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RESEARCH ARTICLE

Elemental and isotopic determination of lead (Pb) in particulate matter in the Brazilian city of Goiânia (GO) using ICP-MS technique

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Abstract The toxic metal lead (Pb) can be harmful to human health in various manners, but is also considered as a distinguished tracer of environmental pollution since the relative abundance of its four stable isotopes with the atomic masses of 204, 206, 207, and 208 varies with the emission source. This study is focused on the Pb concentrations and isotope ratios in the particulate matter of the Brazilian city of Goiânia in order to determine the main Pb emission sources. Particulate matter samples were collected on clean Teflon filters during rainy and dry season in 2014 in the center of Goiânia city near main roads with a high traffic volume. Pb concentrations as well as stable Pb isotope ratios of the particulate matter samples were analyzed by inductively coupled plasma-mass spectrometry. To apply this analytical technique successfully, it was necessary to optimize parameters in case of acquisition time, detector dead time, and mass discrimination, which affect the measurement accuracy and precision. Results showed that Pb concentrations in Goiânia were different between rainy and dry season. Pb concentrations showed higher values and less variation in dry season than in rainy season. Pb isotope ratios demonstrated significant variations between dry and rainy season. An enrichment of ^{206}Pb isotopes related to ^{207}Pb and ^{208}Pb isotopes was observed in dry season. However, the comparison of the obtained isotopic Pb signature with data of potential Pb sources from previous studies indicated that traffic-related sources should be considered as main Pb source in the particulate matter of Goiânia. These assumptions were incorporated by the calculation of the contribution factor of Pb coming from traffic-related sources by applying binary mixing equations.

Keywords Lead isotope ratios · Particulate matter · Industrial emissions · Air pollution · ICP-MS

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Introduction

Atmospheric pollution caused by particulate matter has a high impact on human health. Particulate material is stated as solid or liquid particles in suspension. Especially the finer particles are linked to respiratory diseases and increased mortality, particularly on children and elderly people (Pope et al. 1995; Schwartz et al. 1996).

A trace metal frequently enriched in particulate matter is lead (Pb). It is a cumulative heavy metal toxicant, producing adverse effects on human health already in low concentrations by damaging nervous connections, causing brain and blood diseases, and impairing growth and mental functions (Wang and Zhang 2006). A multiplicity of Pb inputs are anthropogenic. Major sources of Pb in the atmosphere are mining activities, the burning of wood and coal, smelting, non-ferrous metal refining, and waste incineration (Nriagu and Pacyna 1988). The combustion of gasoline also is still an important

atmospheric Pb emission source due to the presence of Pb in its crude (10–300 $\mu g\ L^{-1}$), although leaded fuel is banned from the market in most of the countries in the world (OECD 1993; Aberg et al. 1999; Mastral et al. 2009). The total phase-out of leaded gasoline was achieved in Brazil by 1991 (Lovei 1998). Besides gasoline, there are other traffic-related emission sources of particulate Pb. These emissions are generated from non-exhaust sources such as brakes, tires, clutch, and road surface wear or those that already exist in the form of deposited material at the roadside. They become re-suspended due to traffic-induced turbulence (Grigoratos and Martini 2015). Pb is the only metal listed in ambient air quality standards in the state of São Paulo, though no nationwide regimentation for Pb in particulate matter exists in Brazil. However, the Environmental State Company of São Paulo (CETESB 2014) in the Decree No. 59113/2013 stated an annual maximum acceptable limit for Pb as $0.5\ \mu g\ m^{-3}$. This value is in accordance with the standard value set in the European Union (Directive 2008/50/EC 2008), and in contrast to the USA, where a Pb limit value of $0.15\ \mu g\ m^{-3}$ was set as a rolling 3-month average (U.S. EPA 2016).

The four naturally occurring stable isotopes of Pb, ^{204}Pb (1.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%), and ^{208}Pb (52.4%), can be used as tracers for the origin of atmospheric pollution. This is because the ratios between the different Pb isotopes vary in different geological environments as ^{206}Pb and ^{207}Pb that are products of the radioactive decay of ^{238}U ($T_{1/2} = 4.47 \times 10^9$ years) and ^{235}U ($T_{1/2} = 7.04 \times 10^8$ years), while ^{208}Pb is formed by the decay of ^{232}Th ($T_{1/2} = 1.4 \times 10^{10}$ years). ^{204}Pb is non-radiogenic (Dickin 1995). Thus, each Pb-containing ore has different Pb isotope ratios depending on the initial concentration of Th and U and the time the ore was formed. Therefore, Pb isotope ratios are a useful tool to trace the anthropogenic or natural origin of Pb in the atmosphere (Mukai et al. 1993). The Pb isotope ratios of rock-forming minerals and the soils, dusts, and sediments derived from them vary regionally, depending on the U and Th content in the rocks and their geological age (Shotyk et al. 2015). For example, $^{206}Pb/^{207}Pb$ ratio in Pb minerals decreases with increasing geological age (Cimova et al. 2016). Also, anthropogenic Pb generally is less radiogenic. Lower $^{206}Pb/^{207}Pb$ ratios can be an indicator of anthropogenic activities due to the input/mixture of anthropogenic Pb sources, the relative decrease of natural Pb, and the abundance of Pb in industrial materials, which is derived from various lead sulfide ores (Monna et al. 1997; Gioia et al. 2006; Komárek et al. 2008; Kylander et al. 2010). These show lower $^{206}Pb/^{207}Pb$ isotope ratios as they became physically and chemically separated from crustal rocks and thus giving rise to less radiogenic Pb (Dickin 1995).

Due to the impairment of urban air quality connected with rapid urbanization and industrialization in East and South-East Asia, a multiplicity of studies on Pb isotope ratios in

particulate matter and its application to trace sources of atmospheric pollution were performed in this region (Mukai et al. 1993; Zheng et al. 2004; Xu et al. 2011; Lee et al. 2015). Similar studies have been realized in North and Central America (Bollhöfer and Rosman 2001; Salcedo et al. 2016). In Europe, Pb isotopic signatures of particulate matter were used among others to determine if the phase-out of leaded fuels in the EU was worthwhile (Monna et al. 1997; Veron et al. 1999; Mastral et al. 2009). In contrast, just a few studies on Pb isotope ratios in atmospheric particulate matter were realized in Brazil.

One of the first studies analyzing Pb isotope ratios in Brazil were conducted by Bollhöfer and Rosman (2000). Aerosols collected between 1994 and 1999 for periods of 1 day to 2 months at more than 70 different sites affecting the southern hemisphere have been measured for their $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$, and $^{206}Pb/^{204}Pb$ ratios and Pb concentrations to characterize geographical variations in isotopic Pb signatures. Aerosol samples were collected among others between the year 1995 and 1998 in rainy and dry season in the inner city of São Paulo using small diaphragm pumps connected via 2–3 m of PVC tubing to a plastic monitor fitted with a 0.45-mm-pore-size, 37-mm-diameter Teflon front and a 0–60-mm-pore-size Teflon backing filter.

In the study of Aily (2001), PM_{10} samples were collected on clean Teflon filters applying a sampling time of 24 h between August 1999 and September 2000 on the Campus of the State University (USP) in São Paulo. Pb isotope ratios were measured by thermal ionization mass spectrometry (TIMS) and Pb concentrations were measured by isotopic dilution technique. In order to find possible pollution sources, pollutants such as gasoline and ethanol fuel, soot from vehicle exhaust fumes, street dust and particulate matter from industrial emissions collected on fiberglass filters as well as possible geogenic sources like potassium feldspar-rich rocks were analyzed on their Pb isotope ratios.

Babinski et al. (2003) determined Pb isotope ratios from PM_{10}, collected with Teflon filters between August 1999 and September 2000, and rain water samples at the University of São Paulo, situated in the western part of the city. PM_{10} samples were collected during 7 to 20 days per month, changing the filters every 24 h. Isotopic Pb signature of particulate matter and rain water as well as possible Pb sources like gasoline, soot from vehicle exhaust pipes and PM from industrial emissions were analyzed by TIMS. It was suggested that industrial emissions were the main contributing factor for Pb in the PM_{10} samples since the contribution of Pb in vehicular fuels was insignificant.

In a research performed by Mirlean et al. (2005), Pb concentrations and isotope ratios in atmospheric deposits and potential Pb sources in and around the city of Rio Grande in South Brazil were investigated. Atmospheric deposits were collected at five sampling sites (fishing village, suburban

zone, old town, industrial zone, nature reserve) during 1998 and 2000 with a collector for bulk precipitation consisting of a polypropylene funnel (diameter 30 cm) jointed to a polypropylene collection bottle. Collectors were installed not less than 5 m above soil surface and were exposed for 30 days. Isotope ratios of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ were measured by VG-Sector mass spectrometer and used to trace sources of atmospheric Pb from different sampling locations distributed over the city.

The city of Goiânia, capital of Goiás state, is located in the mid-west of Brazil and possessed 1.43 million inhabitants in 2015, owning a fleet of 1.103 million vehicles, which is a proportion comparable to highly industrialized countries (IBGE 2015). The rapid growth of the quantity of vehicles in the city is a possible contribution factor to recent atmospheric pollution in Goiânia.

In this study, the main objective was to determine and compare Pb concentrations and its isotope ratios in the particulate matter of Goiânia between dry and rainy season. In order to identify possible emission sources, obtained Pb isotope ratio compositions were compared with data from recent studies conducted in Brazil and binary mixing equations, based on $^{206}Pb/^{207}Pb$ ratios, were set. In order to realize an accurate determination of Pb isotope ratios, basic methods using ICP-MS technique had to be previously implemented.

Materials and methods

Sampling program

Sampling of particulate matter was conducted in the city of Goiânia (GO). Sampling point (16°66′31.86″S; 49°26′15.75″ W) was placed in the central area of the city near roads with heavy traffic volume. Samples were collected on clean Teflon filters (Fluoropore™ membrane filters, PTFE-coated, 0.22 μm pore size, 47 mm total diameter, Millipore FGLP04700; Merck Millipore Ltd., USA) using a low-volume NILU-type "open face" stacked filter unit sampler (NILU—Norwegian Institute for Air Research) connected to a diaphragm pump maintaining a sampled air volume of about 40 m^3 per day in 2 m above the ground. This sampling height was chosen to avoid interference with the surface and topsoil, and also to consider the height of exposure to living organisms. Sampling were always launched at 12:00 PM local time and sampling time was 24 h. Samples were taken in two

sampling campaigns. The first campaign was performed in April and May 2014, representing rainy season. The second campaign was carried out in August 2014, representing dry season. A total of 16 samples for each meteorological season were amounted.

Determination of Pb concentrations and Pb isotope ratios

Filter digestion, based on Method IO-3.1 (U.S. EPA 1999), was realized in 10 mL of 22.3% ($v\ v^{-1}$) concentrated aqua regia using microwave digestion system Speedwave® 4 (Berghof, Germany) with parameter settings shown in Table 1.

Standard solutions were prepared on the base of isotopic standard SRM 981 (NIST Common Pb isotopic standard), dissolving the solid SRM 981 standard in 196 mL of HNO$_3$ (2 mol L^{-1}) and completing the solution to 500 mL with ultrapure water. Concentrations of aqua regia in sample solutions were diluted to 5.3% after digestion ($v\ v^{-1}$) with ultrapure water (Milli-Q) to a final volume of 41.7 mL. Pre-cleaning for all materials used to prepare solutions and standards was performed in 10% HNO$_3$ using Speedwave® 4 by Berghof and were later rinsed in ultrapure water.

Pb isotope ratios were measured by ICP-MS type X Series II (Thermo Fisher Scientific, USA) using the instrumental and data acquisition parameters as shown in Tables 2 and 3. Li, In, and U counts were used to align the instrument performance. Pb concentration was estimated from the ^{206}Pb, ^{207}Pb, and ^{208}Pb signals while determining the Pb isotopic composition.

Calculation of dead time of the instrument and correction of mass bias were performed by using isotopic standard SRM 981 (NIST Common Pb isotopic standard). Dead time was estimated according to method 1 of Nelms et al. (2001) and was adopted to the instrument software. The mass bias was corrected by measuring an isotopic standard of Pb (2.5 ng mL^{-1}) based on SRM 981 (NIST Common Pb isotopic standard) and calculating a correction factor by using the following mathematical expression (Eq. 1):

$$\frac{Rtrue}{Robs} = (1 + \varepsilon linear.\Delta m) \tag{1}$$

where R_{true} is the corrected isotope ratio, R_{obs} is the experimental obtained isotope ratio, Δm is the mass

Table 1 Parameter settings of Speedwave® 4 (Berghof, Germany) for the digestion of particulate matter filter samples

Steps	Temperature (°C)	Time (min)	Ramp (min)	Power (%)	Pressure (bar)
1	140	10	5	45	35
2	160	10	5	45	40
3	200	5	5	45	35

Table 2 ICP-MS instrumental parameters

Nebulizer	Mira Mist
RF power (W)	1450
Flow rate nebulizer gas (L min^{-1})	0.8
Flow rate coolant gas (L min^{-1})	13
Flow rate auxiliary gas (L min^{-1})	0.7
Peristaltic pump rotation (rpm)	15
Torch sample depth (mm)	150
Vertical (mm)	93
Horizontal (mm)	53

difference between the two isotopes, and $\varepsilon linear$ is the correction factor.

Statistical analysis

Results were summarized into a multi-element database using Excel and statistically characterized and analyzed with the BioEstat 5.3 and ORIGIN 8 statistical software. As the data was not normally distributed, the non-parametric Kruskal–Wallis test was employed to investigate differences in Pb concentrations and Pb isotope ratios between dry and rainy season.

Results and discussion

Pb concentrations

Prior to and during every sample analysis, prepared standard solutions based on SRM 981 (NIST Common Pb isotopic standard) with Pb concentrations of 0, 0.5, 2.5, and 5 ng mL^{-1} were passed in the ICP-MS to generate a calibration curve. All analytical curves had coefficients of determination of at least $R^2 = 0.9995$. Instrumental detection limit, which is equal to three times the standard deviation of the blank signal at the selected analytical masses, was identified as 0.0035 ng mL^{-1}. The method detection limit had a value of 0.014 ng mL^{-1}. The Pb concentrations show a high disparity between rainy season samples (April/May) and dry season samples

Table 3 Data acquisition parameters

Measuring mode	Peak jump
Points per mass	3
Dwell time	4 ns for ^{206}Pb and ^{207}Pb; 2 ns for ^{208}Pb
Sweeps	20,450
Acquisition time per main run	300 s
Replicates	3

(August). The average Pb concentration from April/May is lower with a mean value of 1.28 ng m^{-3} than the mean Pb concentration from August with 1.89 ng m^{-3} (Table 4). Furthermore, samples of rainy season demonstrate a considerably higher coefficient of variation with 97.31% compared to 45.06% of the samples from dry season, highlighting a high divergence within the rainy season samples. Samples from April/May differ from a minimum Pb concentration of 0.36 ng m^{-3} to a maximum of 4.53 ng m^{-3}. Two PM samples

Table 4 Lead concentration and lead isotope ratios for rainy and dry season samples

Date	Pb (ng m^{-3})	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb
11/04/14	0.61	1.171	2.450
13/04/14	0.58	1.176	2.446
14/04/14	1.98	1.173	2.447
16/04/14	3.89	1.175	2.451
17/04/14	1.33	1.174	2.452
18/04/14	1.65	1.172	2.448
19/04/14	0.63	1.174	2.451
21/04/14	0.53	1.162	2.441
23/04/14	0.52	1.172	2.449
24/04/14	0.75	1.166	2.444
25/04/14	0.36	1.173	2.451
27/04/14	0.37	1.176	2.450
29/04/14	0.38	1.176	2.448
30/04/14	1.51	1.171	2.451
07/05/14	0.92	1.167	2.445
14/05/14	4.53	1.172	2.444
Average	1.28	1.172 ± 0.004	2.448 ± 0.003
RSD%		0.324	0.127
04/08/14	3.70	1.161	2.437
06/08/14	1.79	1.184	2.446
07/08/14	1.36	1.169	2.438
08/08/14	2.92	1.169	2.440
09/08/14	1.23	1.175	2.446
10/08/14	1.74	1.178	2.452
12/08/14	2.41	1.173	2.450
15/08/14	1.16	1.176	2.446
16/08/14	0.90	1.178	2.448
18/08/14	0.72	1.175	2.450
20/08/14	0.98	1.184	2.449
21/08/14	2.47	1.173	2.449
22/08/14	1.50	1.179	2.451
24/08/14	2.66	1.174	2.446
26/08/14	2.75	1.175	2.446
27/08/14	1.91	1.179	2.446
Average	1.89	1.175 ± 0.006	2.446 ± 0.004
RSD%		0.468	0.176

have a higher Pb concentration than 3 ng m^{-3}; no other sample of this campaign shows a higher value than 2 ng m^{-3}. In contrast, August samples differ from 0.72 to 3.70 ng m^{-3}. Six samples from August have a higher Pb concentration than 2 ng m^{-3}, one sample shows a higher concentration than 3 ng m^{-3}. Median (0.690 ng m^{-3}) and arithmetic average of the rainy season samples differ considerably while median (1.765 m^{-3}) and arithmetic average of dry season samples are quite close to each other as observed in the generated boxplot diagram of Fig. 1. The high variation of April/May samples is also expressed in the skewness, where it shows a value of 1.871 in April/May, whereas in August it shows a value closer to 0 with 0.532.

Also, both sample periods show differences in their quartiles. While 25% of April/May samples are lower than 0.528 ng m^{-3}, just 25% of August samples are lower than 1.765 ng m^{-3}. Even with the two high outlier values, just 25% of the April/May samples show higher Pb concentrations than 1.545 ng m^{-3}, while 25% of the August samples reach higher Pb concentrations than 2.518 ng m^{-3}. Due to two outlier values, arithmetic average of rainy season samples is stretched to a higher value. This data demonstrates that generally dry season samples show markedly higher Pb concentrations and differ in a much lower scope than samples from rainy season.

To further examine differences in the Pb concentrations between the two sample periods, a Kruskal–Wallis test was performed. The results of the test demonstrated an H value of 5.818 and P value lower than 0.05 ($P = 0.014$) from the post hoc test, rejecting the H_0 hypothesis that both sample groups are equal and showing that Pb concentrations from April/May and August are statistically different to each other.

Considering the standard value established by CETESB, the exposition to the measured Pb concentrations over the
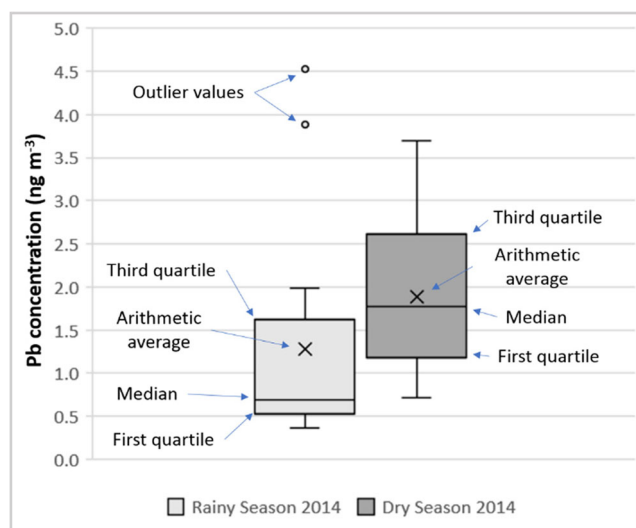

Fig. 1 Boxplot diagram for Pb concentrations of samples from rainy and dry season (2014) from Goiânia

averaging time of 1 year would not carry risks to the human health. In comparison with a previous study by Bollhöfer and Rosman (2000), where Pb concentration in particulate matter from São Paulo City ranged between 3 ± 1 and 52 ± 14 ng m^{-3} with an average of 29 ng m^{-3}, Pb concentrations from Goiânia are relatively low. Also, the study from Aily (2001) shows clearly higher Pb concentrations ranging from 10.23 ng m^{-3} to even 254.52 ng m^{-3} in particulate matter sampled in São Paulo City. In that study, dry season samples with an average value of 60.56 ± 43.38 ng m^{-3} showed higher Pb concentrations than in rainy season with an average of 36.14 ± 37.80 ng m^{-3}.

Isotopic determination of Pb

The mass bias corrected ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb isotope ratios with the aforementioned equation (Eq. 1) are shown in Table 4. For an accurate Pb isotope evaluation, it is intended to have a relative standard deviation (RSD) of <0.1% (Mastral et al. 2009).

Measured ^{208}Pb/^{207}Pb isotope ratios from April/May samples show a good precision with just one RSD value higher than 0.2%, while there are six RSD values higher than 0.2% at the ^{206}Pb/^{207}Pb isotope ratios. In contrast, August samples show a higher precision with just three RSD values higher than 0.2% at the ^{206}Pb/^{207}Pb isotope ratios and no RSD value higher than 0.2% at the ^{208}Pb/^{207}Pb isotope ratios. The higher precision in dry season samples may be explicable with the higher Pb concentrations in this sampling period.

Pb–Pb diagrams were represented in previous studies with the aim of analyzing, interpreting, and comparing data (Mastral et al. 2009). In this paper, it has been used to plot the difference of ^{208}Pb/^{207}Pb and the ^{206}Pb/^{207}Pb ratios between both sampling periods (Fig. 2).

The ^{206}Pb/^{207}Pb isotope ratio varied in the rainy season from 1.162 to 1.176 and the ^{208}Pb/^{207}Pb isotope ratios ranged from 2.446 to 2.452. The ^{206}Pb/^{207}Pb isotope ratios from dry season differed from 1.161 to 1.184 and ^{208}Pb/^{207}Pb isotope ratios from 2.437 to 2.452. Arithmetic averages of ^{206}Pb/^{207}Pb isotope ratios of August samples are slightly higher (1.175) than in April/May (average of 1.172), while the ^{208}Pb/^{207}Pb ratios show just a marginally divergence (2.446 in dry season and 2.448 in rainy season). The RSDs of all ratios demonstrate a higher variation of the ^{206}Pb/^{207}Pb isotope ratios in dry season than in rainy season, while the ^{208}Pb/^{207}Pb isotope ratios show very close relative standard deviations in both months. Kruskal–Wallis tests show that ^{206}Pb/^{207}Pb isotope ratios from rainy season vary significantly from dry season ($H = 4.306$, $P = 0.038$), whereas ^{208}Pb/^{207}Pb isotope ratios between both sample periods show no significant statistical disparities ($H = 1.368$, $P = 0.242$). Thus, while ^{208}Pb/^{207}Pb isotope ratios in rainy and dry season demonstrate quite similar values, ^{206}Pb/^{207}Pb isotope ratios of dry season are in average higher

**Fig. 2** $^{206}Pb/^{207}Pb$–$^{208}Pb/^{207}Pb$ diagram according to the Pb isotope ratios for samples from Goiânia
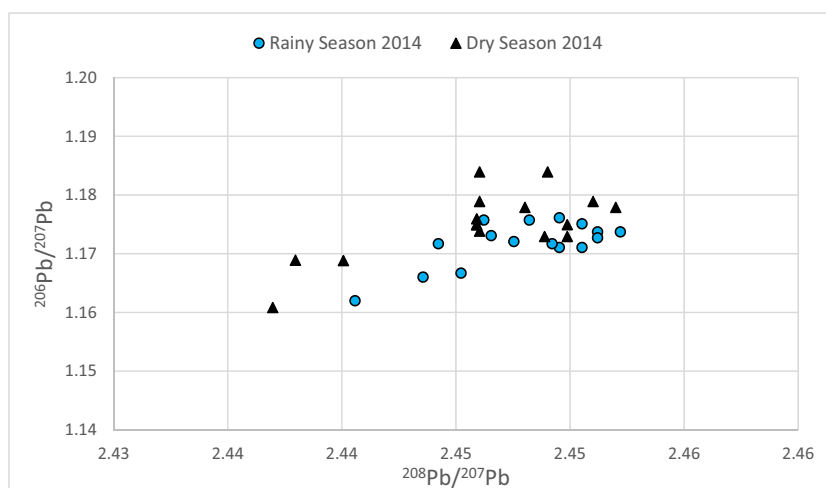
than $^{206}Pb/^{207}Pb$ isotope ratios in rainy season. This observation supposes an enrichment of ^{206}Pb isotopes related to ^{207}Pb isotopes in dry season derived from a more radiogenic emission source.

When considering the natural abundance of Pb isotopes (Berglund and Wieser 2011), $^{206}Pb/^{207}Pb$ is equal to 1.091, while $^{208}Pb/^{207}Pb$ is equal to 2.371. Environmental lead has various origins, including natural origin. As different sources have their specific lead isotopic compositions, it may be possible to identify some evidences for anthropogenic inputs (Zhi et al. 2016). Comparing the natural isotopic abundance, therefore, can give us some idea about the origin of the isotopes. Based on the natural occurrence of the Pb isotopes, ^{207}Pb is slightly depleted relative to ^{206}Pb and ^{208}Pb isotopes in the

studied area when compared with the crustal mean of this element. Geological characteristics could affect this difference, as the Pb isotope abundance is dependent of the U–Th–Pb content in the system and the mixture of different sources of Pb, including human activities. Thus, besides environmental factors, human activities can also be responsible for these differences in Pb isotope ratios in Goiânia.

In order to assess possible emission sources, measured $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ isotope ratios were plotted on a Pb–Pb diagram (Fig. 3) together with data from previous studies from Brazil, which contain Pb isotope ratios of aerosol samples from São Paulo (Bollhöfer and Rosman 2000), gasoline, exhaust fume, street dust, and industrial emission samples from São Paulo (Aily 2001); petroleum and derivates

Fig. 3 $^{206}Pb/^{207}Pb$–$^{208}Pb/^{207}Pb$ diagram according to the Pb isotope ratios for samples from Goiânia compared with Pb isotope ratios from recent studies of other regions in Brazil
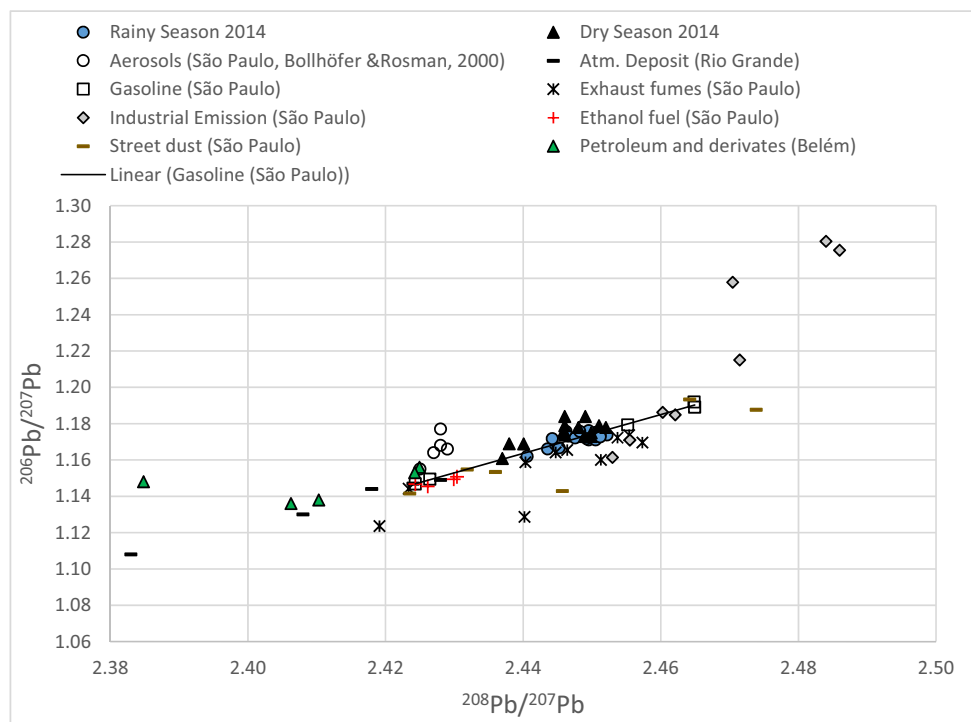
samples from Belém, Pará (Souza de Lima 2010); and atmospheric deposit samples from Rio Grande, Rio Grande do Sul (Mirlean et al. 2005).

Pb isotope ratios in aerosol samples from São Paulo and atmospheric deposit samples from Rio Grande are highly different from Pb isotope ratios in Goiânia samples. Aerosol samples from São Paulo possibly show different Pb isotope ratios than PM from Goiânia samples due to the higher influence of traffic emissions as the mega city São Paulo has one of the highest traffic volumes in the world. Furthermore, samples from São Paulo could have a slightly different matrix as they are aerosol samples and were collected in much higher altitude (2 m above the ground on the roof of a high-rise building). It would be suitable to compare chemical aspects of particulate matter concentrations under the same conditions of atmospheric pressure and temperature, as the altitude can affect the air quality and pollution (Alvarez et al. 2013). Differences of Pb isotope ratios in samples from Rio Grande are explicable as lead used in roof construction appeared to be a major source of atmospheric lead. Both Pb isotope ratios from rainy season and dry season samples of Goiânia are distributed on the line of Pb isotope ratios of gasoline from São Paulo. Thus, gasoline can be considered as a possible influence on Pb isotope ratios of Goiânia even though Pb isotope ratios from gasoline samples are distributed in a high range with a low quantity of samples. Furthermore, other traffic-related sources such as street dust, exhaust fumes, and ethanol fuel are in the range of Goiânia samples indicating a high contribution of traffic emissions. Industrial emissions show a high variability grade in its isotope ratios, but also could be a factor of influence on Pb isotope ratios from Goiânia, especially for August samples, which show higher $^{206}Pb/^{207}Pb$ isotope ratios and, thus, are located closer to the Pb isotope data of industrial emissions.

In order to investigate the contribution from the decay of thorium to the Pb in PM in Goiânia, ratios of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ were calculated and plotted against each other in a diagram (Fig. 4).
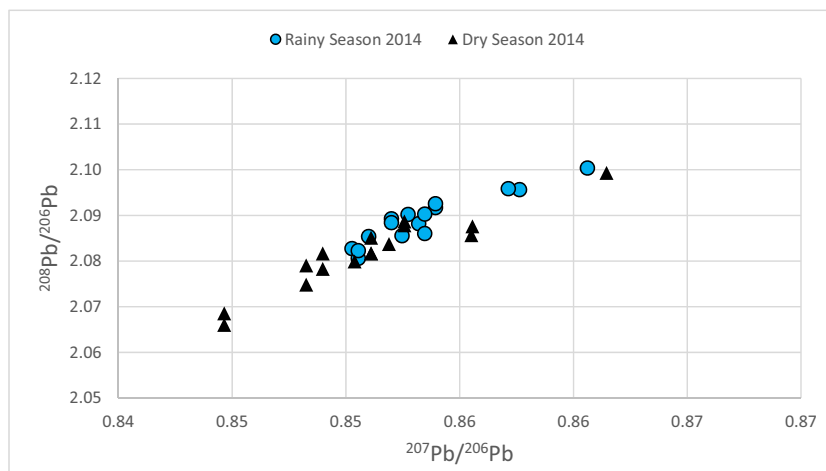
$^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ isotope ratios show significant differences between rainy and dry season. $^{207}Pb/^{206}Pb$ isotope ratios from rainy season are higher than in dry season. The significant variance of $^{207}Pb/^{206}Pb$ ratios between both sampling periods is proved by the consulted Kruskal–Wallis test ($H = 4.306$, $P = 0.038$). $^{208}Pb/^{206}Pb$ ratios demonstrate a highly significant variance between rainy and dry season ($H = 8.872$, $P = 0.003$) with distinctly lower $^{208}Pb/^{206}Pb$ ratios in dry season, indicating a relative enrichment of ^{206}Pb isotopes related to ^{208}Pb isotopes in this period derived from less radiogenic Th-rich environments. In Fig. 5, $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ isotope ratios from PM in Goiânia were adopted in a Pb–Pb diagram together with data of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ isotope ratios from Pb sources taken from the study of Aily (2001). Results demonstrate the location of Pb isotope ratios from PM in Goiânia in the conformity of isotopic signature of gasoline, exhaust fumes, and street dust, indicating a high contribution of traffic emissions. Furthermore, Pb isotope data from PM in Goiânia are in the range of data from industrial emissions, especially data from dry season with their lower $^{208}Pb/^{206}Pb$ isotope ratios. Hence, industrial emissions also should be considered as a possible influence factor.

For a further assessment, $^{206}Pb/^{207}Pb$ isotope ratios of Goiânia samples were plotted together with $^{206}Pb/^{207}Pb$ isotope ratios data from several related studies from Brazil (Fig. 6), as this type of diagram allows to refer on more previous works from the region.

$^{206}Pb/^{207}Pb$ isotope ratios of April/May as well as August samples are in the range of $^{206}Pb/^{207}Pb$ isotope ratios from PM_{10} samples (Aily 2001) and aerosol samples (Bollhöfer and Rosman 2000) from São Paulo. Furthermore, the diagram also illustrates that gasoline, exhaust fumes, street dust, and industrial emission should be considered as possible Pb sources as this data conforms with the $^{206}Pb/^{207}Pb$ isotope ratios from Goiânia.

For a more detailed investigation of the Pb contribution from traffic-related sources and industrial emissions to the

Fig. 4 $^{208}Pb/^{206}Pb$–$^{207}Pb/^{206}Pb$ diagram according to the Pb isotope ratios for samples from Goiânia

Fig. 5 $^{208}Pb/^{206}Pb–^{207}Pb/^{206}Pb$ diagram according to the Pb isotope ratios for samples from Goiânia compared with Pb isotope ratios from recent studies of other regions in Brazil
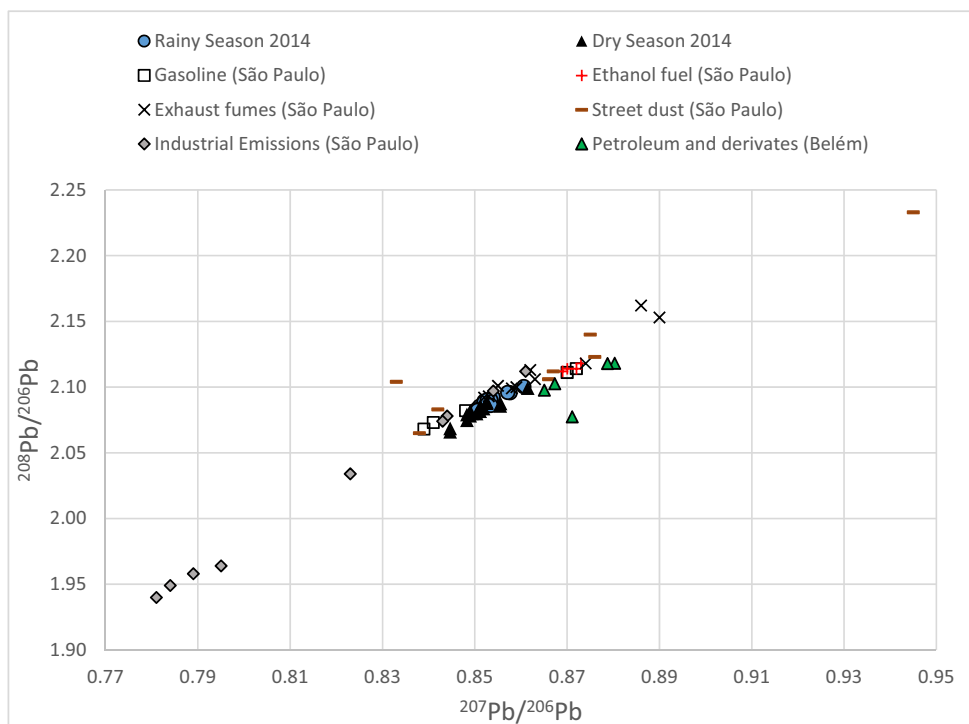
Pb of Goiânia samples, the following binary mixing equation was used with the assumption that Pb in both samplings is considered as a mixture between Pb from traffic-related sources and industrial emissions (Eq. 2):

$$R_{PM} = R_{traffic}X_{traffic} + R_{industry}X_{industry} \quad (2)$$

where R_{PM} is the $^{206}Pb/^{207}Pb$ isotope ratio of the respective PM sample, $R_{traffic}$ (1.155) is the average value for $^{206}Pb/^{207}Pb$

isotope ratios for Pb in traffic-related sources [average of petroleum and derivates (Souza de Lima 2010), exhaust fumes, gasoline, and street dust (Aily 2001)], $R_{industry}$ (1.222) is the average value for $^{206}Pb/^{207}Pb$ isotope ratios for Pb in industrial emissions (Aily 2001), $X_{traffic}$ is the contribution of Pb coming from gasoline in the particulate matter, and $1 − X_{traffic}$ ($=X_{industry}$) is the contribution of Pb from industrial emissions in the particulate matter.

The average $X_{traffic}$ value for samples taken in rainy season was $75.50 \pm 5.64\%$, while the average $X_{traffic}$ value for

Fig. 6 Comparison of the values of $^{206}Pb/^{207}Pb$ isotope ratio here reported with values of recent studies from Brazil
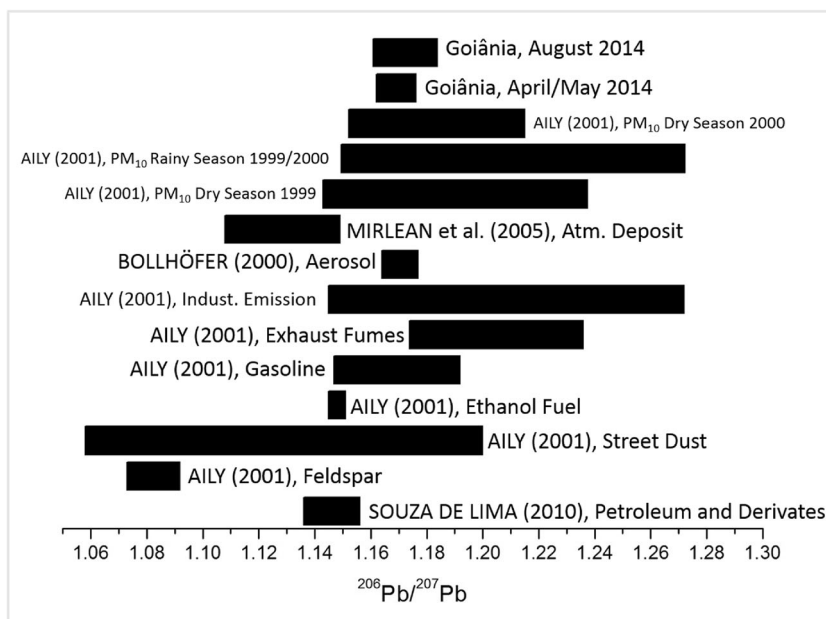
samples taken in dry season was 70.60 ± 8.31%, showing a very high influence of traffic-related sources on Pb in both sampling periods. Hence, contribution of traffic-related sources is dominant in both sampling periods, but also industrial emissions are an influence factor with a contribution of 24.50 ± 5.64% in rainy season and 29.40 ± 8.31% in dry season. Binary mixing equations in order to investigate the contribution of Pb coming from gasoline were also calculated by Zheng et al. (2004) and Mastral et al. (2009). In the research performed by Zheng et al. (2004), contribution of automotive Pb on Pb in PM_{10} samples from Shanghai, China, were around 20%. The studies of Mastral et al. (2009) resulted in a contribution factor of 23 ± 9% of Pb coming from gasoline on Pb in PM_{10} samples from Zaragoza, Spain.

Conclusion

Basic methods using ICP-MS technique in matters of optimization of acquisition time and dead time as well as the correction of mass bias were successfully implemented, which allowed an accurate determination of Pb isotope ratios of the study samples.

Pb concentrations from Goiânia showed differences between rainy and dry season. Samples from dry season had higher Pb concentration values in average and varied in a lower scope than samples from rainy season, possibly due to environmental factors (e.g., rainfall, distinct transport rate of particulate matter). Considering the guide values established by CETESB, the European Union, or the United States Environmental Protection Agency, the exposition to the measured Pb concentrations over the respective averaging times would not carry risks to the human health.

Pb isotope ratio analysis showed slight differences between dry and rainy season and an enrichment of [206]Pb isotopes relative to [207]Pb and [208]Pb isotopes in dry season. Pb in both sample periods were highly influenced by traffic-related emissions. However, binary mixing equations illustrated that there was also an apparent contribution of industrial emissions on Pb in both sampling periods and that also other Pb sources should be considered as potential factor of influence to Pb in Goiânia. Hence, data sets of Pb sources in Brazil are fragmentary and more data of possible Pb sources must be consulted in order to develop a more significant assessment.

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