) Guajará Bay: western margin and (◆)VCC - Val de Cans Channel (Santos *et al.* 2012), (●) MR - Mocajatuba River (Moura *et al.* 2004).

Figure 3. Diagram showing Pb (mg kg^{-1}) *versus* $^{206}Pb/^{207}Pb$ of bottom sediments.

DISCUSSION

Relationship between Pb and levels of Al, Fe, and OM

The correlation matrices showed that there was a significant correlation between Pb and Al and Fe elements on the western margin of Guajará Bay and Carnapijó River, which would suggest that Pb is associated with aluminosilicate minerals (clays) and oxides-Fe hydroxides as already demonstrated in previous studies (Saraiva 2007, Nascimento 2007). The absence of a strong correlation between Pb and OM can be explained by the fact that the efficiency of OM in adsorbing chemical compounds essentially depends on its complexing properties (Lima *et al.* 2004). In this respect, it is possible that the existing OM in most of the sediments from the western margin of Guajará Bay and Carnapijó River lacks sufficient complexing properties to fix Pb, and may therefore consist purely of organic plant matter.

Evaluation of anthropogenic Pb contribution

The isotopic data obtained in this study shown significant variations in the isotopic compositions of the Guajará Bay samples. Some samples had low values, which indicated an anthropogenic contribution. These data coincide slightly with the isotopic composition determined by Santos *et al.* (2012), although a similar trending correlation in the increase of the Pb content was not found. Overall, the isotopic signatures suggest an anthropogenic Pb contribution, but the values are not accompanied by a significant increase in Pb contents.

In Carnapijó River, the isotopic composition values of Pb are higher, and within the value levels found in Guamá River, particularly on the left margin. The average $^{206}Pb/^{207}Pb$ ratio is 1.196 ± 0.004 for Carnapijó River, similar to the value observed in the left margin of the Guamá (1.196 ± 0.002, Santos *et al.* 2012), but different from the average value for the western margin of Guajará Bay (1.188 ± 0.006), despite the averages being close and within the error. There was no evidence of an anthropogenic influence in this sector of the Belém hydrographic system, which is located faraway from the urban center. The B5 sample, which was taken from the confluence of Barcarena River, has a slightly lower value. This may be related to its proximity to the mouth of Barcarena River, which drains the urban and industrial hub of the city of Barcarena. The B1 sample from the confluence of Acará River was obtained at the furthest point of all samples from the city of Belém, and has a higher $^{206}Pb/^{207}Pb$ ratio value of 1.20, which is compatible with having a purely geogenic origin of Pb.

Criteria and limitations for the use of the concentration and isotopic signature of Pb in identifying Pb contamination

Sampling modes

The results obtained on our samples from the western margin of Guajará Bay differ from previous results for the same part of the Bay. Even when there were a partial overlapping of the $^{206}Pb/^{207}Pb$ isotope range, the isotopic composition $^{206}Pb/^{207}Pb$ of the samples by Santos *et al.* (2012) showed lower values ($1.172 < {}^{206}Pb/^{207}Pb < 1.188$), which were not evident in our results ($1.180 < {}^{206}Pb/^{207}Pb < 1.196$) (Fig. 3). Furthermore, there was no evidence of a clear relationship between the increased Pb content and the decreased isotope ratio, unlike the evidence provided by Santos *et al.* (2012). It is considered that this difference in behavior may result from the sampling mode. Santos *et al.* (2012) used a Petersen dredge, in which a surface layer of 5 cm of the bottom sediments is collected. Our study established the isotopic signatures using the top layer of 10 cm from a core of bottom sediments, which therefore corresponded to a different time period of deposition. Based on an approximate rate of sediment deposition of 0.7 cm year^{-1} for Guajará Bay (Dias *et al.* 2010; Santos *et al.* 2012, Oliveira *et al.* in press), the 10 cm analysis of the core corresponds to a period of 16 to 18 years of sedimentation, while the sampling by Santos *et al.* (2012) corresponds to a period of only 8 to 9 years. This difference may justify the less anthropogenic signature found in this study, as the population growth of the city of Belém has accelerated over the past 10 years (Carvalho 2012). The lowest isotope ratio in the sediments from Carnapijó River was found in sample B5, which was the only sample collected in this area using a Petersen dredge. Therefore, this could also reflect the differences in the sampling time rather than any anthropogenic influence from the Barcarena city.

Total and partial concentration of Pb (exchangeable)

The anthropogenic Pb component is preferably located in the exchangeable fraction of bottom sediments removed by acid leaching, while geogenic Pb is located in the structure of minerals (mainly silicate minerals), and is obtained by total dissolution of the sample (Bur *et al.* 2009). In studies involving Pb and its isotopic signature, correlations have been established using both the total concentration (Ferrand *et al.* 1999, Bindler *et al.* 2001, Moraes *et al.* 2004, Miller *et al.* 2007, Gioia *et al.* 2006, Dong *et al.* 2010) and the exchangeable Pb fraction (Bird *et al.* 2010; Gioia *et al.* 2006). For the hydrographic system of Belém, results have been presented using either the total Pb (Santos *et al.* 2012) or exchangeable Pb concentrations (Moura *et al.* 2004). In the Pb content vs. isotopic signature diagrams, exchangeable Pb should be normally used because the isotopic signatures are obtained by acid leaching, which preferentially remove the anthropogenic lead component. However, there is a relationship between exchangeable (leachate) and total Pb concentrations, considering that the geogenic Pb value content must remain constant and the total concentration varies only due to the increase in the anthropogenic contribution. Ettler *et al.* (2004) suggested using the Pb/Al ratio instead of Pb contents to identify the presence of anthropogenic Pb. It is evident that in the $^{206}Pb/^{207}Pb$ *versus* Pb/Al diagram, there is a clear tendency of the $^{206}Pb/^{207}Pb$ ratio to decrease as the Pb/Al ratio increases, with respectively lower and higher values for the Guajará Bay samples than the samples from Carnapijó River (Fig. 4). The sample taken from the Acará River confluence, despite having a Pb content similar to that of the more concentrated samples from Guajará Bay, has the lowest Pb/Al ratio and the highest $^{206}Pb/^{207}Pb$ ratio (1.20). This suggests that the Pb/Al ratio is an appropriate parameter to be considered with the isotopic signature of Pb, for use in indicating an anthropogenic contribution. The B2 sample has a distinct behavior, and it stands out because it has the highest Pb/Al ratio and a high isotopic signature ($^{206}Pb/^{207}Pb = 1.192$). However, the fact that this sample has a much higher percentage of sand (>95%) than all other samples (Oliveira *et al.* in press) may have caused the increase in the Pb/Al ratio in relation to the low Al content, and not because of the high Pb content.

Variation in the background for Pb content and isotopic signature

The background value for the Pb concentration of bottom sediments is difficult to determine, especially in estuarine systems with fairly complex hydrodynamics. This undermines the ability to obtain a reliable determination of

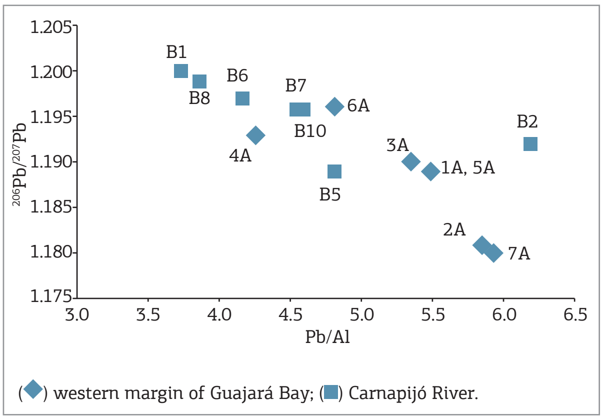


Figure 4. $^{206}Pb/^{207}Pb$ *versus* Pb_{total}(mg kg^{-1})/Al (weight %) diagram of bottom sediments;

anthropogenic contributions, as contamination levels (Geoaccumulation Index, Enrichment Factor etc.) depend on the choice of a reference value for natural Pb (such as the average continental crust value or the natural local value). A background value about 18 mg kg^{-1} for total Pb was proposed by Santos *et al.* (2012) for the Belém hydrographic system with a corresponding $^{206}Pb/^{207}Pb$ isotopic signature of 1.196. It is considered that the average total Pb content of 19.3 ± 3.7 mg kg^{-1} (20.5 ± 4.3 mg kg^{-1}, when including the B1 sample from the confluence with Acará River) and the average $^{206}Pb/^{207}Pb$ ratio of 1.196 ± 0.004 obtained for Carnapijó River also reflect the geogenic background.

Sources and transport of anthropogenic Pb

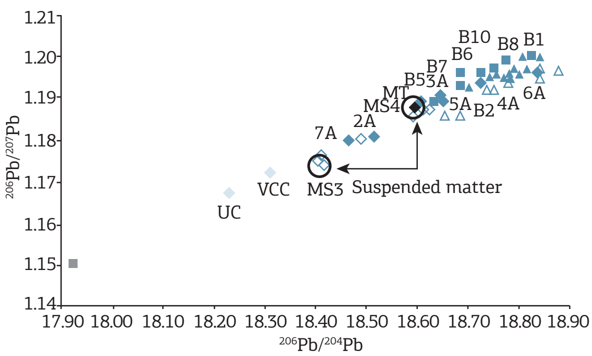
Previous studies have determined that the accumulation of anthropogenic Pb, which is found in natural environments such as lakes, peat bogs, and oceanic waters, is linked to industrial atmospheric sources rather than to the dumping of domestic sewage and industrial waste (Komarék *et al.* 2008, Bollhöfer & Rosman 2000). However, the transport and accumulation of anthropogenic Pb in estuarine environments occurs mainly by sorption to suspended matter (Helland *et al.* 2002, Callender 2011).

Bollhöfer and Rosman (2000) determined an isotope $^{206}Pb/^{207}Pb$ ratio of 1.15 in particulate matter (aerosols) found in the industrial district of Icoaraci, in the northern sector of Belém. It has also been considered that the anthropogenic Pb contribution in relation to atmospheric transport could explain the isotopic signatures of bottom sediments on the western margin of Guajará Bay. However, Santos et al., (2012) dismissed such a hypothesis, and suggested suspended matter to be the main vehicle for Pb transport to the western margin of the Bay.

In $^{206}Pb/^{207}Pb$ *versus* $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$ *versus* $^{206}Pb/^{207}Pb$ diagrams (Figs. 5 and 6, respectively), the isotopic signatures of the two samples of suspended matter from the Belém waterfront were inserted, in addition to those of bottom sediments from Carnapijó River and western margin Guajará Bay (this study). Also inserted were those from bottom sediments obtained from the left and right margins of Guamá River (Santos *et al.* 2012), three samples from the Belém waterfront (Santos *et al.* 2012; Oliveira *et al.* 2013) and the values from aerosols in Icoaraci district (Bollhöfer & Rosman 2000). All samples show a linear arrangement, which is compatible with binary mixing between a geogenic pole, as marked by samples from Carnapijó and Guamá Rivers ($^{206}Pb/^{207}Pb_{average}$ = 1.196), and an anthropogenic pole, marked by the isotopic signature from aerosols obtained in the industrial district. The two suspended matter samples showed distinct isotopic compositions of geogenic Pb, particularly in the case of the sample taken from the western margin of the Bay ($^{206}Pb/^{207}Pb$ = 1.174). This sample was obtained close to that of the bottom sediment sample, which had a more anthropogenic isotopic signature of $^{206}Pb/^{207}Pb$ = 1.170 (Santos *et al.* 2012).

The Pb isotopic signatures point to the southern sector where the Bay is narrower as the area from the western margin of the Bay most affected by the anthropogenic contribution. The main drivers of the deposition and dispersion of sediments in Guajará Bay are the topography, river inflow, and tidal currents (Gregório & Mendes 2009). These authors also identified that the hydrodynamic regime of Guajará Bay is controlled by a flooding stream at the eastern margin of the Bay, and an ebb on the western margin. The suspended matter is thus transported during the flood and ebb tide from the Belém waterfront on the eastern margin to the western margin, and the water discharge from Guamá River promotes the transport in that direction (Fig. 7). This hydrodynamic behavior would thus be responsible for increasing the anthropic influence along the entire length of the Bay, not only on the Belém waterfront, in relation to transport by suspended particulate matter.

The fact that the samples from the Belém waterfront (Una and Val de Cans channels; Santos *et al.* 2012; Oliveira *et al.* 2013) and aerosols (Bolhöfer & Rosman 2000) plot on the same linear trend in both Pb isotopic diagrams (Figs. 5 and 6) indicates that the isotopic signature of the contaminant end-member of industrial aerosols and urban wastewaters is probably similar. In addition, Petroleum byproducts like gasoline or used motor oil may also be involved as



(◆) western margin of the Guajará Bay (this study); (■) Carnapijó River (this study); (o) suspended matter from Guajará Bay (this study); (▲) left margin of Guamá River (Santos **et al.** 2012); (△) right margin of Guamá River (Santos **et al.** 2012); (◇) western margin of the Guajará Bay (Santos **et al.** 2012); Belém riverfront: (◆)VCC - Val de Cans Channel (Santos **et al.** 2012), (◆) UC - Una Channel, (◆) MT - Miramar Terminal (Oliveira **et al.** 2013); (■) aerosols from the Icoaraci area (Bollhöfer & Rosman 2000).

Figure 5. $^{206}Pb/^{207}Pb$ ***versus*** $^{206}Pb/^{204}Pb$ **diagram of bottom sediments, suspended matter, and aerosols.**

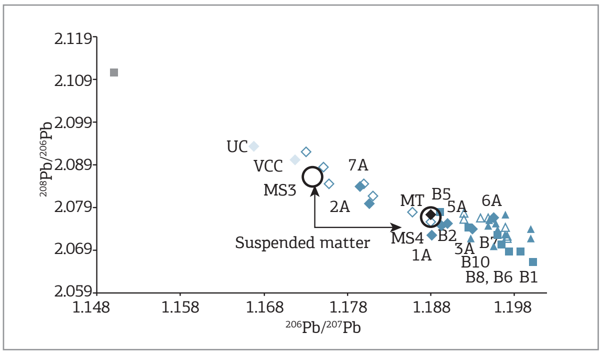


Figure 6. $^{206}Pb/^{207}Pb$ *versus* $^{208}Pb/^{206}Pb$ diagram of bottom sediments, suspended matter, and aerosols (same symbols as those used in Fig. 5).

their Pb isotopic signatures (Lima *et al.* 2010) also fit the linear trend (not shown in the diagrams).

The isotopic composition of suspended matter is within the range of bottom sediment samples from the Bay and from the mouth of the Una and Val de Cans channels, which is compatible with anthropogenic Pb dispersal in the hydrographic system mainly by particulates-associated transport. However, the behavior of the isotopic signatures in the $^{206}Pb/^{204}Pb$ *versus* $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ *versus* $^{206}Pb/^{207}Pb$ diagrams indicates that aerosols cannot be discarded as a possible contributor to the anthropic influence in the bottom sediments of the Guajará bay.

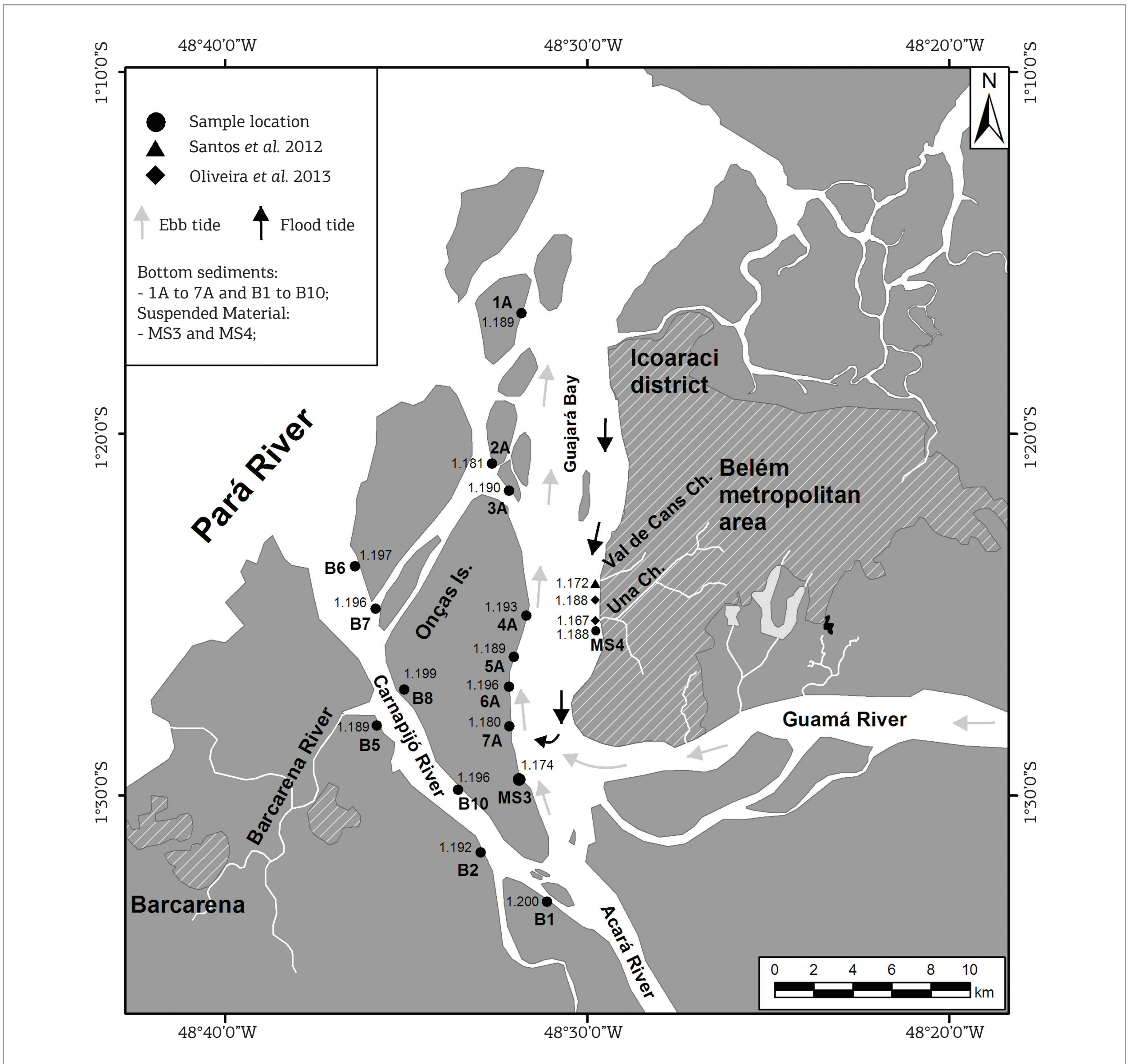


Figure 7. Simplified map of the Belém hydrographic system. $^{206}Pb/^{207}Pb$ values of the bottom sediments and suspended matter are reported, including those of bottom sediments from the Belém waterfront (Val de Cans Channel – Santos *et al.* (2012); Miramar terminal and Una Channel – Oliveira *et al.* (2013)). Tidal and fluvial currents according to Gregório and Mendes (2009) are also displayed.

CONCLUSIONS

The isotopic signatures of sediments from the western margin of Guajará Bay confirm an anthropogenic contribution in relation to the presence of Pb, as shown by Santos *et al*. (2012). However, this contribution is incipient, and as yet no associated environmental damage has occurred.

Throughout the Bay, the accumulation of lead with an anthropogenic origin is related to recent processes that have become more efficient in the last 10 years, as shown by the isotopic signature differences between the Guajará Bay sediments analyzed in this study and those analyzed by Santos *et al*. (2012). It is considered that such changes may be connected to the rapid population growth within the city of Belém.

In Carnapijó River, isotopic signatures show that this area has not yet been affected by human activity. The mean Pb concentration (20.5 ± 4.5 mg kg^{-1}) and isotopic signature ($^{206}Pb/^{207}Pb = 1.196 \pm 0.004$) confirm the background values previously proposed by Moura *et al*. (2004) and Santos *et al*. (2012).

The isotopic signatures of suspended matter from the eastern Belém waterfront ($^{206}Pb/^{207}Pb = 1.188$) and western margin (the island region: $^{206}Pb/^{207}Pb = 1.174$) of Guajará Bay show that domestic sewage from Belém is a major anthropogenic source of Pb in the Guajará Bay bottom sediments, and that this suspended matter is an efficient transport mechanism of metals to the western margin of the bay. In this respect, there is greater accumulation in the southern part, which is the narrowest section of the Bay, due to the effect of the tides at the confluence with Guamá River. However, the isotopic signatures of Pb indicate that aerosols cannot be ruled out as possibly contributing to the anthropogenic influence of lead accumulation in Guajará Bay.

Finally, the isotopic results demonstrate the potential of using the isotopic signature of Pb as a prospective tool for the indication of human activity and the future contamination of bottom sediments, even in a complex hydrodynamic environment within an area that is currently only minimally impacted by human occupation.

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