The use of lead isotope composition as a tool to investigate the anthropogenic impacts on the environment in the metropolitan region of Belém (PA)

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ABSTRACT *The lead isotope composition of sediment and soil samples was used to investigate the anthropogenic impacts on the environment in the metropolitan region of Belém (MRB), state of Pará, Brazil. The sampling program was conducted in three different areas, including a sediment core in the city water reservoir, with indications of anthropogenic contribution of heavy metals to the environment. The $^{206}Pb/^{207}Pb$ ratio of the samples ranged between 1.20 to values lower than 1.16. The highest ratio values were related to bedrock erosion while the lowest values were associated with human induced lead in the environment due to industrial activities and/or urban occupation. As the geogenic and anthropogenic lead isotope composition of the studied sediments and soils samples are quite different, the lead isotopic ratios can be used to investigate anthropogenic impacts on the environment in the MRB. As the changes in the isotopic ratios were more evident than changes in the lead concentration, it is suggested that the use of the lead isotope composition may be more effective for monitoring the anthropogenic heavy metal input to the environment.*

Introduction

The toxicity of lead in the environment has been known for many years, but until recently this toxicity has been generally confined to certain occupations. The more recent use (50 to 100 years) of large quantities of lead in gasoline, pigments, batteries, ceramics, and other industrial products has led to a more widespread exposure of populations to lead concentrations well above natural background levels (Hill 1992, Onel 1991). Where problems of toxicity or pollution occur, tracing the source of the problem can often be difficult because of the multiplicity of sources, both anthropogenic and natural (geogenic). Detailed analyses and mapping of concentrations around the sites of pollution can sometimes delineate source but are often not definitive. The financial and time burdens of such studies can also be extensive. Tracing sources is even more difficult in cases of toxicity where lead from soil, dust, water and air can all contribute to the problem.

Lead does have one advantage over other heavy metals as a tracer of pollution and toxicity, since the relative amounts of the lead isotopes in nature vary significantly. Different sources of lead have different isotopic ratios and the variation in these ratios acts as a tracer for the source of lead.

Natural lead is normally composed of four stable isotopes of masses 204, 206, 207 and 208 with average ratios of 204:206:207:208 = 1:16.97:15.56:36.9. Most of this is the initial compliment of lead incorporated into the Earth at its formation. However, three of these isotopes are also derived from the radioactive decay of both uranium and thorium: ^{206}Pb is derived from the decay of ^{238}U, ^{207}Pb from ^{235}U and ^{208}Pb from ^{232}Th. As a consequence of this radioactive decay the ratios of these three isotopes to ^{204}Pb will vary. Since there are significant amounts of uranium and thorium in the Earth, especially in the crust, and since the half-lives of uranium and thorium are on the order of the age of the Earth, significant amounts of ^{206}Pb, ^{207}Pb and ^{208}Pb have been produced over time. The isotopic ratios of lead in the crust are thus changing with time.

The measured isotopic ratios of lead in any geologic situation will depend on two major factors: 1) the U/Pb and Th/Pb ratios in the geologic environment under consideration; and, 2) the time over which the U, Th and Pb are associated with one another. However, lead has a much different geochemical behavior than either uranium and thorium. Lead can be strongly concentrated under certain geological conditions to produce lead ore bodies, usually in the form of lead sulfides. Uranium and thorium are almost completely excluded from such environments and as a result the isotopic ratios of the lead in such ore bodies remain constant with time after formation. Because every lead ore body forms in what are essentially unique conditions of time, process and source, each ore body will have a unique set of isotopic ratios. Indeed, so sensitive are the isotopic ratios to small variations in conditions that even within ore bodies variations in isotopic ratios can be discerned, such variations being the result of differences in the time of formation, differences in source and differences in processes of formation. Such ore bodies are the major sources of lead used by humans. Thus, anthropogenic lead will have isotopic ratios reflecting these sources and in most cases these ratios are different from other geogenic sources such as soil and bedrock. The ability to distinguish human-use leads from geogenic leads is further aided by geologic and economic constraints. World lead production over the last 75 years has tended to be dominated by a few large well-defined ore bodies. This is reflected in Pb isotopic ratios of human-use leads. Thus, measurement of lead isotopic ratios can in most cases distinguish between anthropogenic sources and geogenic sources as well as distinguish different human sources.

Lead isotopic ratios have been used for over thirty years by isotope geologists as a method for age dating and as a geologic tracer. They have also been used for some time to determine the provenance of archaeological artifacts. The measurement of lead isotopes in environmental samples also began early (Tatsumoto and Patterson 1963, Chow and Johnstone 1965) but was not used extensively until the early 1970's. Pioneering work in using lead isotopes in tracing pollution was done by Ault *et al*. (1970), Chow (1971), Chow *et al*. (1975), Manton (1973, 1977) and Manton *et al.* (1978).

The anthropogenic contribution of lead to the earth on a global scale was investigated by Settle and Paterson (1982), Shen and Boyle (1987), Sturges and Barrie (1989), Rosman *et al*. (1993), Bollhofen and Rosman (2000) among others, using aerosols, corals and ice cores. More detailed lead isotope studies were developed by Hirao *et al.* (1986) in the sediments of Tokyo Bay; Elbay-Poulichet *et al.* (1986) in major French rivers and estuaries; and, Graney *et al.* (1995) in sediments of lakes in the United States. The utilization of organic matter in such studies has been demonstrated by Carignan and Gariepy (1995) using lichens, and Hoven *et al.* (1999) with marine eelgrass (*Zostera marina*).

However, most of the lead isotope investigation has been conducted in the northern hemisphere, and very few data are available for the southern hemisphere. The recent paper of Bollhofen and Rosman (2000) has given a broad picture of the lead isotopic signature for atmospheric lead in the southern hemisphere. The lead isotopic ratios measured in aerosol samples collected in four metropolitan regions of Brazil (Belém, Recife, Rio de Janeiro and São Paulo) indicate $^{206}Pb/^{207}Pb$ ranging from 1.14 to 1.18. These were interpreted as the anthropogenic contribution to the atmosphere (Bollhofen and Rosman 2000).

In this paper, the lead isotope composition of sediment and soil samples in the metropolitan region of Belém (MRB), state of Pará, Brazil was investigated in order to distinguish the lead isotopic signature of the bedrock from that related to the anthropogenic sources. The MRB underwent a fast urban development in the last 40 years, without effective land-use planning (Fig. 1). As result, anthropogenic emission of heavy metals is now a serious threat to the surface water reservoirs and the mangrove ecosystem that surrounds part of this region. Monitoring the anthropogenic heavy metals inputs to the environment in the MRB is fundamental to preserve the water resources and the ecosystems of this region, necessary requirements for developing a sustainable society. Thus, this paper contributes to the use of lead isotope composition as a tool for monitoring the introduction of heavy metals, especially lead, to the environment.

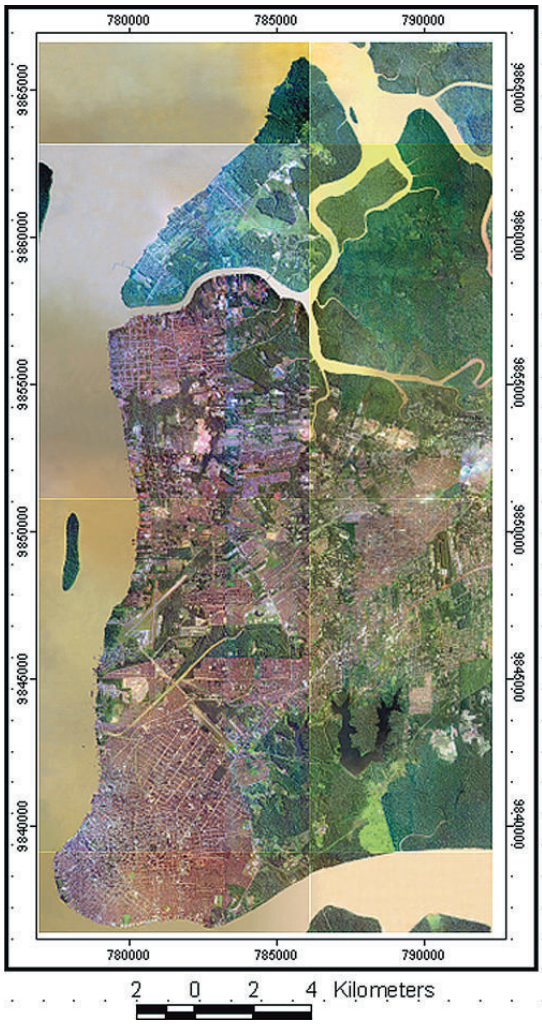

Figure 1 – Aerial photography of part of the Metropolitan Region of Belém (PA) showing the urbanized and not occupied areas (CODEM 1998)

Sampling and analytical methods

Lead isotope studies were carried out in three different areas of the MRB (Fig. 2). In these areas, there were previous indications or strong evidence of anthropogenic influence in the environment. The first area was in the Maguari channel located nearby the Icoaraci Industrial District. Bottom sediments were collected along the channel and also in the Mocajatuba River, a tributary where a large ceramic industry operated for several years. The other area was Lake Água Preta, the main municipal water reservoir of the city of Belém that was built during the first half of the 20th century by damming the Água Preta and Catu creeks (COSANPA, 1982). Although this reservoir is located in the Utinga Environmental Protection Area, there is uncontrolled urban occupation in the catchment basin. Bottom sediments and a sediment core were sampled in the Lake Água Preta. The third studied area was the Aurá Landfill. Soil samples were collected in a former solid-waste disposal site and in an area nearby not used for solid-waste disposal. In addition, bottom sediments of the Aurá River and of the pond that receives the leachate were collected.

Bottom sediments were collected using a precleaned Ekman bottom grab sampler. The top two-centimeter part of the sediments was sampled and stored in a refrigerator until the laboratory treatment. The sediment core was collected with a precleaned 6-meter aluminum pipe. After coring, the sediment core was sectioned and the sub-samples stored in the refrigerator. Before the chemical analyses, the samples were dried in an oven at 50 °C and disaggregated. Around 3 grams of sample were weighed and stored in polyethylene vials for dissolution. The partial extraction of metals was done by adding 20 ml of 3N HNO_3 into the vials, which

were put in a shaking machine for 24 hours at room temperature. Then, the samples were filtered through filter paper, completed to 50 ml in a volumetric flask, and stored in cleaned polyethylene vials. One milliliter of the solution was taken for lead extraction for isotopic analysis. Lead chromatographic separation was done with EIChroM strontium resin (Sr-spec) leaching the samples with HCl (Gale 1996). Lead was loaded onto a single Re filament using phosphoric acid and silica gel. Isotopic ratios were determined by solid source thermal ionization mass spectrometry using a single-collector VG 54E instrument of Pará-Iso, the Laboratory of Isotope Geology of the Federal University of Pará (UFPA). Lead isotope analyses were corrected for fractionation (0.12% per a.m.u.) by repeated analysis of the NIST 982. Total blank procedure was less then 1.5 nanograms. Although it is not an ideal blank level, the amount of sample used for leaching the metals (~ 3 g) overcame this problem. The uncertainties in the isotope ratios are given in 2σ. Lead concentrations were determined by atomic absorption spectrometry using a Perkin Elmer 3300 instrument at the Atomic Absorption Laboratory of the UFPA. The concentrations reported for bottom sediments were corrected for the proportion of silt and clay (< 0.063 mm fraction) in the sample.

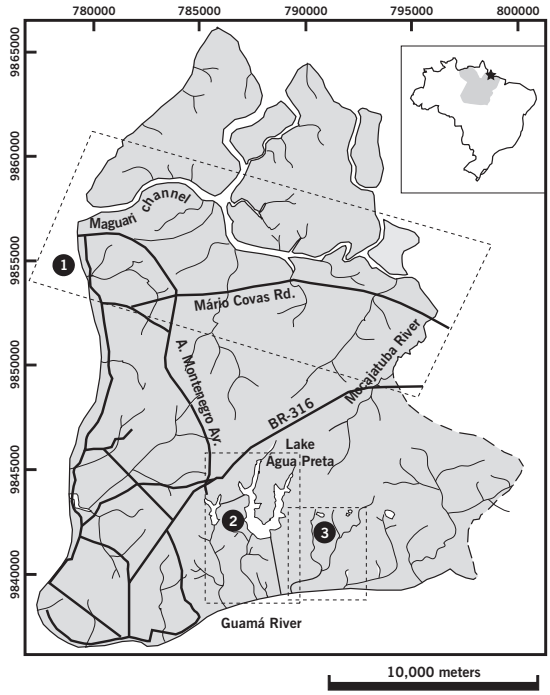

Figure 2 – Simplified planimetric map of the Metropolitan Region of Belém showing the selected studied areas of Maguari channel (1), Lake Água Preta (2) and, Aurá Landfill (3)

Results

Maguari channel area

The lead isotope bottom sediment data of the Maguari channel area are presented in table 1, along with the lead concentration of some samples. The $^{206}Pb/^{207}Pb$ ratios of these samples are located in a simplified map of this area (Fig. 3). Samples 99MG-1 and 99MG-02, collected in the Mocajatuba River, have the highest Pb concentration (30 and 89 ppm) and the lowest $^{206}Pb/^{207}Pb$ ratio (1.179 and 1.162). Near this location, a ceramic industry operated for several years and lead-base substances were used to give the glazing finish to the ceramics. It is important to note that the sample with the highest lead concentration has the lowest $^{206}Pb/^{207}Pb$ ratio. As the sampling goes into the Maguari channel itself, the lead concentration decreases and the $^{206}Pb/^{207}Pb$ increases until values near 1.199 (Table 1).

Lake Água Preta

Initially, a bottom sediment survey was carried out in order to determine the distribution of the Pb isotope composition in the different portions of the reservoir (Table 2). The lowest $^{206}Pb/^{207}Pb$ ratios (1.165) of the bottom sediments are in those portions of the reservoir near the areas of more recent urban occupation (Guanabara and Águas Lindas neighborhoods) and interstate road BR-316 (Fig. 4). The $^{206}Pb/^{207}Pb$ ratio increases to 1.194 as the sampling moves toward the better preserved portions of the lake (Fig. 4). The $^{206}Pb/^{207}Pb$ ratio of the suspended load of the Guamá River, whose water has been pumped into the reservoir since the earlier 1960's, is 1.192 (Table 2 and Fig. 4). This isotopic ratio is similar to the highest values of the bottom sediments of Lake Água Preta. Correlation between the lead concentration and the isotopic ratios is not clear, since the bottom sediments with the lowest $^{206}Pb/^{207}Pb$ ratio display both relatively high and low lead concentration (Table 2).

A sediment core was collected in Lake Água Preta, where the lowest $^{206}Pb/^{207}Pb$ ratio and the highest lead concentration have been found (Fig. 4). Lead concentration and the $^{206}Pb/^{207}Pb$ ratio were determined along the 80 cm of this core (Table 3). The variation of the $^{206}Pb/^{207}Pb$ ratio is clearly seen when the lead isotope data is plotted against depth (Fig. 5). Four segments can be readily identified. From 77.5 cm to 55.7 cm, the $^{206}Pb/^{207}Pb$ ratio is around 1.20. Then, from 55.7cm to 42.6 cm there is a marked decrease in the $^{206}Pb/^{207}Pb$ ratio that

Table 1 – Lead concentration and isotopic composition of the bottom sediment samples of the Maguari channel area

Sample #	Pb (μg/g)	$^{206}Pb/Pb^{204}$	$^{207}Pb/Pb^{204}$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$
99MG-01	30	18.453 (23)	15.671 (30)	38.478 (94)	1.1787 (01)
99MG-02	89	18.152 (22)	15.635 (24)	38.092 (91)	1.1624 (09)
99MG-03	12	18.491 (22)	15.684 (28)	38.572 (94)	1.1805 (07)
99MG-04	14	18.450 (23)	15.689 (29)	38.549 (95)	1.1773 (02)
99MG-05	12	18.561 (23)	15.676 (28)	38.649 (93)	1.1854 (12)
99MG-06	9	18.719 (23)	15.714 (28)	38.878 (93)	1.1928 (08)
99MG-08	11	18.560 (27)	15.730 (28)	38.713 (93)	1.1812 (15)
99MG-07	23	18.730 (23)	15.702 (29)	38.860 (94)	1.1944 (02)
E3*	–	18.892 (24)	15.804 (30)	39.184 (966)	1.1971 (03)
E2*	–	18.880 (26)	15.780 (16)	39.152 (99)	1.1989 (03)
E1*	–	18.844 (24)	15.782 (15)	39.100 (104)	1.1962 (03)

*Data from Belucio (1999)

reaches 1.174. From 42.6 cm to 15.3 cm the $^{206}Pb/^{207}Pb$ ratio continued to decrease, but at a lower rate, to a value of 1.164.

From this point, this isotope ratio increases to 1.184 at the top of the profile. The lead concentration does not display the same kind of variation along the profile. Only in the last 10 cm of the top of the core does the content of lead in the sediment increase significantly, reaching values over 50 μg/g (Table 3 and Fig. 5).

Aurá landfill

Four samples were collected in the Aurá landfill (Fig. 6 and Table 4). A soil sample of a former solid waste disposal site not used for more than 10 years (GD-04), gave a $^{206}Pb/^{207}Pb$ ratio of 1.145. Another soil sample (GD-02), collected in an area not affected by the solid waste disposal site, gave a $^{206}Pb/^{207}Pb$ ratio of 1.202. In a bottom sediment sample collected in the pond that receives the leachate from the landfill, the $^{206}Pb/^{207}Pb$ ratio was 1.174, and in a

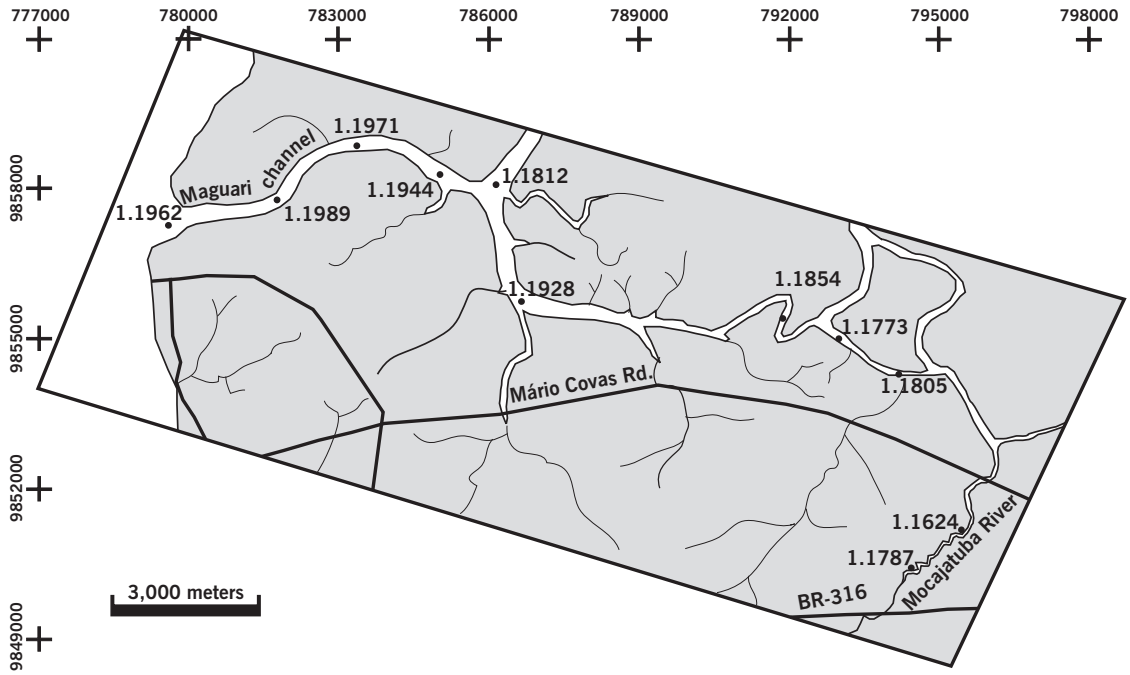

Figure 3 - $^{207}Pb/^{206}Pb$ isotope ratio of the bottom sediments of the Maguari channel area

Table 2 – Lead concentration and isotopic composition of the bottom sediment samples of Lake Água Preta and of the suspended load of the Guamá River

Sample #	Pb (μg/g)	$^{206}Pb/Pb^{204}$	$^{207}Pb/Pb^{204}$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$
AP-01	19	18.265 (22)	15.685 (28)	38.401 (92)	1.1657 (02)
AP-02	20	18.340 (23)	15.697 (29)	38.491 (93)	1.1676 (03)
AP-03	33	18.621 (22)	15.692 (29)	38.725 (94)	1.1880 (04)
AP-04	32	18.769 (22)	15.762 (29)	39.055 (94)	1.1922 (02)
AP-05	13	18.706 (22)	15.706 (28)	38.852 (93)	1.1925 (02)
AP-06	30	18.762 (23)	15.732 (28)	38.972 (94)	1.1942 (02)
AP-07	36	18.747 (22)	15.726 (29)	38.927 (94)	1.1936 (02)
AP-08	38	18.398 (21)	15.666 (28)	38.444 (92)	1.1758 (01)
AP-09	51	18.284 (21)	15.677 (28)	38.336 (92)	1.1676 (02)
AP-10	39	18.650 (23)	15.735 (28)	38.863(93)	1.1867 (02)
AP-11	18	18.776 (23)	15.742 (29)	39.004 (93)	1.1943 (02)
Guamá River	–	18.715 (25)	15.714 (31)	38.855 (96)	1.1922 (02)

bottom sediment sampled in the Aurá River this ratio was 1.193 (Table 4).

Discussion

The $^{206}Pb/^{207}Pb$ ratio of different types of samples collected in the MRB ranges from 1.145 to around 1.20. Plotting the data presented for the MRB in a $^{206}Pb/^{207}Pb$ *vs* $^{206}Pb/^{204}Pb$ diagram, the samples lie on a straight line, which can be interpreted as a mixing line with two end members (Fig. 7). The lead isotopic ratios of these end members can be estimated using the available data for the MRB. One of the end members must have a $^{206}Pb/^{207}Pb$ ratio lower than 1.16, perhaps reaching 1.14, while the other one has a $^{206}Pb/^{207}Pb$ ratio around 1.20.

This suggests the contribution of two different sources of lead for the sediments of the MRB. One source is probably related to the erosion of the bedrock ($^{206}Pb/^{207}Pb \approx 1.20$), and the other, to the anthropogenic contribution ($^{206}Pb/^{207}Pb < 1.16$), mainly during the last 40 years.

The sediment core in Lake Água Preta is the data set that best shows the contribution of the geogenic and the anthropogenic sources. The variation of the $^{206}Pb/^{207}Pb$ ratio probably recorded the history of the lead incorporated into the lake sediments, since the reservoir was built almost 100 years ago. Unfortunately, it was not possible to perform a Pb-210 analysis of this sediment core in order to determine the rate of sediment deposition in Lake Água Preta

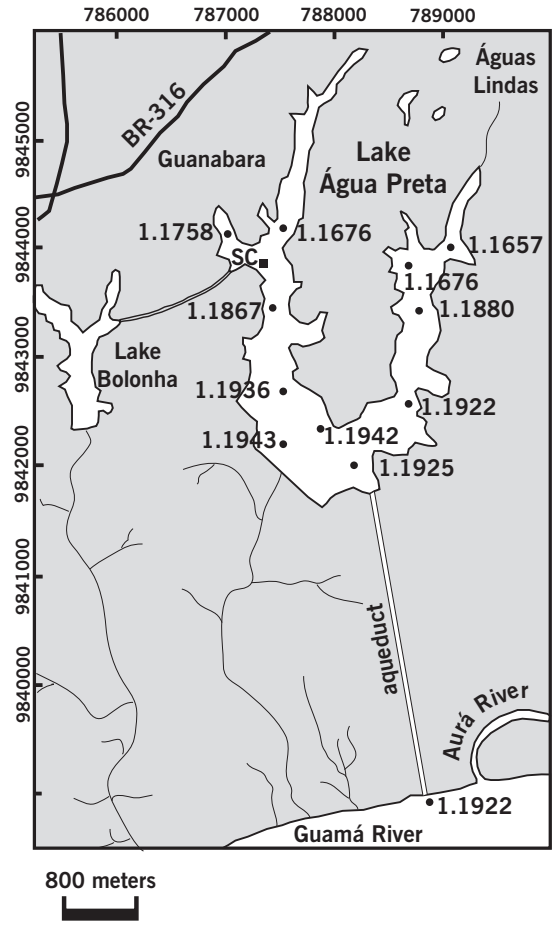

Figure 4 – $^{207}Pb/^{206}Pb$ isotope ratio of the bottom sediments of Lake Água Preta.
SC- Sediment Core

to estimate the ages where the changes in the Pb isotope ratio have occurred. However, as the history of the urban occupation of the MRB and the construction of the dam are well documented, some interpretation concerning the changes on the lead isotopic ratios may be drawn.

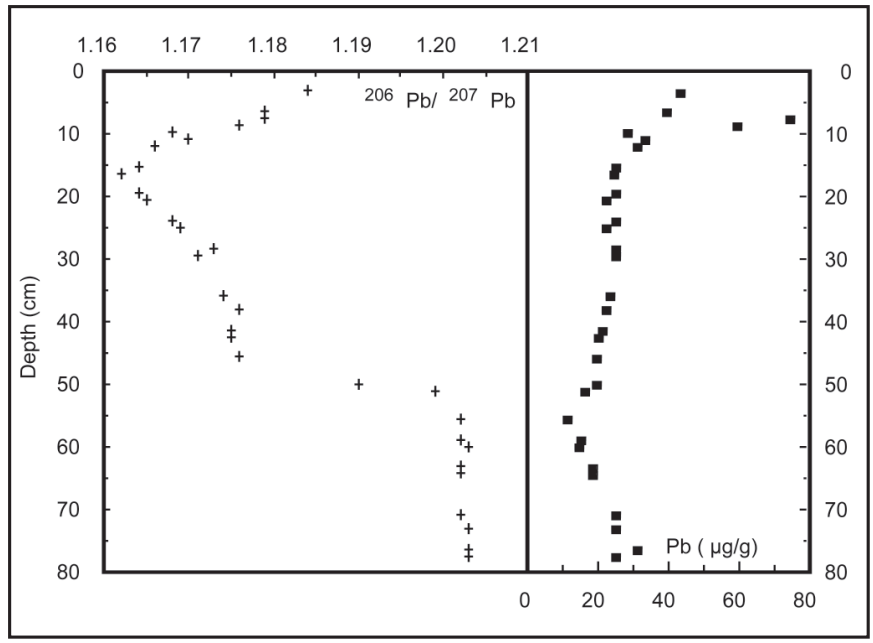

Figure 5 – Diagram showing the variation of the $^{207}Pb/^{206}Pb$ isotope ratio and lead concentration of the core sediment samples of Lake Água Preta with depth

During the first half of the 20th Century, when the dam of Lake Água Preta was constructed, the sediment incorporated in the reservoir had the lead isotopic signature of the bedrock since the urban occupation of the catchment basin was very small, and the secondary forest surrounding the lake was well preserved. The $^{206}Pb/^{207}Pb$ ratio of this period, which is recorded in the first 25 cm of the bottom of the core, is around 1.20. In the early 60's, the construction of interstate road BR-316 contributed to drastically change this scenario. The urban occupation of the MRB begins to increase as a result of the intense migration of population (formation of the Guanabara and Águas Lindas neighborhood for instance) and, the anthropogenic contribution to the catchment basin of the lake was inevitable. This new scenario is well recorded in the sediment core as the $^{206}Pb/^{207}Pb$ ratio decreases systematically until 1.16 toward the top of the profile. The increase of the $^{206}Pb/^{207}Pb$ ratio in top 15 centimeters of the core is not well understood. However, it is probably a specific situation of the sampling site that was very near the margins of the lake. It is important to notice that the bottom sediment sample collected nearby record a lower $^{206}Pb/^{207}Pb$ ratio of 1.16 (Fig. 4).

The interpretation that the $^{206}Pb/^{207}Pb$ ratio around 1.20 indicates the bedrock as a source of lead is supported by the soil sample collected in the Aurá landfill in a place not affected by solid waste deposit ($^{206}Pb/^{207}Pb = 1.202$), and also by most of the bottom sediment samples of the Maguari channel area whose values of the $^{206}Pb/^{207}Pb$ ratio are very near 1.20. On the other hand, there are strong indications that the $^{206}Pb/^{207}Pb$ ratio near, or lower than, 1.16 may be interpreted as result of anthropogenic contribution. First, the bottom sediment samples of the Lake Água Preta, collected in those parts of the reservoir nearer the urban occupation, have the lowest $^{206}Pb/^{207}Pb$ ratios (≈1.16). Secondly, the lead isotope composition of the soil sample collected in the Aurá landfill shows the lowest $^{206}Pb/^{207}Pb$ ratio of MRB (1.145). Third, in the Mocajatuba River, near the place where a ceramic industry operated for several years, the highest lead concentration is accompanied with the lowest $^{206}Pb/^{207}Pb$ ratio (1.164) recorded for the Maguari channel area. Finally, Bollhofen and Rosman (2000) have published a $^{206}Pb/^{207}Pb$ ratio of 1.15 for atmospheric particulates collected in the Icoaraci Industrial District, Belém (PA). Comparing this data with those obtained in other metropolitan areas of Brazil, they interpreted this low $^{206}Pb/^{207}Pb$ ratio as indicative of anthropogenic contribution.

It is interesting to notice that the changes in the lead isotope ratios due to anthropogenic inputs are more visible than the changes in the lead concentration itself. Thus, the use of the lead isotope ratios for monitoring heavy metal perturbations of the environment caused by industrial activities or urban developments can be more effective than the determination of heavy metal concentrations themselves.

Table 3 – Lead concentration and isotopic composition of the core sediment samples of Lake Água Preta

Sample depth (cm)	Pb μg/g	$^{206}Pb/Pb^{204}$	$^{207}Pb/Pb^{204}$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$
3.3	43	18.559 (27)	15.688 (32)	38.642 (97)	1.1844 (04)
6.5	39	18.510 (26)	15.716 (30)	38.659 (96)	1.1791 (01)
7.6	74	18.420 (25)	15.646 (30)	38.414 (97)	1.1787 (02)
8.7	59	18.403 (25)	15.675 (30)	38.483 (97)	1.1757 (01)
9.8	28	18.273 (25)	15.671 (30)	38.321 (96)	1.1675 (02)
10.9	33	18.295 (31)	15.665 (37)	38.360 (103)	1.1698 (01)
12	31	18.284 (41)	15.668 (39)	38.289 (110)	1.1660 (06)
15.3	25	18.190 (23)	15.647 (29)	38.200 (93)	1.1642 (01)
16.4	24	18.174 (36)	15.644(29)	38.203 (102)	1.1622 (02)
19.6	25	18.157 (37)	15.614 (35)	38.135 (123)	1.1643 (01)
20.7	22	18.208 (26)	15.649 (33)	38.257 (105)	1.1648 (02)
24	25	18.346 (30)	15.727 (32)	38.543 (106)	1.1682 (01)
25.1	22	18.332 (24)	15.697 (31)	38.418 (98)	1.1692 (01)
28.4	25	18.339 (25)	15.660 (30)	38.339 (95)	1.1727 (02)
29.5	25	18.310 (31)	15.647 (40)	38.362 (126)	1.1713 (06)
36	23	18.376 (36)	15.684 (41)	38.433 (123)	1.1737 (04)
38.2	22	18.362 (27)	15.632 (31)	38.306 (97)	1.1757 (04)
41.5	21	18.400 (25)	15.682 (30)	38.448 (96)	1.1746 (04)
42.6	20	18.410 (33)	15.686 (38)	38.426 (110)	1.1748 (02)
45.8	19	18.477 (27)	15.729 (31)	38.663 (98)	1.1762 (01)
50.2	19	18.707 (27)	15.728 (62)	38.959 (98)	1.1903 (02)
51.3	16	18.900 (33)	15.766 (38)	39.334 (121)	1.1988 (02)
55.7	11	18.940 (27)	15.781 (31)	39.387 (99)	1.2016 (01)
58.9	15	18.942 (32)	15.788 (33)	39.396 (105)	1.2017 (04)
60	14	18.922 (27)	15.755 (31)	39.301 (99)	1.2026 (02)
63.3	18	18.925 (33)	15.761 (35)	39.318 (106)	1.2022 (04)
64.4	18	18.958 (32)	15.787 (33)	39.381 (113)	1.2016 (04)
71	25	19.105 (112)	15.933 (91)	39.791 (260)	1.2018 (06)
73.1	25	18.945 (24)	15.767 (29)	39.346 (96)	1.2031 (02)
76.4	31	18.930 (30)	15.775 (36)	39.323 (99)	1.2029 (02)

Table 4 – Lead concentration and isotopic composition of the soil and bottom sediment samples of Aurá Landfill

Sample #	Pb (μg/g)	$^{206}Pb/Pb^{204}$	$^{207}Pb/Pb^{204}$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$
GD-01	23	18.778 (31)	15.767 (34)	38.984 (99)	1.1929 (14)
GD-02	20	18.859 (27)	15.733 (31)	39.064 (99)	1.2003 (07)
GD-03	52	18.367 (33)	15.662 (29)	38.378 (93)	1.1741 (04)
GD-04	64	17.845 (22)	15.598 (28)	37.712 (91)	1.1455 (07)

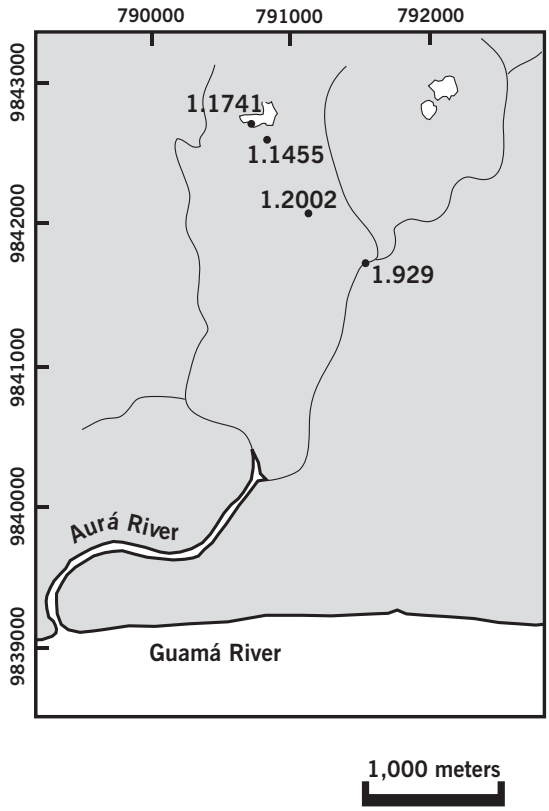

Figure 6 - $^{207}Pb/^{206}Pb$ isotope ratio of the sediment and soil samples of Aurá Landfill

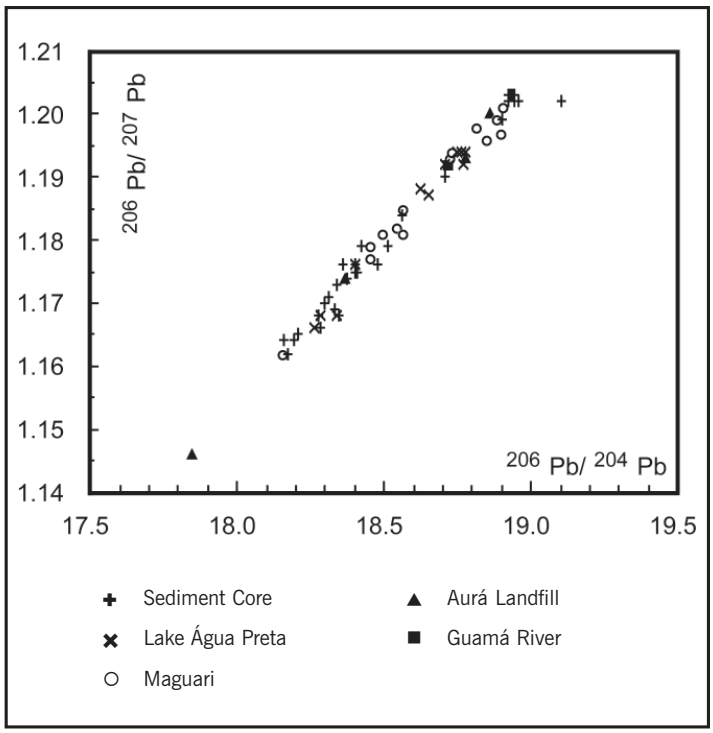

Figure 7 – $^{206}Pb/^{207}Pb$ *vs.* $^{206}Pb/^{204}Pb$ diagram for the soil and sediment samples in the Metropolitan Region of Belém (PA)

This study does not allow identification of a specific anthropogenic source for the lead in the MRB. However, considering the sampling sites, there are no doubts that the release of municipal and industrial effluents associated with the consumption of lead-based products is an important anthropogenic source. The atmospheric input may also be considered, however the extent of its influence has yet to be investigated. Fossil fuel could have been an important source until 1989, when alkyl-leaded gasoline was banned in Brazil. In order to discriminate the different sources of anthropogenic lead, a detailed investigation needs to be carried out to determine their lead isotope compositions. Nevertheless, this study has shown that the lead isotope composition of the sediments and soil can be used to trace the anthropogenic contribution to the environment in the MRB, since the geogenic source has a quite distinct $^{206}Pb/^{207}Pb$ ratio (1.20), which is very different from the $^{206}Pb/^{207}Pb$ ratio of 1.16 or less of the anthropogenic sources.

Conclusions

The geogenic and anthropogenic lead isotope composition of the sediment and soil samples in the MRB are quite different. This permits the use of lead isotope ratios as a tool in the investigation of the anthropogenic impacts on the environment in this region. The $^{206}Pb/^{207}Pb$ ratio of the geogenic source is around 1.20 while the anthropogenic sources have $^{206}Pb/^{207}Pb$ ratios around 1.16, or even lower. The use of lead isotope composition in environmental studies seems to be more effective for monitoring the heavy metal input caused by industrial activities or urban development than the determination of the heavy metal concentration itself.

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