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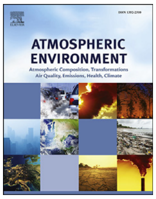

An isotopic study of atmospheric lead in a megacity after phasing out of leaded gasoline

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HIGHLIGHTS

- Air mass transport from eastern industrial area to São Paulo was identified.
- Pb concentration still is significant after phasing out leaded gasoline.
- Pb pollution is a serious consequence of having an intensely urbanized city.
- São Paulo city has a diverse number of atmospheric lead sources.

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ABSTRACT

Atmospheric lead (Pb) concentrations in São Paulo city, Brazil, remain significant, despite the fact that leaded gasoline was phased out. The use of its isotope signature allows tracing emissions to the increasing number of cars, urban construction, and industrial emissions in this densely populated area. High-precision and accurate stable isotope ratio determinations using isotope dilution thermal ionization mass spectrometry (ID-TIMS) combined with particle induced X-ray emission (PIXE) and multivariate analysis were used to identify the main sources of lead present in São Paulo atmospheric particulates. Throughout a period of sixty days, aerosol samples were collected every 12 h during the summer of 2005 at the University of São Paulo (USP) and simultaneously during one week in an industrial area (Cubatão) and in two more remote areas (São Lourenço da Serra and Juquitiba). The data suggests that aerosols from São Paulo are mainly derived from vehicular exhaust (mostly gasoline) and traffic dust resuspension, with the admixture of industrial emissions, including cement. Lead isotopic compositions (expressed as $^{206}Pb/^{207}Pb$ ratios) measured in São Paulo aerosols range from 1.1491 to 1.2527 and are similar to those determined from tunnel dust, fuels, and vehicular exhaust; therefore, those are likely to be the main lead sources in the atmosphere of São Paulo. Vehicular traffic (fuel combustion, dust from vehicular components, and road dust) remains an important source of lead in the atmosphere. The maximum concentration occurring during the summer was 0.055 μg m^{-3} in fine particles, which is detrimental for human health and may lead to exceedances of the Air Quality Standard for lead of 0.15 μg m^{-3} (3-month average) during other seasons when the dispersion of pollutants is less favourable.

1. Introduction

Leaded gasoline was phased out in the late 20th century to address health and economic concerns, (Pacyna et al., 1995; Bollhöfer and Rosman 2001; Cheng and Hu, 2010). This was triggered by high lead concentrations ([Pb]) in atmospheric particulate matter and subsequent warnings from researchers devoted to the reduction of the emissions of anthropogenic lead into the environment. In 1962, Chow and Patterson reported the first evidence

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of high lead concentrations in the environment which subsequently lead to the concern about anthropogenic lead pollution (Chow and Patterson 1962).

The "Pró-Álcool" program, started in 1975, and aimed to increase the use and production of ethanol as vehicular fuel, and currently is added 27% to gasoline. An increasing fleet of so called flex-fuel vehicles is operating with different blends The phasing out of leaded gasoline in the country began only after 1989, following public demands to reduce the air pollution levels.

The phasing out of leaded gasoline in Brazil resulted in a significant decrease of [Pb] in the atmosphere of Brazilian cities (Castanho and Artaxo, 2001). The Metropolitan Area of São Paulo (MASP) is the most developed and industrialized region in Brazil with a population of twenty million inhabitants and more than seven million vehicles powered by diesel, gasoline, ethanol and/or natural gas, emitting or enabling the generation of several pollutants in the atmosphere. Air pollution in São Paulo has been studied since the early 1980's by a group of pioneers in atmospheric science from the University of São Paulo (Orsini et al., 1986; Andrade et al., 1993; Massambani and Andrade, 1994; Ulke and Andrade 2001; Castanho and Artaxo, 2001; Sánchez-Ccoyllo and Andrade, 2002; Miranda et al., 2002). In 1989, various aspects of atmospheric pollution in São Paulo were intensively studied as part of the São Paulo Atmosphere Characterization Experiment (SPACEX) and since 1968, the Air Quality Centre in São Paulo (CETESB) has been responsible for air quality in this megacity, and since 1985 publishes air quality annual reports for the MASP and some other São Paulo State areas (CETESB, 2016).

Thermal Ionization Mass Spectrometry (TIMS) is widely used to determine stable lead isotope composition in particulate matter to trace atmospheric lead sources, which in turn assists identifying specific types of sources using their isotopic fingerprints (Volkening and Heumann, 1990; Radlein and Heumann, 1992; Erel et al., 1997; Véron et al., 1998; Chiaradia and Cupelin, 2000; Alleman et al., 2001; Luke and Othman, 2002; Velde et al., 2005; Komarek et al., 2008). Studies using lead isotopic variations as tracers of pollutant sources in several cities in Brazil were reported by Bollhöfer and Rosman (2000), in São Paulo city by Aily (2001) and by Gioia et al. (2010), and in Brasília by Gioia (2004). The study of Aily (2001) produced the first lead isotope data for atmospheric particulate matter collected in São Paulo, leading to the identification of natural and anthropogenic sources. That study revealed important seasonal variations in the relative contribution of different sources of atmospheric lead during the summer in 2000. Moreover, it identified industrial emissions as the main type of source for atmospheric lead. A follow up study by Gioia et al. (2010), determined [Pb] and isotopic ratios in aerosols collected in short intervals throughout a period of three days and suggested that vehicular emissions were quantitatively still important in São Paulo. However, more data are necessary to ratify those conclusions and to improve our understanding of the factors that control atmospheric lead in São Paulo.

In order to better identify and quantify the sources of pollutant detected in the MASP atmosphere after the phasing-out of leaded gasoline, the present study uses lead isotopic compositions and multi-element data that were obtained on aerosol collected during a 12-h sampling campaign in São Paulo for sixty days during the summer of 2005 (December 2005 to February 2006). Simultaneous sampling was carried out in three other locations close to São Paulo, representing different source areas. Meteorological parameters were combined with chemical and isotopic data to characterize aerosols, their natural and anthropogenic sources, and investigate the effect of air mass transport.

2. Methods

2.1. Site description

São Paulo city is located at the southeast of Brazil, approximately 60 km from the coast (Fig. 1). The Metropolitan Area of São Paulo (MASP, UTM 23K 333284 7394644) includes the city of São Paulo and 38 other cities and had a population of 19.2 million inhabitants in 2005 (IBGE, 2007). It is the most industrialized and economically developed region of South America and has one of the largest urban motor vehicles fleet in the world. The sampling site in São Paulo City is at the University of São Paulo (USP), which is a very large and green campus, surrounded by intense vehicular traffic.

Three additional sites (Fig. 1) were selected: (i) Cubatão (Mogi Valley, UTM 23K 0360595 7363775, 40 km southeast from São Paulo city), an industrial area, dominated by fertilizer plants and intense traffic of heavy vehicles and a possible source region for atmospheric pollutants; (ii) Juquitiba, located 70 km southwest from São Paulo, a forest area close to the Jurupará State Park and considered here as the 'background' location (UTM 23K 289458 7351766); and (iii) São Lourenço da Serra, a neighbouring municipality of Juquitiba, less forested and receiving significant contribution of vehicular emissions due to its proximity to the federal highway (Regis Bittencourt, UTM 23K 302148 7360716).

2.2. Sampling and meteorological data

An in-house inlet system was used to select particles with aerodynamical diameter (ϕ)<10 μm (Hopke et al., 1997). Two polycarbonate membranes were changed every 12 h, and particle fractions $PM_{10-2.5}$ ($2.5 < \phi < 10$ μm) and $PM_{2.5}$ ($\phi < 2.5$ μm) were sampled separately. Inhalable particulate matter corresponds to $PM_{10} = \sum(PM_{10-2.5}$ and $PM_{2.5})$. An inlet tube downstream from the filter holder collected the air into a twin cylinder diaphragm pump. The air was forced through a standard volumeter, where it was exhausted to the atmosphere. The flow rate was approximately 16 L/min.

Aerosol collections in São Paulo were performed at the Campus of the University of São Paulo (USP) (Fig. 1) during the summer season from December 2005 until February 2006 (Table 1). During this sampling period, 214 filters (polycarbonate membranes) were collected. Sampling at the other sites were performed for seven days in February 2006 (Table 1). Vehicular emissions from diesel and regular gasoline were also collected. Meteorological data in São Paulo were obtained from stations at the *Instituto de Astronomia, Geofísica e Ciências Atmosféricas*, IAG-USP. Relevant meteorological parameters including temperature, atmospheric pressure, precipitation, and wind velocity and direction were taken into account for data interpretation.

Dust sources from road, tunnel, phosphogypsum from residual pile, cement, and soil were collected in indicates plastic bags. These materials were artificially resuspended using an in-house built system to segregate fine and coarse fractions. For sample numbers see Table 1.

2.3. Sample processing

Two hundred and fourteen filters were weighed to determine particulate matter concentration in coarse, fine, and inhalable fractions. One hundred and thirty aerosol samples were analyzed for lead isotopes. They were dissolved over three days in a mixture of 2 mL (40%) HF with 0.5 mL (14.5 M) HNO_3. After evaporation, 2 mL of 6 M HCl were added, and the solution was heated (80 °C) for

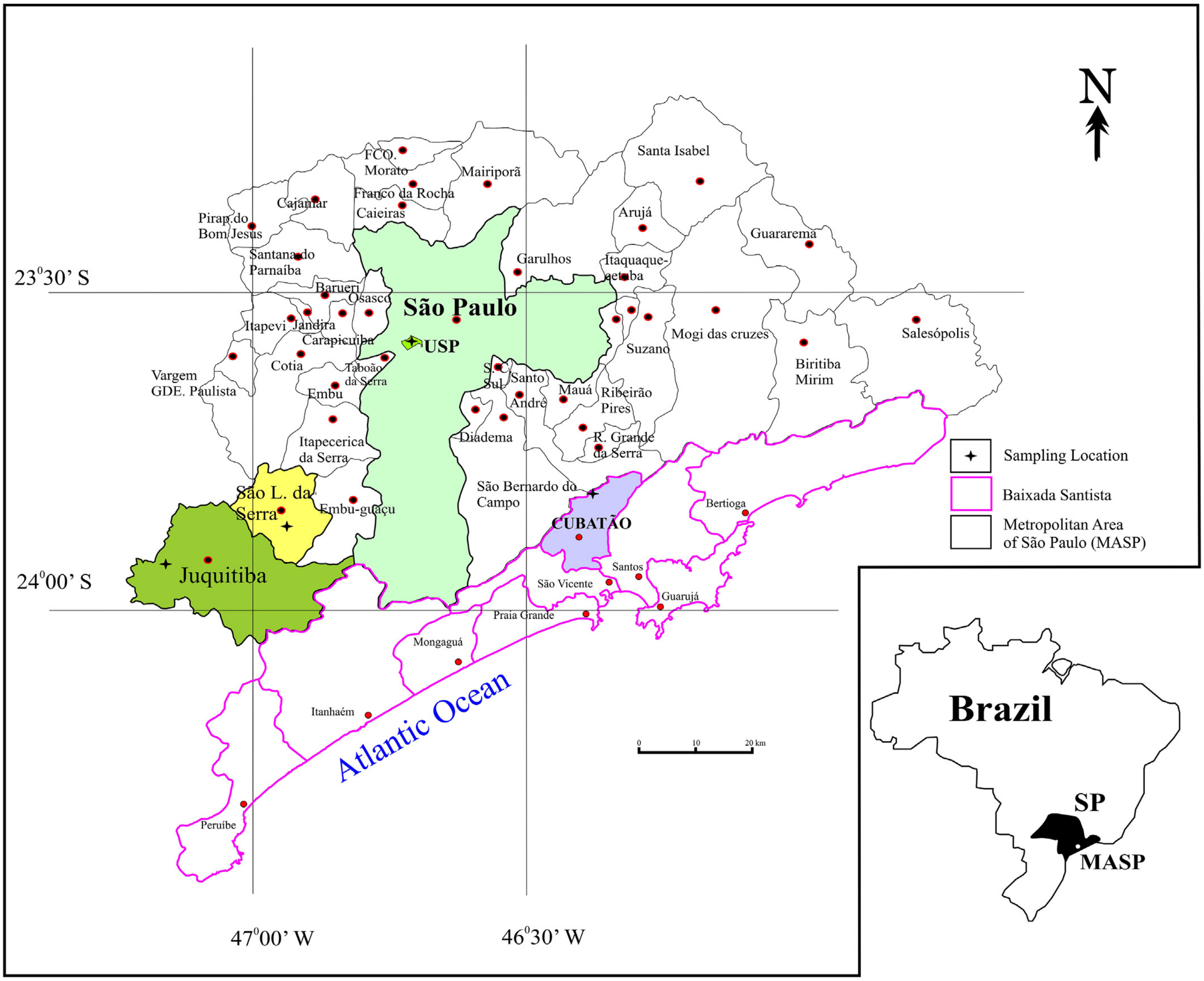

Fig. 1. Map of Metropolitan Area of São Paulo and coastal area (Baixada Santista). The crosses indicate the air sampling stations in the cities of São Paulo, Juquitiba, São Lourenço da Serra, and Cubatão.
Source: Modified from Instituto Geográfico e Cartográfico, 2003.

Table 1
Sampling stations and collection parameters during the summer of 2005.

Experiments	Sampling interval	Particle size	Period	No of samples
USP –São Paulo city	Every 12 h	$PM_{10\text{-}2.5}$ and $PM_{2.5}$	Dec/2005 Feb/2006	214
CUBA- Cubatão Mogi Valley	Every 12 h	$PM_{10\text{-}2.5}$ and $PM_{2.5}$	1 to 8 Feb/2006	25
SL- São Lourenço da Serra	Every 12 h	$PM_{10\text{-}2.5}$ and $PM_{2.5}$	2 to 6 Feb/2006	8
CBA - Juquitiba	Every 12 h	$PM_{10\text{-}2.5}$ and $PM_{2.5}$	1 to 6 Feb/2006	9
Vehicular Emissions	–	$PM_{10\text{-}2.5}$ and $PM_{2.5}$	–	04
Sources –Dust Cubatão	–	$PM_{10\text{-}2.5}$ and $PM_{2.5}$	–	14
Industrial Filters Cubatão	–	–	–	04
Sources – Dust São Paulo	–	$PM_{10\text{-}2.5}$, and $PM_{2.5}$	–	10
Other sources cited in Fig. 9			Aily (2001)	

one day. The final solution was dried and added 1 mL of 6M HBr. This solution was split into two aliquots: one aliquot (consisting 80% of solution) was used for the determination of the Pb isotopic compositions (IC), and the remaining 20% was used to measure [Pb] concentration using isotope dilution (ID). The IC and ID solutions were evaporated to dryness and diluted with 0.6 M HBr; Pb was extracted using columns packed with BioRad AG1-X8 anionic exchange resin in HBr media. The procedure for separation of Pb from the matrix of the digested aerosol samples consists of: an anion exchange resin (0.15 mL) was loaded into a heat-shrink Teflon tubing with 4 mm diameter. The resin bed was cleaned using 1.5 mL of 6 N HCl, followed by 1.5 mL of water. The resin was then conditioned using 1.5 ml of 0.6 M HBr. The supernatant of the sample, dissolved in 1 ml of 0.6 M HBr, was loaded onto the column. A 1.5 mL of acid solution 0.6 M HBr − 0.6 M HNO_3 was then introduced to remove elements other than Pb, because HBr−HNO_3 mixture is more efficient than using HBr alone with respect to the separation of zinc from lead (Kuritani and Nakamura, 2002). The lead sample fraction was eluted with 1.0 mL of water. Prior to evaporation, one drop of 0.05 N H_3PO_4 was added to the solution to prevent complete dryness.

Chemical procedures were conducted in clean room conditions and with ultra-pure reagents (sub-boiling distillation in Teflon® bottles) at the Center of Geochronological Research, University of São Paulo. Lead isotope ratios were measured by Thermal Ionization Mass Spectrometry (TIMS) using a multi-collector TRITON mass spectrometer at the Laboratory of Geochronology and Radiogenic Isotopes (LAGIR), of the Rio de Janeiro State University. Each sample was loaded onto a single Re filament with 2 μL silica gel and 2 μL H_3PO_4, to improve the lead ionization during the mass spectrometric analysis (Cameron et al., 1969). Mass fractionation was ≤0.10%/a.m.u. determined by repeated measurements of the NBS 981 Common Pb Standard, an external precision of 0.08% (2σ) for ratios $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$. Lead analytical blanks were typically lower than 50 pg and around 400 pg including membrane filter blanks. Dust samples followed the same dissolution process and lead chemical separation procedure used for aerosol filter analysis.

One hundred and thirty-four aerosol samples (68 fine fractions and 66 coarse fractions) collected at the USP station, were analyzed by PIXE (Particle Induced X-ray Emission, Johansson and Campbell, 1988; Johansson et al., 1995). One quarter of each original filter was used. The system calibration for atmospheric aerosol samples does not require matrix absorption correction (Cesareo et al., 1998). We used Micromatter-XRF calibration standards, prepared by evaporation of metals and salts evaporation under vacuum (thickness around tenths of μg/cm^2, with 5% uncertainty). The analysis was carried out at the Laboratory for Material Analysis by Ion Beam, at the Institute of Physics, University of São Paulo. The calibration standard thickness was controlled by Rutherford Backscattering Spectrometry (RBS), with an estimated uncertainty below 3%.

3. Results

We report here all the data from all the sampling stations. This includes: (i) meteorological data to assess air mass transport; (ii) particulate matter concentrations, [Pb], and lead isotopic compositions to identify the source and air mass transport; and (iii) chemical composition to evaluate statistically multi-elemental factor analysis for source discrimination and to constrain relations with lead isotopic compositions.

3.1. Meteorological data from the city of São Paulo

The wind direction is mainly distributed around the N-W and S-E quadrants centres in São Paulo (Fig. 2). This is in agreement with the typical large scale general circulation system in this area, often associated to the regional circulation coupling the sea and mountain breezes generated at the near coast and the "Serra do Mar" mountain range. SE wind dominates during daytime periods, while at nighttime less intense NW winds prevail, with 23.5% of calm periods. The approximately 60 km distance separating São Paulo from the coast, introduces a time delay in the possible air masses exchange between the MASP area and the coast, where Mogi Valley is located.

The predominant circulation system expressed in Fig. 2 and Supplementary Fig. S1, and based in study areas location (Fig. 1), indicate that there is the possibility of air mass transport from the coast (Cubatão - Mogi Valley) to São Paulo may occur mainly during the day (Fig. 2).

Temperature and atmospheric pressure between December 25 and 28 were below 25 °C and above 930 mbar. In January 2006, the wind directions were predominantly southeast (SSE-SE) and occasionally N-NW, mostly during the day. February showed large variations, mainly from the NW-NNW-N and SE-SSE (Supplementary Fig. S1). There was low atmospheric pressure, high temperature, and the highest levels of atmospheric precipitation (Fig. 3).

Atmospheric precipitation favours the removal of pollutants during the Brazilian summer, reducing particulate matter concentration in the atmosphere and hence [Pb] in the atmosphere (Gioia et al., 2010).

3.2. Particulate matter concentrations

Particulate matter concentrations are reported in detail in Supplementary Table S1. The PM_{10} concentrations at the USP station range from 9.1 to 57.4 μgm^{-3} during the entire period of December 2005 to February 2006 (Figs. 3 and 4), and inhalable particles concentrations are higher at night. In the fine fraction, the concentrations are between 5.4 and 34.8 μgm^{-3}, and the coarse fraction ranges from 3.5 to 26.7 μg m^{-3} (Fig. 3). USP samples show that PM_{10} (24 h) at USP range from 24.6 to 42.6 μg m^{-3}

PM_{10} concentrations in Cubatão (industrial area) range from 21.3 to 77.2 μg m^{-3} (Figs. 4 and 5). Concentrations of the fine fraction vary between 6.9 and 41.8 μg m^{-3} and of the coarse fraction range from 9.8 to 46.4 μg m^{-3}. Particulate matter concentrations in Cubatão are the highest, especially the coarse fraction collected during the daytime. PM_{10} (24 h) values vary between 21.7 and 58.1 μg m^{-3}. This result exceeds the National Air Quality Standard for the annual arithmetic average concentration (50 μg m^{-3}) (CETESB, 2016).

In the São Lourenço rural area, PM_{10} concentrations range from 17.3 to 24.7 μg m^{-3}. The concentrations of the fine fraction vary between 8.1 and 17.4 μg m^{-3}, and the coarse fraction ranges from 4.3 to 11.7 μg m^{-3} (Figs. 4 and 5). Juquitiba presents the lowest PM_{10} concentrations, ranging from 8.4 to 20.3 g m^{-3}. The concentrations of the fine fraction vary between 4.3 and 13.4 μg m^{-3}, and the coarse fraction ranges from 2.4 to 9.4 μg m^{-3} (Figs. 4 and 5).

At USP, São Lourenço da Serra, and Juquitiba various national standard limits for air quality were not exceeded including: i. Standard for Air Quality daily for PM_{10} (24 h) of 150 μg/m^3 admissible at most once a year; ii. annual limit of 50 μg m^{-3}; iii. Standard for Air Quality for $PM_{2.5}$ annual standard of 15 μg m^{-3} established by the U.S. Environmental Agency (USEPA) for the arithmetic mean of annual averages (24 h) the last three years).

3.3. Lead concentrations and isotopic compositions

3.3.1. [Pb] and Pb isotopic compositions on USP aerosol samples

The aerosol samples collected at USP show [Pb] ranging from

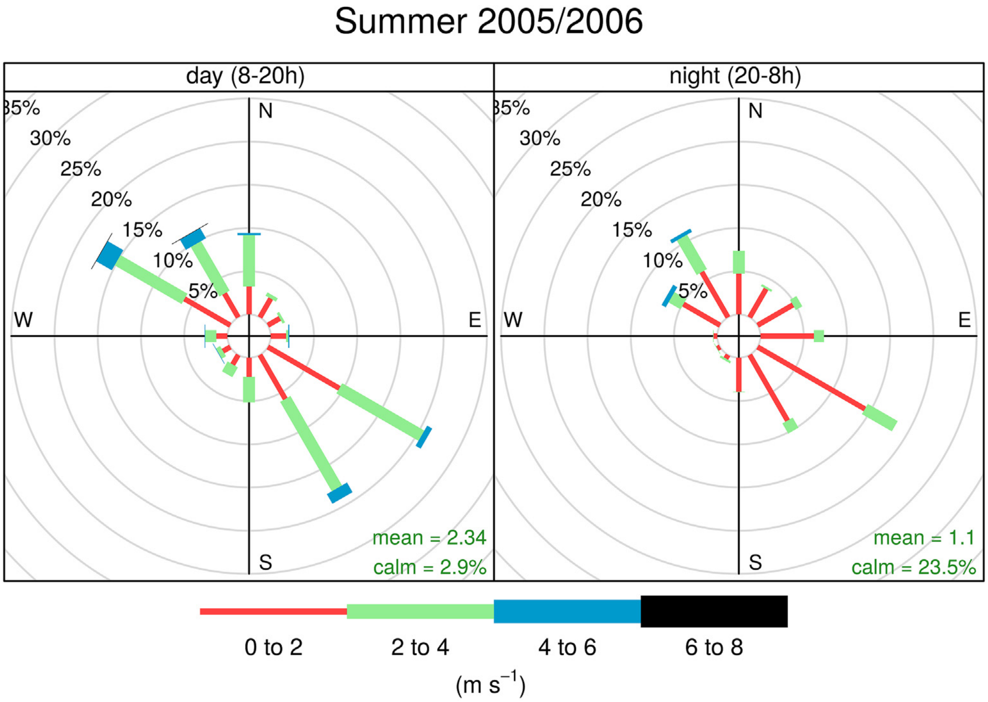

Fig. 2. Wind rose during the throughout summer sampling period, for day and night-time. Calm stands for wind speed of below 0.4 m s^{-1}.

0.50 to 54.99 ng.m^{-3} (Table 2, Fig. 6). The [Pb] in the fine fraction range between 1.75 and 54.99 ng.m^{-3}, and in the coarse fraction from 0.50 to 29.63 ng.m^{-3}.

The ^{206}Pb/^{207}Pb isotopic ratios vary between 1.1491 and 1.2527 in the coarse fractions (Table 2, Fig. 6). The most radiogenic ratios (^{206}Pb/^{207}Pb > 1.20) were observed on days with predominantly SE winds and when lead concentrations were lower. These conditions are mostly observed on weekends and Mondays (Supplementary Table S2).

The [Pb] observed in MASP are much lower than those found in other major urban world centres such as Shanghai, China (167–854 ng m^{-3} in PM$_{10}$ fraction; Zheng et al., 2004), but they are higher compared to those recorded in Brasilia (Brazil) during the summer of 2003 (1.66 ± 2.11 ng m^{-3}; Gioia, 2004). The concentrations found in MASP are lower than those determined in the past.

Orsini and Bouéres (1977) determined the [Pb] in the atmosphere of São Paulo using the particle induced X-ray emission (PIXE) technique and found in a small set of samples an average of 1 µg m^{-3} (24 h PM$_{10}$). [Pb] (24 h PM$_{10}$) ranging from 0.83 to 1.60 µg m^{-3} were determined in São Caetano city (east of São Paulo city), in 1978. These concentrations decreased to an interval of 0.22–0.41 µgm^{-3} in 1983, which was attributed to a reduction of tetraethyl lead as an additive to gasoline (Orsini et al., 1986).

In São Paulo during 1989, [Pb] in fine fractions ranged from 42.0 to 58.1 ng.m^{-3} during the winter (Andrade et al., 1994) and from 22.6 to 16.4 ng.m^{-3} during the summer (Castanho and Artaxo 2001). Aily (2001) determined a [Pb] ranging from 3.02 to 254.52 ng.m^{-3} in PM$_{10}$ (24 h) fractions collected between August 1999 and September 2000, and generally lower concentrations were found in the summer (36 ± 38 ng m^{-3}).

3.3.2. *[Pb] and isotopic compositions at USP, Cubatão, São Lourenço da Serra, and Juquitiba*

One of the main objectives of this project was to determine the Pb isotopic compositions in the four areas (São Paulo, Cubatão, São Lourenço da Serra, and Juquitiba cities) during the summer of 2005–2006. The isotopic characterization of each site would identify whether there are connections between these regions through air mass transport processes, especially between São Paulo and Cubatão, where winds from SE sector are predominant in the summer. Results from samples collected simultaneously at four locations during the period from February 1 to 6, 2006 are presented here (Table 2, Figs. 7, and 8a–d).

Lead concentrations at USP range from 3.52 to 54.99 ng m^{-3}, and the highest concentrations are found in the fine fraction and generally during nighttime (Fig. 8a and c). The ^{206}Pb/^{207}Pb values range from 1.1590 to 1.2527 (average of 1.183 ± 0.025, n = 12) and are slightly higher in the fine fraction and in aerosols collected during daytime (Fig. 8b and d).

In Cubatão, the [Pb] range from 1.53 to 28.30 ng m^{-3} and are higher in fine particles collected during daytime (Fig. 8a,c). The low range of Pb concentrations suggests an effect of rain washout during the rainy summer days in Cubatão, which results in an effective removal of particulate matter. The ^{206}Pb/^{207}Pb ratios range from 1.1854 to 1.3279 (average of 1.257 ± 0.042), and the slightly higher ones were determined on the fine fractions collected during the daytime (Fig. 8b and d).

The most radiogenic lead isotopic compositions measured in aerosols at USP are in the same range as of those from Cubatão, suggesting that some particles from Cubatão reached São Paulo by SE wind direction transport (Fig. 6).

In contrast, [Pb] in aerosols collected at São Lourenço da Serra and Juquitiba are the lowest ones, as seen in Table 2, averaging 5.21 ± 4.5 ng m^{-3} and 0.60 ± 0.58 ng m^{-3}, respectively. The ^{206}Pb/^{207}Pb ratios are similar; however, at São Lourenço da Serra, the range is narrower (1.1750–1.1879) than at Juquitiba (1.1674–1.1924). The aerosols from Juquitiba show the lowest Pb concentrations, and possibly represent the background and a natural geogenic source.

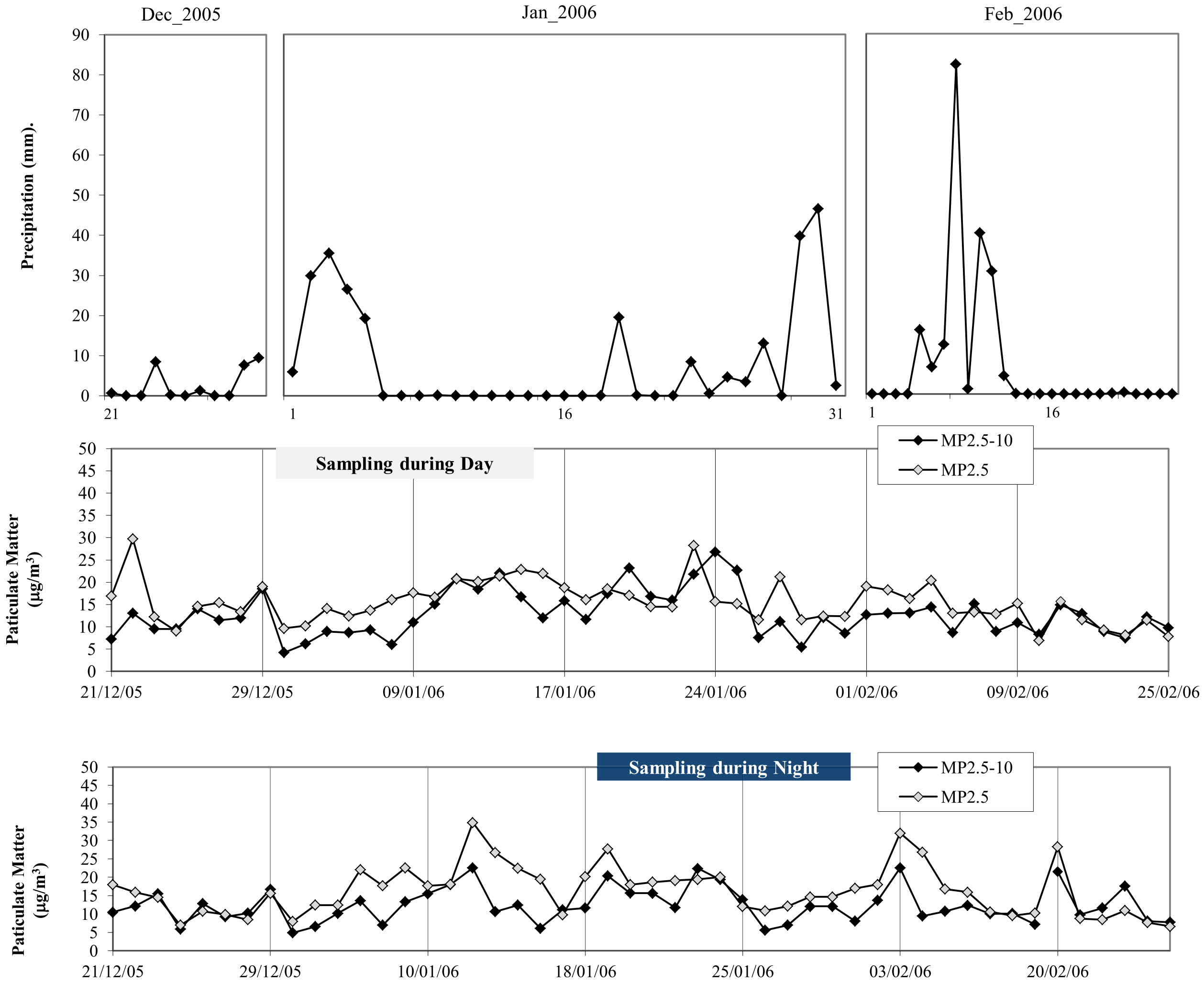

Fig. 3. Precipitation and concentrations of $PM_{2.5-10}$ and $PM_{2.5}$ samples collected at day and night in the whole period on summer of 2006, at the USP station. Summer in São Paulo is characterized by intense precipitation, which decreases the particulate matter concentration.

3.4. *Assessment of the chemical composition*

3.4.1. *Aerosols*

Multi-element concentration determinations by PIXE in the fine and coarse fractions of particulate matter collected during day and nighttime periods is given in Supplementary Fig. S2. Mean concentrations ($ng.m^{-3}$) were obtained for twenty elements and are shown in Table 3.

Sulphur typically present in metropolitan areas, shows high concentrations in the fine fraction (average of 930 ng m^{-3}), indicating a significant contribution from industrial and vehicular emissions, because it derives from combustion processes (Miranda and Tomaz, 2008), and subsequent conversion of the SO_2 gas into particles. Its presence in the coarse fraction may indicate the contribution of biogenic material and soil resuspension, as already suggested by Castanho and Artaxo (2001).

High concentrations of calcium (338 ng m^{-3}) and phosphorous (30.5 ng m^{-3}) are found in the coarse fraction, which reveals important contributions from urban construction activities, which is one of the most common sources of these elements in large urban cities of emerging economies (Zheng et al., 2004). Calcium is the most important indicators of this source, and the presence in the coarse fraction demonstrates its dominance at the local scale. Likewise, phosphorus is a good indicator for this source due to the addition of gypsum during cement manufacturing. Phosphorous may also be associated to the transport of fertilizer plants emissions at Cubatão.

Concentrations of lead (11.1 ng m^{-3}) and zinc (60.6 ng m^{-3}) in the fine fraction suggest a contribution from fossil fuel combustion processes and, therefore, the influence from vehicle emissions (Huang et al., 1994). Low concentrations of vanadium (1.41 $ng.m^{-3}$) and nickel (3.05 $ng.m^{-3}$), in contrast, suggest a less influence of oil burning and heavy vehicle traffic during the sampling period (Miranda and Tomaz, 2008).

The presence of chlorine in the São Paulo aerosols (181.9 $ng.m^{-3}$ in the coarse fraction) and 22 $ng.m^{-3}$ in fine fraction) could be explained by sea breeze transport from the east coast, as already suggested by Castanho and Artaxo (2001).

Samples collected at the other two sampling locations (Cubatão and Juquitiba) during seven days show different fingerprint elements typical for each area, i.e., the Cubatão aerosols have high phosphorous concentrations in the coarse fraction, which is related to the presence of phosphogypsum from fertilizer factories, and Juquitiba aerosols show the predominance of elements derived from soil (Al, Si, Ti, K, and Fe), indicating soil resuspension.

3.4.2. *Multi-element statistical analysis — USP data*

Factor analysis (FA) was used to analyze the chemical and

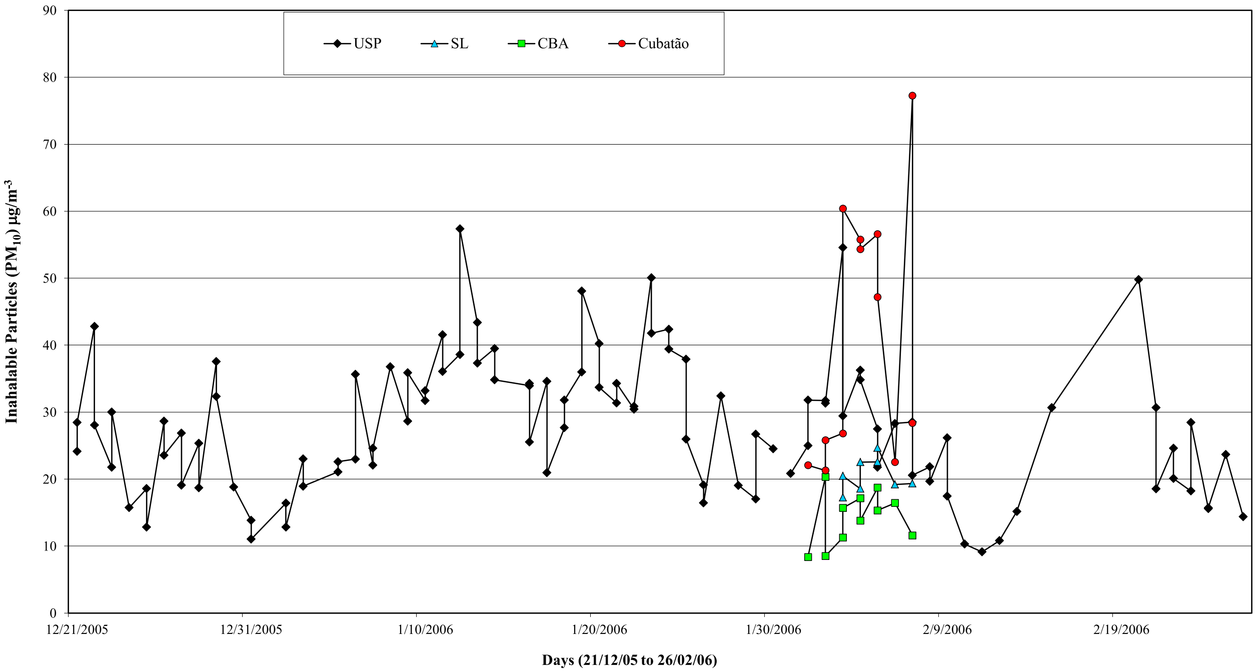

Fig. 4. PM_{10} concentrations of samples collected in the period of 21st December 2005 to 26th February 2006 in USP station and six days at the Juquitiba (CBA), São Lourenço da Serra (SLS), and Cubatão stations.

isotope data and to assist in the identification of the main sources of the atmospheric aerosols, as reported in Tables 4 and 5. Factor analysis is a widely used statistical data treatment, that seeks the least number of factors explaining the major fraction of the common variance of a database. The factors were rotated to maximize the variance of the extracted rotated factors, and the most common treatment, VARIMAX, maximizes its squared loadings (Johnson and Winchern, 1982; Miranda and Tomaz, 2008). The species with higher rotated loadings in a factor, provides a way to associate it to a source in the environment, with similar composition.

The factors obtained for São Paulo show most variables with extractions greater than 0.8, indicating a very reliable data set. Four factors were extracted for the fine fraction of the aerosols collected in São Paulo. The first factor is the high correlation among $PM_{2.5}$, Mn, Fe, Ni, Cu, Zn, Pb, and Br, indicating a vehicle emissions source due to the presence of the marker elements (Zn, and Br), based in Huang et al. (1994). The second factor correlates Al, Si, K, Ca, Ti, Mn, and Fe, which clearly shows the influence of soil dust resuspension. The mass of the fine fraction has a great significance for the production of sulphate particles as well as K, Mn, Fe, Ni, Cu, Br, and Pb(ID) (Pb concentration was obtained by isotope dilution mass spectrometry technique), representing the third factor: a mixture between soil dust, vehicle emissions, and biomass combustion (association with sulphates and potassium). The fourth factor may be associated to metallurgy, but we cannot rule out an industrial source related to chromium and manganese. The last factor shows the relationship between sulphur with high values of $^{206}Pb/^{207}Pb$.

The first factor of the coarse fraction presents the association with K, Ti, Cr, Mn, Sr, and Hg. This factor is odd and not easy to interpret. The presence of mercury is incompatible with soil resuspension, and we suggest a mix between industrial and natural sources. The second factor is likely associated with the resuspension of soil (dust) due to the presence of Al, Si, Ca, Fe, $PM_{2.5-10}$ and a minor loading of Pb. The third factor correlates sulphate particles with Fe, Ni, Cu, Zn, and Pb as vehicular emissions. The fourth factor is dominated by Cu, Zn and Pb, which could be explained by direct vehicular emissions (break, electric motors, exhaustion).

3.5. Chemical characterization of sources

Potential sources were characterized in the course of this study, including tunnel dust, road dust, diesel, and gasoline vehicular exhaust emissions, cement in São Paulo, and industrial plant dust, phosphogypsum, soil, and industrial filters from Cubatão (Fig. 9, Supplementary Table S3) to enable an improved source identification in the aerosols collected in São Paulo and Cubatão.

Gioia et al. (2010) suggested that traffic emissions are an important atmospheric lead source due to the large vehicular fleets in São Paulo, combining contributions from fuel combustion, brake wear, tyre wear, road surface abrasion, and resuspension of road dust with passing traffic, characterizing vehicular traffic emissions. Even considering the very low lead concentrations in fuels (Aily 2001; Gioia et al., 2010), the large number of vehicles must magnify lead emissions to the atmosphere (Gioia et al., 2010). Two distinct samples were used in this study to characterize vehicular emissions: car exhaust, representing the influence on fuel combustion into the motor (to gasoline and diesel); and dust from main roads and a tunnel used by light vehicles to characterize lead isotopic signature to all possible contributions from vehicular traffic. We assume a closed system to determine the impact of vehicular contribution in the São Paulo atmosphere.

The road dust collected at high traffic avenues in São Paulo (Avenida dos Bandeirantes and Marginal Pinheiros) have non-radiogenic lead with $^{206}Pb/^{207}Pb$ ratios ranging between 1.1365 and 1.1752 and $^{208}Pb/^{206}Pb$ from 2.0817 to 2.1885. The tunnel dust collected at the Ayrton Senna Tunnel in São Paulo showed [Pb] around 33 $\mu g.g^{-1}$ and 104 $\mu g.g^{-1}$ in fine fraction and coarse fraction, respectively, and $^{206}Pb/^{207}Pb$ between 1.1727 and 1.1772, and $^{208}Pb/^{206}Pb$ from 2.0809 to 2.0848, which are very similar to the lead isotopic compositions of aerosols collected in São Paulo (Fig. 9).

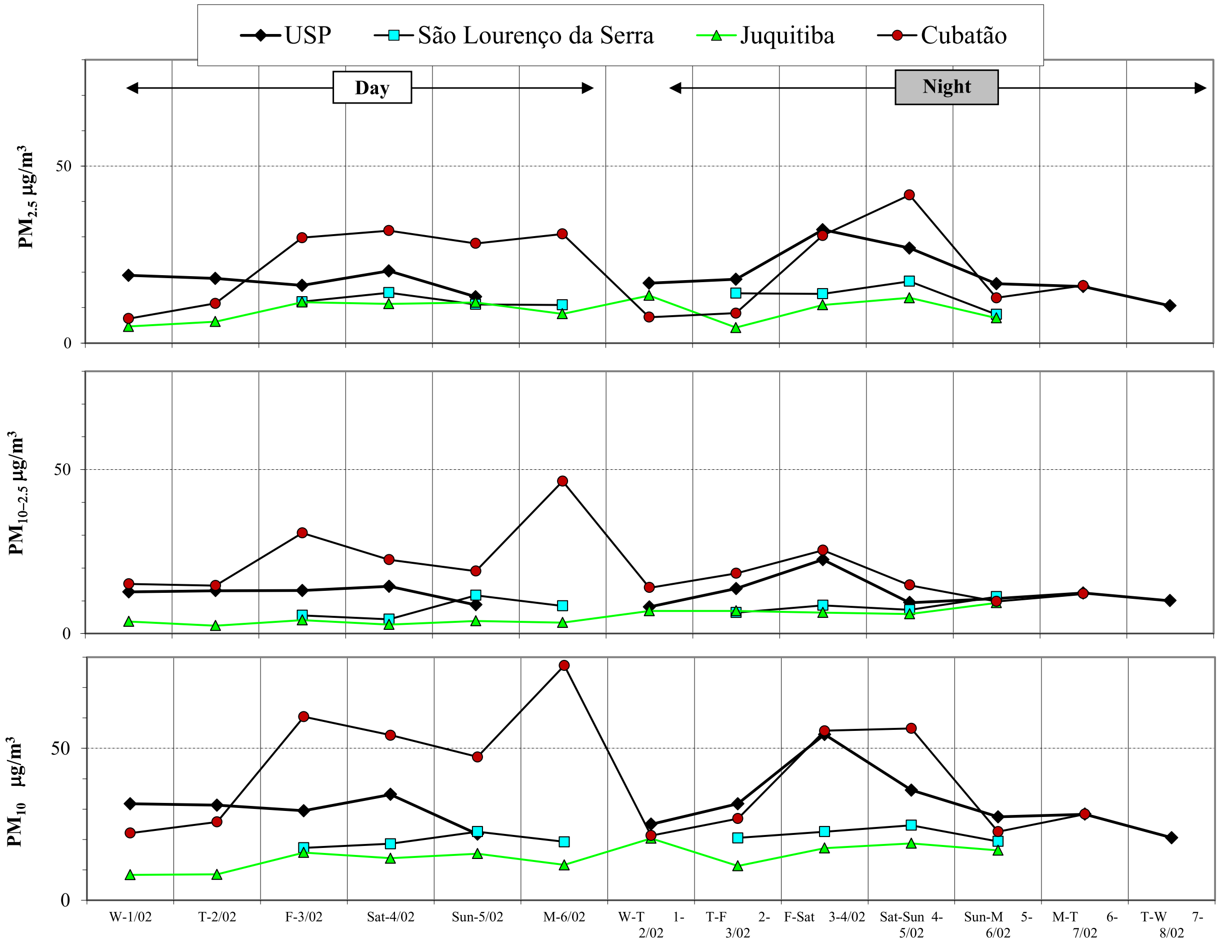

Fig. 5. Concentration of PM$_{10}$, of coarse (PM$_{10-2.5}$), and of fine (PM$_{2.5}$) fraction samples collected between February 1 and 7, 2006 at the station of USP and Cubatão, and between February 1 and 6, 2006 at the station of Juquitiba, São Lourenço da Serra, during day and night. Data are compared to the annual limit of 50 µg m^{-3}. No samples were taken at São Lourenço da Serra on 1st and 2nd Feb. São Paulo PM concentrations were higher during night, and Cubatão PM concentrations were higher during day periods. Letters on axis corresponds days in week in sequence.

Table 2
[Pb] and isotopic compositions obtained by ID-TIMS of fine and coarse particles collected in São Paulo, Cubatão, São Lourenço da Serra, and Juquitiba sampling stations.

Parameters	PM$_{2.5}$				PM$_{2.5-10}$			
	Average	SD	Minimum	Maximum	Average	SD	Minimum	Maximum
USP – São Paulo								
^{206}Pb/^{204}Pb	18.5621	0.3311	17.9444	19.5149	18.5180	0.3520	17.9619	19.8431
^{206}Pb/^{207}Pb	1.1852	0.0180	1.1511	1.2359	1.1822	0.0190	1.1491	1.2527
^{208}Pb/^{206}Pb	2.0538	0.0315	1.9525	2.1058	2.0608	0.0333	1.9169	2.1115
[Pb] ng.m^{-3}	16.89	12.71	1.75	54.99	6.97	6.12	0.50	29.63
Vale do Mogi – (Vila Parisi-Cubatão)								
^{206}Pb/^{204}Pb	20.0828	0.9067	18.7812	21.2046	19.7741	0.7359	18.5839	21.0018
^{206}Pb/^{207}Pb	1.2732	0.0443	1.2015	1.3279	1.2506	0.0406	1.1854	1.3180
^{208}Pb/^{206}Pb	1.8800	0.0899	1.7737	2.0391	1.9180	0.0801	1.7880	2.0570
[Pb] ng.m^{-3}	16.53	8.12	4.45	28.30	5.60	3.27	1.53	10.81
São Lourenço da Serra								
^{206}Pb/^{204}Pb	18.3896	0.0267	18.3633	18.4262	18.5416	0.0813	18.4304	18.6035
^{206}Pb/^{207}Pb	1.1759	0.0012	1.1750	1.1776	1.1844	0.0046	1.1782	1.1879
^{208}Pb/^{206}Pb	2.0682	0.0024	2.0660	2.0715	2.0578	0.0099	2.0490	2.0719
[Pb] ng.m^{-3}	8.44	4.28	4.23	13.88	1.98	1.42	1.1021	4.08
CBA - Juquitiba								
^{206}Pb/^{204}Pb	18.5149	0.1998	18.2196	18.6615	18.5796	0.0656	18.4892	18.6679
^{206}Pb/^{207}Pb	1.1823	0.0109	1.1674	1.1924	1.1843	0.0054	1.1784	1.1895
^{208}Pb/^{206}Pb	2.0620	0.0169	2.0484	2.0866	2.0620	0.0128	2.0435	2.0744
[Pb] ng.m^{-3}	0.752	0.640	0.213	1.5890	0.473	0.566	0.094	1.460

Particulate matter collected from car exhausts were analyzed because these are the most representative sources for fuel emissions to the atmosphere. ^{206}Pb/^{207}Pb compositions of gasoline vehicular exhaust pipes range from 1.1635 to 1.1752 and ^{208}Pb/^{206}Pb

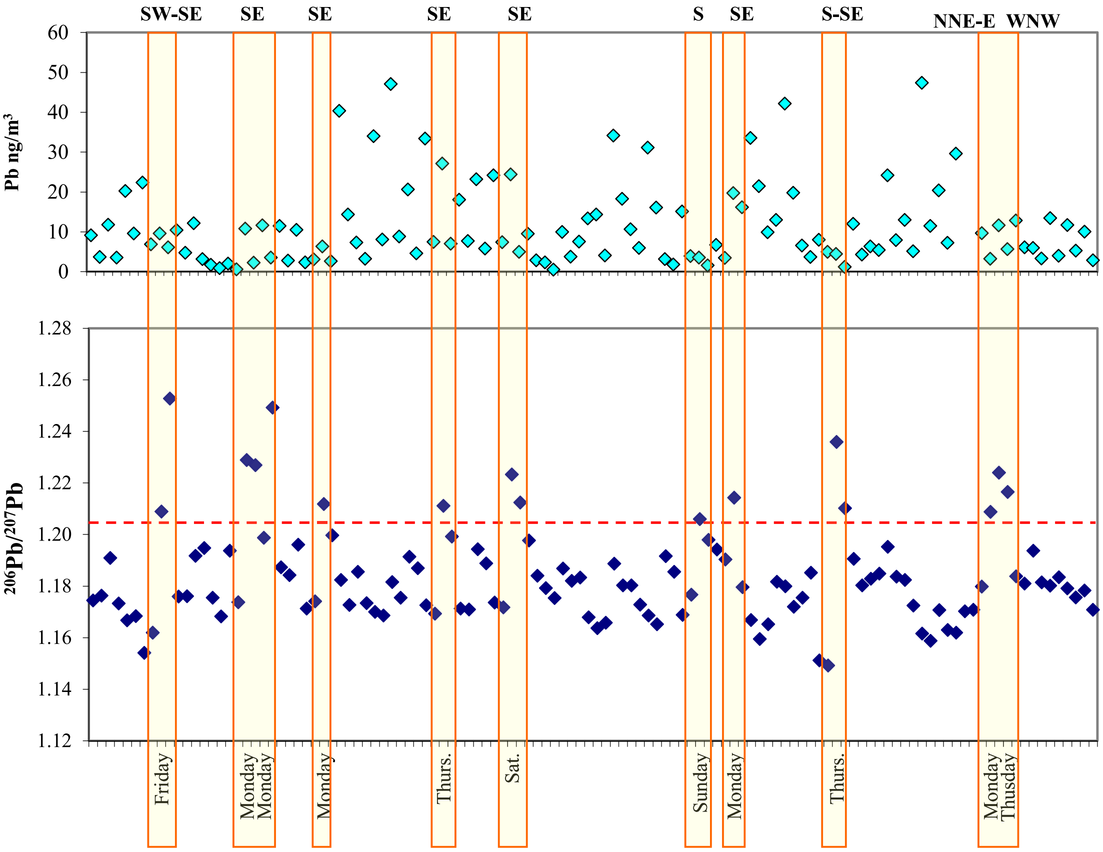

Fig. 6. Variation in lead isotopic composition ratios ($^{206}Pb/^{207}Pb$) and concentrations in aerosols collected during the summer of 2005 at USP. Note that the most radiogenic isotopic ratios ($^{206}Pb/^{207}Pb > 1.20$) are associated with lower lead concentration samples (Pb limit of 150 ng m^{-3} according CETESB and USEPA) and SE wind direction.

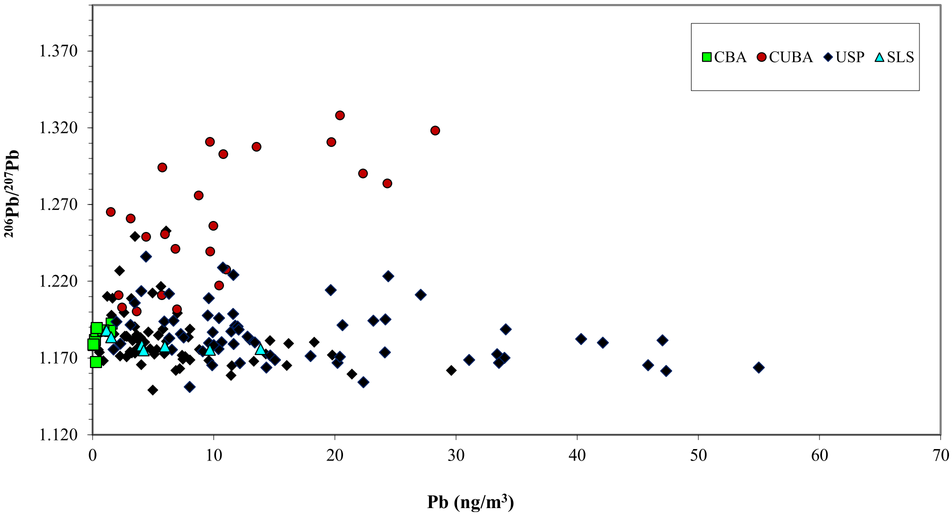

Fig. 7. $^{206}Pb/^{207}Pb$ versus [Pb] determined on aerosol samples collected in São Paulo (USP) between December 2005 and February 2006. Data from aerosol samples collected in Juquitiba (CBA), and São Lourenço da Serra (SLS) between February 1 and 6, 2006, and Cubatão (CUBA) between February 1 and 7, 2006, are also shown.

from 2.0751 to 2.0894, with average [Pb] of 1.5 ng.m^{-3}. A greater range of isotope ratios was observed for diesel vehicular exhaust, where the $^{206}Pb/^{207}Pb$ compositions vary from 1.1569 to 1.1894 and the $^{208}Pb/^{206}Pb$ from 2.0613 to 2.0916 with [Pb] ranging from 0.5 to of 1.2 ng.m^{-3}. The isotopic ratios observed from pipe exhausts are similar to those measured in tunnel dust.

Emissions of dust from construction sites have a high contribution around USP, with local construction of buildings, and presence of cement mixing plants, located four km to the north and six km west of USP. Samples were collected close to the plant located in the northern part and near of the São Paulo station, and a commercial cement sample. This potential source of resuspended particulate matter in São Paulo shows $^{206}Pb/^{207}Pb$ signatures between 1.1964 and 1.1994 and $^{208}Pb/^{206}Pb$ between 2.0365 and

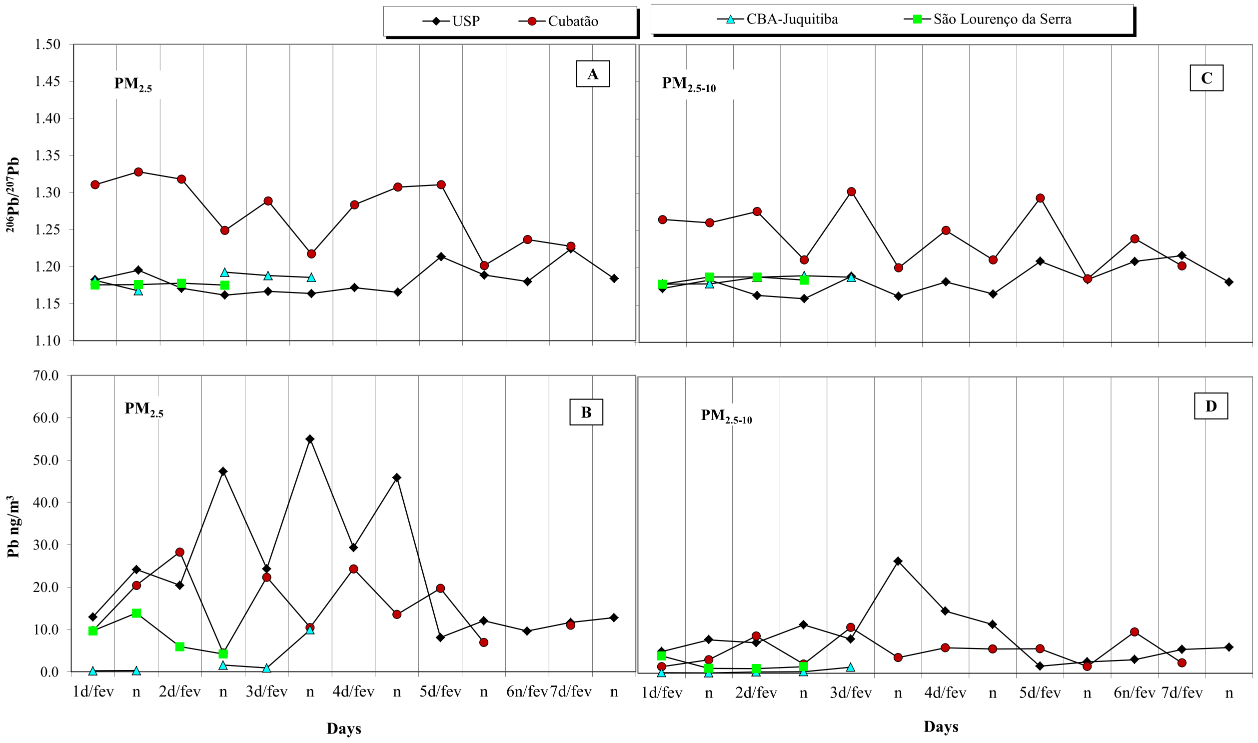

Fig. 8. Lead isotopic composition ($^{206}Pb/^{207}Pb$) (**A and C**) and (**B and D**) results in the aerosols collected in all stations, during February 1 to 7, 2006, in fine ($PM_{2.5}$) and in coarse fractions ($PM_{2.5\text{-}10}$), during day (**d**) and night (**n**).

Table 3
Statistical results of the particulate matter collected during the summer of 2005, in USP station. The concentrations of the particulate material were determined by gravimetric determinations and a multi-element PIXE.

$PM_{2.5}$ aerosol				$PM_{2.5\text{-}10}$ aerosol			
Species	Mean ($ng\ m^{-3}$)	±σ	Sample Qty	Species	Mean ($ng\ m^{-3}$)	±σ	Sample Qty
$PM_{2.5}$ ($\mu g\ m^{-3}$)	17.53	6.97	68	$PM_{2.5\text{-}10}$ ($\mu g\ m^{-3}$)	14.22	5.19	66
Al	174.07	6.45	68	Al	385.68	12.47	66
Si	161.68	5.07	68	Si	548.93	15.54	66
P	11.57	1.94	14	P	30.51	2.94	22
S	930.11	25.30	68	S	241.92	7.16	65
Cl	22.42	1.57	53	Cl	181.92	5.66	66
K	110.75	3.30	68	K	135.14	4.14	66
Ca	63.11	2.14	68	Ca	337.99	9.47	66
Ti	6.32	0.81	63	Ti	26.97	1.46	64
V	1.41	0.72	20	V	0.97	0.96	17
Cr	2.50	0.54	66	Cr	4.01	0.72	64
Mn	11.28	0.67	68	Mn	15.27	0.88	66
Fe	198.97	5.80	68	Fe	450.19	12.70	66
Ni	3.05	0.28	68	Ni	2.88	0.33	66
Cu	7.70	0.42	67	Cu	6.00	0.43	65
Zn	60.57	1.96	68	Zn	40.82	1.44	65
Se	3.64	0.40	48	Se	2.97	0.48	8
Br	15.73	0.92	68	Br	16.86	1.03	66
Sr	3.36	0.71	25	Sr	3.48	0.77	46
Hg	–	–	–	Hg	3.47	0.47	39
Pb	11.10	0.65	64	Pb	3.89	0.46	25

2.0436; [Pb] in coarse and fine fractions are 20.31 and 11.18 $\mu g\ g^{-1}$, respectively.

A phosphogypsium sample collected in Cubatão shows $^{206}Pb/^{207}Pb$ values between 1.1870 and 1.1878 and $^{208}Pb/^{206}Pb$ between 2.1236 and 2.1285. Dust from parking lots in the industrial plants and roads show $^{206}Pb/^{207}Pb$ values between 1.1742 and 1.2155 and $^{208}Pb/^{206}Pb$ between 2.0331 and 2.0808. The surface soil has $^{206}Pb/^{207}Pb$ values ranging from 1.1816 to 1.1891 and road dust close to fertilizer plants show $^{206}Pb/^{207}Pb$ ratios between 1.1742 and 1.1801 (Supplementary Table S2). The isotopic signatures identified in these sources are much less radiogenic than the compositions measured in aerosols collected in Cubatão. This indicates that a source having a more radiogenic Pb ratios, which has not been identified, predominates in the Cubatão aerosols signature, and is different from the fertilizer plants emissions investigated in this study.

Table 4
Results Matrix rotation VARIMAX for the proportion of elementary fine fraction of particulate matter sampled during the summer of 2005 on the USP.

Species	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Extraction
	Vehicular	Soil Dust	Sulphates	Metallurgy	Lead isotope ratios	
PM$_{2,5}$	**0.320**	0.169	**0.779**	–	–	0.898
Al	**0.206**	**0.656**	0.399	–	–	0.903
Si	–	**0.940**	–	–	–	0.906
S	–	–	**0.784**	0.129	**0.257**	0.768
K	**0.215**	**0.273**	**0.766**	–	–	0.577
Ca	–	**0.877**	–	–	0.109	0.814
Ti	–	**0.931**	0.139	0.125	–	0.902
Cr	–	–	–	**0.930**	–	0.874
Mn	**0.314**	**0.316**	**0.502**	**0.592**	0.108	0.743
Fe	**0.317**	**0.638**	**0.513**	0.303	0.202	0.651
Ni	**0.686**	0.224	0.306	0.133	0.135	0.774
Cu	**0.806**	–	0.336	–	–	0.726
Zn	**0.938**	–	–	0.111	–	0.694
Br	**0.569**	–	**0.450**	0.194	0.116	0.817
Pb	**0.906**	–	0.127	–		0.898
^{206}Pb/^{207}Pb	–	–	0.174	–	**0.883**	0.827
Pb(ID)	**0.504**	–	**0.427**	0.113		0.734

Values in bolds indicates correlation between elements.

Table 5
Results Matrix rotation VARIMAX for the proportion of elementary coarse fraction of particulate matter sampled during the summer of 2005on the USP.

Species	Factor 1	Factor 2	Factor 3	Factor 4	Extraction
	Industrial	Soil Dust	Sulphates	Vehicular	
PM$_{2,5\text{-}10}$	0.207	**0.855**	–	0.286	0.858
Al	–	**0.889**	0.147	–	0.962
Si	–	**0.841**	0.161	–	0.926
S	–	–	**0.710**	**-**	0.889
K	**0.921**	–	–	0.123	0.953
Ca	–	**0.886**	**-**	–	0.953
Ti	**0.929**	–	–	–	0.976
Cr	**0.909**	–	–	–	0.992
Mn	**0.918**	–	–	–	0.993
Fe	–	**0.715**	0.319	0.224	0.951
Ni	–	–	**0.625**	0.294	0.890
Cu	–	0.235	**0.651**	**0.618**	0.928
Zn	–	0.185	**0.415**	**0.775**	0.919
Sr	**0.896**	–	–	–	0.899
Hg	**0.917**	–	–	–	0.986
^{206}Pb/^{207}Pb	–	0.189	0.277	**−0.868**	0.899
Pb (ID)	0.217	**0.426**	0.270	**0.737**	0.845

Values in bolds indicates correlation between elements.

4. Discussion

4.1. Sources of atmospheric lead around USP sampling station

The isotopic compositions of aerosols from São Paulo are plotted on a ^{208}Pb/^{206}Pb vs. ^{206}Pb/^{207}Pb diagram along with data from sources and aerosols collected on Juquitiba, São Lourenço and Cubatão (Fig. 9, Supplementary Table S2). This allow us to identify the contributions of these sources to the São Paulo atmosphere composition. Lead ratios from São Paulo aerosol plot along a trend, where the end members are represented by geogenic and anthropogenic lead signatures. The more thorogenic ratios were determined on geogenic lead end member which is represented by rocks and minerals collected at USP (Aily, 2001). Their ratios are distinct from those determined on SP aerosols suggesting this end member does not contribute significantly to the aerosols of São Paulo. The anthropogenic lead sources can be separated in three end members, namely: end member 1 - vehicular, smelting and alcohol fuel; end member 2 - aerosols from Cubatão industrial area; and end member 3 - industrial emissions from São Paulo (Aily, 2001). ^{206}Pb/^{207}Pb ratios from São Paulo aerosols are ranging from 1.1491 to 1.2527, and ^{208}Pb/^{206}Pb from 1.9169 to 2.1115, defined by the blue field in Fig. 9. Although these lead ratios show a large spread in the diagram, the average of ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios (1.1840 ± 0.0187, and 2.0567 ± 0.0331, respectively) are very similar to those from end member 1, suggesting that fuels and traffic are the most important pollutant sources of the São Paulo atmosphere, and will be discussed below.

4.1.1. Traffic sources

Gasoline has a wide range of isotope composition (Fig. 9, Supplementary Table S3), and the ratios are similar to the isotopic composition of aerosols collected in São Paulo (Fig. 9). Gioia et al. (2005) determined lead isotopic compositions of different fuels in Brazil and found typical range from 1.1438 to 1.1529 (^{206}Pb/^{207}Pb) and from 2.114 to 2.102 (^{208}Pb/^{206}Pb) for alcohol, from 1.1651 to 1.1938 (^{206}Pb/^{207}Pb) and from 2.096 to 2.050 (^{208}Pb/^{206}Pb) for regular gasoline, from 1.1825 to 1.1913 (^{206}Pb/^{207}Pb) and from 2.0943 to 2.0680 (^{208}Pb/^{206}Pb) for premium gasoline, and from 1.1939 to 1.1989 (^{206}Pb/^{207}Pb) and from 2.063 to 2.082 (^{208}Pb/^{206}Pb) for diesel. Our data show that the isotopic signature of gasoline fuel fits better with those measured on São Paulo aerosols, suggesting that it represents one of the main source of lead in the atmosphere. However, the most significant Pb isotopic compositions was determined in gasoline and diesel vehicular exhaust pipes, which Pb ratios show that vehicular exhaust has significant influence from gasoline (^{206}Pb/^{207}Pb $= 1.1635$ to 1.1752, and ^{208}Pb/^{206}Pb $= 2.0894$ to 2.0751) and diesel (^{206}Pb/^{207}Pb $= 1.1569$ to 1.1814, and ^{208}Pb/^{206}Pb $= 2.0613$ to 2.0916) emissions and are correlated with USP aerosol Pb isotopic compositions (Supplementary Table S3).

The dust material collected in a tunnel is representing a mix of soot and fine dust, which has ^{206}Pb/^{207}Pb ratios between 1.1727 and 1.1772, and ^{208}Pb/^{206}Pb between 2.0809 and 2.0848. This ratio represents the fleet of cars in the metropolitan area, and is labelled in this study as indication for vehicular traffic. This is reinforced by the high [Pb] measured on the soot samples (104.51 and 33.30 $\mu g.g^{-1}$, for coarse and fine particles, respectively).

It is important to mention that vehicular traffic is also considered a relevant pollution source in other megacities (Zhu et al., 2010; MacKinnon et al., 2011). The occurrence of Ni, Cu, Zn, Br, and Pb in fine particles collected in São Paulo support this assessment (Ni $= 3.05$ ng.m^{-3}, Cu $= 7.70$ ng.m^{-3}, Zn $= 60.57$ ng.m^{-3}, Br $= 15.73$ ng.m^{-3}, Pb $= 11.10$ ng.m^{-3}).

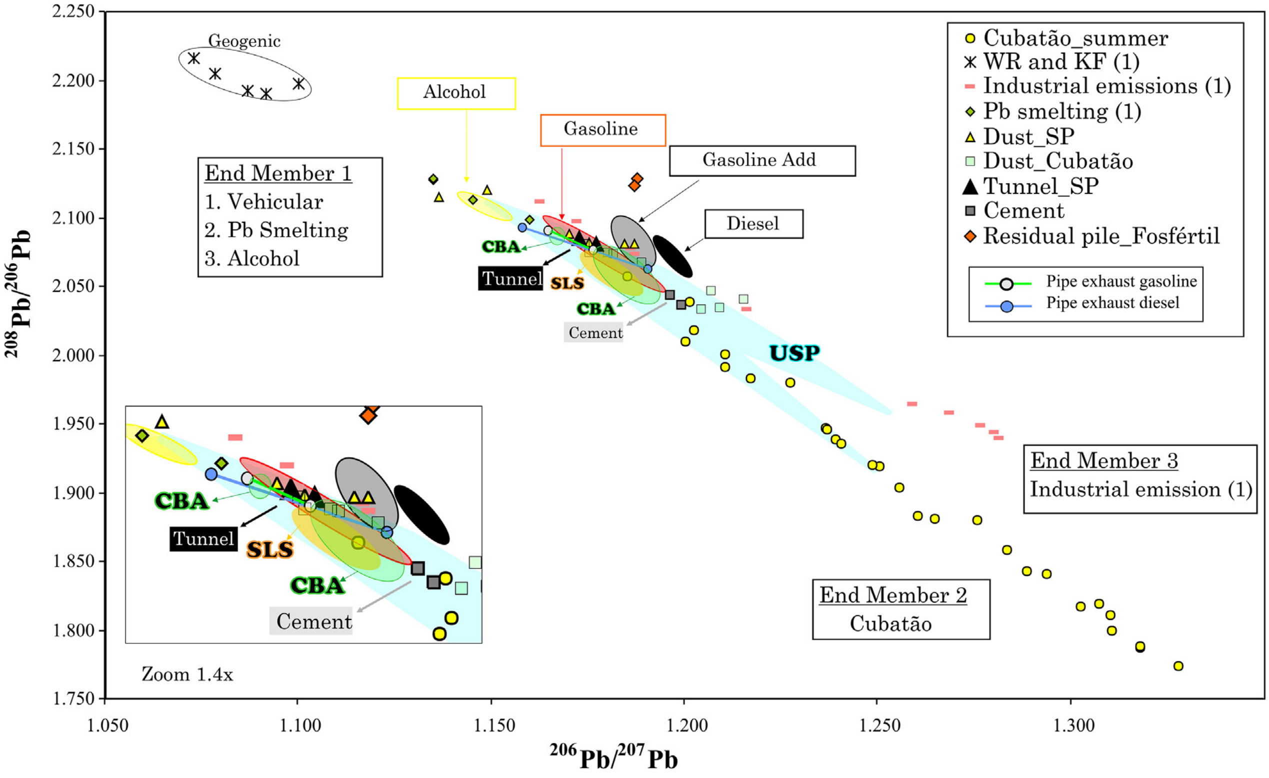

Fig. 9. $^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$ diagram of potential pollutant and of natural sources in São Paulo. (1) Aily (2001) and fuel from Gioia et al. (2005). Gasoline (common, with alcohol); additive gasoline (special for better performance, with alcohol); WR (whole rock from USP); KF (K-feldspar from WR); Industrial emissions in São Paulo city; Dust USP (belt roads, and street close to cement plant and 5 km from USP station); Dust Cubatão (close to fertilizer plants and Cubatão sampling station); Cement (commercial material used in construction); Residual pile Fertilizer Plant (pile of scrap of phosphogypsum, close Cubatão station). The blue area constrains lead isotope compositions found in aerosols collected at **USP** between the summer of December of 2005 and February of 2006; in yellow and green area constrains lead isotope compositions found in aerosols collected at São Lourenço da Serra (**SLS**) e Juquitiba (**CBA**), respectively.

Although, São Lourenço da Serra is a rural area, it is already influenced by its proximity to the highway, and lead concentrations are almost 3-fold higher than the background area, Juquitiba, which is located in a State Park, without traffic influence.

4.1.2. *Industrial emission sources at cubatão*

One of the end-members of the ternary mixing diagram (Fig. 9) can be correlated to aerosols from the industrial area in Cubatão (Gioia et al., 2010). Radiogenic anthropogenic sources have $^{206}Pb/^{207}Pb$ signatures ranging between 1.1854 and 1.3279, and they are quite distinct from natural aerosols (1.1870–1.1878). The industrial emissions analyzed at Mogi Valley (Cubatão) are most similar to dust collected from parking areas in the industrial plants and roads in Cubatão (1.1742–1.2155). The surface soil has a lead isotopic composition (1.1816–1.1891) close to the composition of road dust collected near the fertilizer plants (1.1742–1.1801). The aerosols collected in Cubatão have more radiogenic lead composition, suggesting the source is not derived from the local fertilizer plants, and still unknown.

4.1.3. *Dust resuspension from urban construction*

The dust derived from urban construction sites is composed mainly by coarse particles and is transported only locally. Dust collected close to the road, in front of a cement mixing plant, shows a higher similarity with vehicular emissions (Fig. 9), confirming that the lead contribution from vehicular traffic is relevant. The isotopic composition obtained for cement dust from road most likely represent a mixture of cement with traffic dust and emissions.

4.2. *Evidence for significant air mass transport from Cubatão to São Paulo*

The lead isotopic signature of aerosols in São Paulo shows possible contribution from industrial emissions and or resuspension of particulate matter from Cubatão. This pathway has been previously invoked from dispersion modelling (Kerr et al., 2001; Silva et al., 2016) and the findings are in line with the daytime predominant SE wind direction (Figs. 2 and 3). In line with this predominant circulation system, Fig. 1 shows possible air mass transport from the coast to São Paulo during the day and the opposite way during the night. There seems also a strong effect of precipitation (Figs. 3 and 6), as industrial radiogenic sources derived from Cubatão dominate in SP aerosols after rain events in São Paulo. The Pb isotope ratios increase, suggesting that the aerosols in São Paulo with high [Pb] and non-radiogenic signatures are rained out and aerosols from Cubatão with low [Pb] and radiogenic signatures are detected. These radiogenic signatures indicate that long distance air mass transport plays an important role in the aerosol budget in MASP (Figs. 1, 2 and 6). The deposition of trace substances via cloud droplets was observed in other studies (Gonçalves et al., 2000; Vautz et al., 2003).

Although, transport of aerosols with high [Pb] from the industrial areas of Cubatão to São Paulo is favoured by the diurnal SE wind, the lead isotopic signature of this source is only dominant when aerosols with low [Pb] are collected at the USP station (Fig. 6). Normally the [Pb] in USP aerosols are higher than those coming from Cubatão and suggest that an important local source is present in São Paulo, likely construction material resuspension and vehicular traffic emissions (Fig. 6).

In contrast, our data do not show air mass transport towards SW because the [Pb] determined on the São Lourenco and Juquitiba stations are low. The two forested areas, São Lourenço da Serra and Juquitiba, were selected to characterize the background lead isotopic signature of aerosols in the region. The lead isotopic composition of aerosols in Juquitiba is close to those found for aerosols collected at USP, representing soil dust resuspension, possibly from rural tracks (Figs. 7 and 8). The highest $^{206}Pb/^{204}Pb$ ratio determined on Juquitiba is 18.67 (Table 2), which is similar to the isotopic composition of the natural atmospheric lead (Kylander et al., 2010).

The background atmospheric composition is composed of low [Pb] unlike USP and Cubatão areas. This is the most important characteristic to evaluate the anthropic impact already present in USP, and it is evident that according to the predominant wind direct in São Paulo (S-E sector), these background areas, located to the west, have very little influence on the lead isotope signatures in São Paulo.

5. Conclusions

1) The phasing out of leaded gasoline and its replacement with ethanol in Brazil, which started in 1989, brought about 10-fold decreases in [Pb] in São Paulo city. Between the 1970's and the summer of 2005, these values decreased from 1 $\mu g\ m^{-3}$ to 0.042 $\mu g\ m^{-3}$ in 24 h PM_{10} fraction, respectively. Pb concentrations showed to be significant, even during the Brazilian summer when pollutant dispersion and removal is higher. The [Pb] in the USP area are lower than the revised lead level of the primary and secondary (health-based) standard of 0.15 $\mu g\ m^{-3}$, measured as total suspended particles (TSP), which is explained by favourable meteorological conditions to particulate matter dispersion during hot days and high precipitation occurrences, which characterize the summer period. This study demonstrates that although [Pb] are not as high as in the 1970's, they are significant, especially the increase in fine fractions (0.055 $\mu g\ m^{-3}$). This points to a serious public health hazard, of an intensely urbanized city, which is densely populated and contains and is surrounded by many industrial areas.
2) The sources of atmospheric lead sampled in São Paulo city are diverse. The analytical techniques applied to characterize sources and aerosols in São Paul, i.e. isotope dilution thermal ionization mass spectrometry (ID-TIMS), particle induced X-ray emission (PIXE) and multivariate analysis (Factor Analysis) suggest a predominance of vehicular traffic emissions (fuel combustion, brake wear, tyre wear, road surface abrasion, and resuspension of road dust) and admixing of cement from urban construction and local cement mixing plants. The main evidence is lead isotopic compositions of vehicular exhaust and tunnel dust, which mostly characterize emissions from light vehicles.
3) Industrial emissions from Cubatão have a distinguished radiogenic Pb isotopic compositions ($^{206}Pb/^{207}Pb > 1.20$). On cloudy and rainy days, more radiogenic lead is detected in aerosols collected at USP (São Paulo city), suggesting an important contribution via air mass transport, to Metropolitan Area of São Paulo (MASP) from the eastern industrial area, via SE winds. Our data are the first evidence of a distinct impact of industrial emissions in the megacity of São Paulo.
4) The remote sampling station at Juquitiba, a nature reserve located west of the MASP, shows that a chemical composition of the aerosol samples is distinct and different from those of the industrial sources investigated in Cubatão and the emissions from São Paulo. The low [Pb] average of 0.597 ± 0.5 $ng.m^{-3}$ indicates that the Juquitiba area is indeed shielded from the influence of the megacity and the industrial areas.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.10.049.

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