

1 AN ISOTOPIC STUDY OF ATMOSPHERIC LEAD IN A MEGACITY AFTER PHASING OUT OF  
2 LEADED GASOLINE

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20  
21 **Abstract**

22  
23 Atmospheric lead (Pb) concentrations in São Paulo city, Brazil, remain significant, despite the fact that leaded  
24 gasoline has been phased out. The use of its isotope signature allows tracing emissions from increasing car  
25 numbers, urban construction, and industrial emissions in this extremely populated area. High-precision and  
26 accurate stable isotope ratio determinations using isotope dilution thermal ionization mass spectrometry (ID-  
27 TIMS) combined with particle induced X-ray emission (PIXE) and multivariate analysis were used to identify  
28 the main sources of lead present in São Paulo atmospheric particulates. Throughout a period of sixty days,  
29 aerosol samples were collected every 12 hours during the summer of 2005 at the University of São Paulo (USP)  
30 and simultaneously during one week in an industrial area (Cubatão) and in two more remote areas (São  
31 Lourenço da Serra and Juquitiba). The data suggests that aerosols from São Paulo are mainly derived from  
32 vehicular exhaust (mostly gasoline) and traffic dust resuspension, with admixing of industrial emissions,  
33 including cement. Lead isotopic compositions (expressed as <sup>206</sup>Pb/<sup>207</sup>Pb ratios) measured in São Paulo aerosols  
34 range from 1.1491 to 1.2527 and are similar to those determined from tunnel dust, fuels, and vehicular exhaust;  
35 therefore, those are likely to be the main lead sources in the atmosphere of São Paulo. Vehicular traffic (fuel  
36 combustion, dust from vehicular components, and road dust) remains an important source of lead in the

37 atmosphere. The maximum concentration occurring during the summer was  $0.055 \mu\text{g}\cdot\text{m}^{-3}$  in fine particles, which  
38 is detrimental for human health and may lead to exceedances of the Air Quality Standard for lead of  $0.15 \mu\text{g}\cdot\text{m}^{-3}$   
39 (3-month average) during other seasons that are less favourable to pollutant dispersion.

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## 42 1. Introduction

43 Leaded gasoline has been phased out in the late 20<sup>th</sup> century to address health and economic concerns,  
44 (Pacyna et al. 1995; Bollhöfer & Rosman 2001; Cheng & Hu, 2010). This was triggered by high lead  
45 concentrations ([Pb]) in atmospheric particulate matter and subsequent warnings from researchers devoted to the  
46 reduction of the emissions of anthropogenic lead into the environment. In 1962, Chow and Patterson reported the  
47 first evidence of high lead concentrations in the environment which subsequently lead to the concern about  
48 anthropogenic lead pollution (Chow & Patterson 1962).

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

53 The phasing out of leaded gasoline in Brazil resulted in a significant decrease of [Pb] in the atmosphere  
54 of Brazilian cities (Castanho & Artaxo, 2001). The Metropolitan Area of São Paulo (MASP) is the most  
55 developed and industrialized region in Brazil with a population of twenty million inhabitants and more than  
56 seven million vehicles powered by diesel, gasoline, ethanol and/or natural gas, emitting or enabling the  
57 generation of several pollutants in the atmosphere. Air pollution in São Paulo has been studied since the early  
58 1980’s by a group of pioneers in atmospheric science from the University of São Paulo (Orsini et al., 1986;  
59 Andrade et al., 1990; Massambani & Andrade, 1994; Andrade et al., 1994; Ulke & Andrade 2001; Castanho &  
60 Artaxo, 2001; Sánchez-Ccoyllo & Andrade, 2002; Miranda et al., 2002; CETESB, 2006). In 1989, various  
61 aspects of atmospheric pollution in São Paulo were intensively studied as part of the São Paulo Atmosphere  
62 Characterization Experiment (SPACEX) assessed various aspects of atmospheric pollution in São Paulo and  
63 since 1985, the Air Quality Centre in São Paulo (CETESB) has been responsible for air quality in this megacity.

64 Thermal Ionization Mass Spectrometry (TIMS) is widely used to determine stable lead isotope  
65 composition in particulate matter to trace atmospheric lead sources, which in turn assists identifying specific  
66 types of sources using their isotopic fingerprints (Volkening & Heumann, 1990; Radlein & Heumann, 1992; Erel  
67 et al., 1997; Véron et al., 1998; Chiaradia & Cupelin, 2000; Alleman et al., 2001; Luke & Othman, 2002; Velde  
68 et al., 2005; Komarek et al., 2008). Studies using lead isotopic variations as tracers of pollutant sources in  
69 several cities in Brazil were reported by Bollhöfer & Rosman (2000), in São Paulo city by Aily (2001) and by  
70 Gioia et al. (2010), and in Brasília by Gioia (2004). The study of Aily (2001) produced the first lead isotope data  
71 for atmospheric particulate matter collected in São Paulo, leading to the identification of natural and  
72 anthropogenic sources. That study revealed important seasonal variations in the relative contribution of different

73 sources of atmospheric lead during the summer in 2000. Moreover, it identified industrial emissions as the main  
74 type of source for atmospheric lead. A follow up study by Gioia et al. (2010), determined [Pb] and isotopic ratios  
75 in aerosols collected in high intervals throughout a short period (three days) and suggested that vehicular  
76 emissions were quantitatively still important in São Paulo. However, more data are necessary to ratify those  
77 conclusions and to improve our understanding of the factors that control atmospheric lead in São Paulo.

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

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## 87 **2. Experimental methods**

### 88 *2.1. Site Description*

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

95 Three additional sites (Fig. 1) were selected: (i) Cubatão (Mogi Valley, UTM 23K 0360595 7363775,  
96 40 km southeast from São Paulo city), an industrial area, dominated by fertilizer plants and intense traffic of  
97 heavy vehicles and a possible source region for atmospheric pollutants; (ii) Jucitiba, located 70 km southwest  
98 from São Paulo, a forest area close to the Jurupará State Park and considered here as the ‘background’ location  
99 (UTM 23K 289458 7351766); and (iii) São Lourenço da Serra, a neighbour municipality of Jucitiba, less  
100 forested and receiving significant contribution of vehicular emissions due to its proximity to the federal highway  
101 (Regis Bittencourt, UTM 23K 302148 7360716).

102

### 103 *2.2. Sampling and Meteorological Data*

104 An in-house inlet system was used to select particles with aerodynamical diameter ( $\phi$ ) < 10  $\mu\text{m}$  (Hopke et  
105 al., 1997). Two polycarbonate membranes were changed every 12 hours, and particle fractions  $\text{PM}_{10-2.5}$  ( $2.5 < \phi <$   
106  $10 \mu\text{m}$ ) and  $\text{PM}_{2.5}$  ( $\phi < 2.5 \mu\text{m}$ ) were sampled separately. Inhalable particulate matter corresponds to  $\text{PM}_{10} = \Sigma$   
107 ( $\text{PM}_{10-2.5}$  and  $\text{PM}_{2.5}$ ). An inlet tube downstream from the filter holder collected the air into a twin cylinder

108 diaphragm pump. The air was forced through a standard volumeter, where it was exhausted to the atmosphere.  
109 The flow rate was approximately 16 L/min.

110 Aerosol collections in São Paulo were performed at the Campus of the University of São Paulo (USP)  
111 (Fig. 1) during the summer season from December 2005 until February 2006 (Table 1). During this sampling  
112 period, 214 filters (polycarbonate membranes) were collected. Sampling at the other the sites were performed for  
113 seven days in February 2006 (Table 1). Dust sources from road, tunnel, phosphogypsum from residual pile,  
114 cement, and soil were collected in plastic bags. These materials were artificially resuspended using an in-house  
115 built system to segregate fine and coarse fractions (see table 1). Vehicular emissions from diesel and regular  
116 gasoline were also collected. Meteorological data in São Paulo were obtained from stations at the *Instituto de*  
117 *Astronomia, Geofísica e Ciências Atmosféricas*, IAG-USP). Relevant meteorological parameters including  
118 temperature, atmospheric pressure, precipitation, and wind velocity and direction were taken into account for  
119 data interpretation.

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

123

### 124 2.3. Sample Processing

125 Two hundred and fourteen filters were weighed to determine particulate matter concentration in coarse,  
126 fine, and inhalable fractions. One hundred and thirty aerosol samples were analyzed for lead isotopes. They were  
127 dissolved over three days using a mixture of 2 mL (40%) HF with 0.5 mL (14.5 M) HNO<sub>3</sub>. After evaporation, 2  
128 mL of 6 M HCl were added, and the solution was heated (80 °C) for one day. The final solution was dried. This  
129 solution was split into two aliquots: one aliquot (consisting 80% of solution) was used for the determination of  
130 the Pb isotopic compositions (IC), and the remaining 20% was used to measure [Pb] concentration using isotope  
131 dilution (ID). The IC and ID solutions were evaporated to dryness and diluted with 0.6N HBr; Pb was extracted  
132 using columns packed with BioRad AG1-X8 anionic exchange resin in HBr media. The procedure for separation  
133 of Pb from the matrix of the digested aerosol samples consists of was following: an anion exchange resin (0.15  
134 mL) was loaded into a heat-shrink Teflon tubing with 4 mm diameter. The resin bed was cleaned using 1.5 mL  
135 of 6 N HCl, followed by 1.5 mL of water. The resin was then conditioned using 1.5 ml of 0.6 N HBr. The  
136 supernatant of the sample, dissolved in 1 ml of 0.6 N HBr, was loaded onto the column. A mixture of acid 1.5  
137 mL of 0.6 N HBr–0.6 N HNO<sub>3</sub> was then introduced to remove elements other than Pb, considering the HBr–  
138 HNO<sub>3</sub> mixture is more efficient than using HBr alone with respect to the separation of zinc from lead (Kuritani  
139 & Nakamura, 2002). The lead sample fraction was eluted with 1.0 mL of water. Prior to evaporation, one drop of  
140 0.05 N H<sub>3</sub>PO<sub>4</sub> was added to the solution to prevent complete dryness.

141 Chemical procedures were conducted in clean room conditions and with ultra-pure reagents (sub-boiling  
142 distillation in Teflon® bottles) at the Center of Geochronological Research, University of São Paulo. Lead  
143 isotope ratios were measured by Thermal Ionization Mass Spectrometry (TIMS) using a multi-collector

144 TRITON mass spectrometer at the Laboratory of Geochronology and Radiogenic Isotopes (LAGIR), of the Rio  
145 de Janeiro State University. Each sample was loaded onto a single Re filament with 2  $\mu\text{L}$  silica gel and 2  $\mu\text{L}$   
146  $\text{H}_3\text{PO}_4$ , to improve the lead ionization during the mass spectrometric analysis (Cameron et al. 1969). Mass  
147 fractionation was  $\leq 0.10\%$ /a.m.u. determined by repeated measurements on the NBS 981 Common Pb Standard,  
148 an external precision of 0.08% ( $2\sigma$ ) for ratios  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$ . Lead analytical blanks were typically  
149 lower than 50 pg and around 400 pg including membrane filter blanks. Dust samples followed the same  
150 dissolution process and lead chemical separation procedure used for aerosol filter analysis.

151 Exactly 134 aerosol samples (68 fine fractions and 66 coarse fractions) collected at the USP station, was  
152 analyzed by PIXE (Particle Induced X-ray Emission, Johansson & Campbell, 1988; Johansson et al., 1995), One  
153 quarter of the original filter was used. The system calibration for atmospheric aerosol samples does not require  
154 matrix absorption correction (Cesareo et al., 1998). We used Micromatter-XRF calibration standards, prepared  
155 by evaporation of metals and salts evaporation under vacuum (thickness around tenths of  $\mu\text{g}/\text{cm}^2$ , with 5%  
156 uncertainty). The analysis was carried out at the Laboratory for Material Analysis by Ion Beam, at the Institute  
157 of Physics, University of São Paulo. Three calibration standard thickness was controlled by Rutherford  
158 Backscattering Spectrometry (RBS), with an estimated uncertainty of below 3%.

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160

### 161 3. Results

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

166

#### 167 3.1. Meteorological Data from the City of São Paulo

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

174 December 21-31, 2005, the predominant wind directions were NNW and SSE-E during both night and  
175 daytime (Fig. 2). Temperature and atmospheric pressure between December 25 and 28 were below 25  $^\circ\text{C}$  and  
176 above 930 mbar. In January 2006, the wind directions were predominantly southeast (SSE-SE) and occasionally  
177 N-NW, mostly during the day (Fig. 2). February showed large variations, mainly from the NW-NNW-N and  
178 SE-SSE. There was low atmospheric pressure, high temperature, and the highest levels of atmospheric

179 precipitation (Fig. 3). Atmospheric precipitation favours the removal of pollutants during the Brazilian summer,  
180 reducing particulate matter concentration in the atmosphere and hence [Pb] in the atmosphere (Gioia et al. 2010).

181

### 182 3.2. Particulate matter concentrations

183 Particulate matter concentrations are reported in detail in [Supplementary Table S1](#). The PM<sub>10</sub>  
184 concentrations at the USP station range from 9.1 to 57.4 µg.m<sup>-3</sup> during the entire period of December 2005 to  
185 February 2006 (Fig. 3 and 4), and inhalable particles concentrations are higher at night. In the fine fraction, the  
186 concentrations are between 5.4 and 34.8 µg.m<sup>-3</sup>, and the coarse fraction ranges from 3.5 to 26.7 µg.m<sup>-3</sup> (Fig. 3).  
187 USP samples show that PM<sub>10</sub> (24h) at USP range from 24.6 to 42.6 µg.m<sup>-3</sup>

188 PM<sub>10</sub> concentrations in Cubatão (industrial area) range from 21.3 to 77.2 µg.m<sup>-3</sup> (Figs. 4 and 5).  
189 Concentrations of the fine fraction vary between 6.9 and 41.8 µg.m<sup>-3</sup> and of the coarse fraction range from 9.8 to  
190 46.4 µg.m<sup>-3</sup>. Particulate matter concentrations in Cubatão are the highest, especially the coarse fraction collected  
191 during the daytime. PM<sub>10</sub> (24h) values vary between 21.7 and 58.1 µg.m<sup>-3</sup>. This result exceeds the National Air  
192 Quality Standard for the annual arithmetic average concentration (50 µg.m<sup>-3</sup>) (CETESB, 2016).

193 In the São Lourenço rural area, PM<sub>10</sub> concentrations range from 17.3 to 24.7 µg.m<sup>-3</sup>. The concentrations  
194 of the fine fraction vary between 8.1 and 17.4 µg.m<sup>-3</sup>, and the coarse fraction ranges from 4.3 to 11.7 µg.m<sup>-3</sup>  
195 (Figs. 4 and 5). Juititaba presents the lowest PM<sub>10</sub> concentrations, ranging from 8.4 to 20.3 µg.m<sup>-3</sup>. The  
196 concentrations of the fine fraction vary between 4.3 and 13.4 µg.m<sup>-3</sup>, and the coarse fraction ranges from 2.4 to  
197 9.4 µg.m<sup>-3</sup> (Figs. 4 and 5).

198 At USP, São Lourenço da Serra, and Juititaba various national standard limits for air quality were not  
199 exceeded including: i. Standard for Air Quality daily for PM<sub>10</sub> (24) of 150 µg/m<sup>3</sup> admissible at most once a year;  
200 ii. annual limit of 50 µg.m<sup>-3</sup>; iii. Standard for Air Quality for PM<sub>2.5</sub> annual standard of 15 µg.m<sup>-3</sup> established by  
201 the U.S. Environmental Agency (USEPA) for the arithmetic mean of annual averages (24) the last three years).

202

### 203 3.3. Lead concentrations and isotopic compositions

#### 204 3.3.1 [Pb] and Pb isotopic compositions on USP aerosol samples

205 The aerosol samples collected at USP show [Pb] ranging from 0.50 to 54.99 ng.m<sup>-3</sup> (Table 2, Fig. 6).  
206 The [Pb] in the fine fraction range between 1.75 and 54.99 ng.m<sup>-3</sup>, and in the coarse fraction from 0.50 to 29.63  
207 ng.m<sup>-3</sup>.

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

212 The [Pb] observed in MASP are much lower than those found in other major urban world centers such as  
213 Shanghai, China (167-854 ng.m<sup>-3</sup> in PM<sub>10</sub> fraction; [Zheng et al., 2004](#)), but they are higher compared to those

214 obtained in Brasilia (Brazil) during the summer of 2003 ( $1.66 \pm 2.11 \text{ ng.m}^{-3}$ ; Gioia, 2004). The concentrations  
215 found in MASP are lower than those determined in the past.

216 Orsini & Bouéres (1977) determined the [Pb] in the atmosphere of São Paulo using the X-ray emission  
217 particle-induced (PIXE) technique and found in a small set of samples an average of  $1 \text{ } \mu\text{g.m}^{-3}$  (24h  $\text{PM}_{10}$ ). [Pb]  
218 (24h  $\text{PM}_{10}$ ) ranging from 0.83 to  $1.60 \text{ } \mu\text{g.m}^{-3}$  were determined in São Caetano city (east of São Paulo city), in  
219 1978. These concentrations decreased to an interval of 0.22 to  $0.41 \text{ } \mu\text{g.m}^{-3}$  in 1983, which was attributed to a  
220 reduction of tetraethyl lead as an additive to gasoline (Orsini et al. 1986).

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

225

### 226 3.3.2. [Pb] and isotopic compositions at USP, Cubatão, São Lourenço da Serra, and Juquitiba

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

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

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

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

245 In contrast, [Pb] in aerosols collected at São Lourenço da Serra and Juquitiba are the lowest ones, as seen  
246 in table 2, averaging  $5.21 \pm 4.5 \text{ ng.m}^{-3}$  and  $0.60 \pm 0.58 \text{ ng.m}^{-3}$ , respectively. The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios are similar;  
247 however, at São Lourenço da Serra, the range is narrower (1.1750 to 1.1879) than at Juquitiba (1.1674 to

248 1.1924). The aerosols from Jucituba show the lowest Pb concentrations, and possibly represent the background  
249 and a natural geogenic source.

250

### 251 3.4. Assessment of the chemical composition

#### 252 3.4.1. Aerosols

253 Multi-element concentration determinations by PIXE in the fine and coarse fractions of particulate  
254 matter collected during day and nighttime periods is given in [Supplementary Figure S1](#). Mean concentrations  
255 ( $\text{ng.m}^{-3}$ ) were obtained for twenty elements and are shown in [Table 3](#).

256 Sulphur typically present in metropolitan areas, show high concentrations in the fine fraction (average of  
257  $930 \text{ ng.m}^{-3}$ ), indicating a significant contribution from industrial and vehicular emissions, because it derives from  
258 combustion processes ([Miranda & Tomaz, 2008](#)), and subsequent gas to particle conversion of the  $\text{SO}_2$  gas into  
259 particles. Presence in the coarse fraction may indicate the contribution of biogenic material and soil  
260 resuspension, as already suggested by [Castanho & Artaxo \(2001\)](#).

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

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

272 The presence of chlorine in the São Paulo aerosols ( $181.9 \text{ ng.m}^{-3}$  in the coarse fraction) and  $22 \text{ ng.m}^{-3}$  in  
273 fine fraction) could be explained by sea breeze transport from the east coast, as already suggested by [Brown &](#)  
274 [Artaxo \(2001\)](#).

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

280

#### 281 3.4.2. Multi-elemental statistical analysis – USP data

282 Factor analysis (FA) was used to analyze the chemical and isotope data and to assist in the identification  
283 of the main sources of the atmospheric aerosols, as reported in [Tables 4 and 5](#). Factor analysis is a widely used



284 statistical data treatment, that seeks the least number of factors explaining the major fraction of the common  
285 variance of a database. The factors were rotated to maximize the variance of the extracted rotated factors, and the  
286 most common treatment, VARIMAX, maximizes its squared loadings (Johnson & Winchern, 1982; Miranda &  
287 Tomaz, 2008). The species with higher rotated loadings in a factor, provides a way to associate it to a source in  
288 the environment, with similar composition.

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

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

306

### 307 3.5. Chemical Characterization of Sources

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

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

319 isotopic signature to all possible contributions from vehicular traffic. We assume a closed system to determine  
320 the impact of vehicular contribution in the São Paulo atmosphere.

321 The road dust collected at high traffic avenues in São Paulo (Avenida dos Bandeirantes and Marginal  
322 Pinheiros) have non-radiogenic lead with  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios ranging between 1.1365 and 1.1752 and  $^{208}\text{Pb}/^{206}\text{Pb}$   
323 from 2.0817 to 2.1885. The tunnel dust collected at the Ayrton Senna Tunnel in São Paulo showed [Pb] around  
324  $33 \mu\text{g}\cdot\text{g}^{-1}$  and  $104 \mu\text{g}\cdot\text{g}^{-1}$  in fine fraction and coarse fraction, respectively, and  $^{206}\text{Pb}/^{207}\text{Pb}$  between 1.1727 to  
325 1.1772, and  $^{208}\text{Pb}/^{206}\text{Pb}$  from 2.0809 to 2.0848, which are very similar to the lead isotopic compositions of  
326 aerosols collected in São Paulo (Fig. 9).

327 Particulate matter collected from car exhausts were analyzed because these are the most representative  
328 sources for fuel emissions to the atmosphere.  $^{206}\text{Pb}/^{207}\text{Pb}$  compositions of gasoline vehicular exhaust pipes range  
329 from 1.1635 to 1.1752 and  $^{208}\text{Pb}/^{206}\text{Pb}$  from 2.0751 to 2.0894, with average [Pb] of  $1.5 \text{ ng}\cdot\text{m}^{-3}$ . A greater range of  
330 isotope ratios was observed for diesel vehicular exhaust, where the  $^{206}\text{Pb}/^{207}\text{Pb}$  compositions vary from 1.1569 to  
331 1.1894 and the  $^{208}\text{Pb}/^{206}\text{Pb}$  from 2.0613 to 2.0916 with [Pb] ranging from 0.5 to of  $1.2 \text{ ng}\cdot\text{m}^{-3}$ . The isotopic ratios  
332 observed from pipe exhausts are similar to those measured in tunnel dust.

333 Emissions of dust from construction sites have a high contribution around USP, with local construction  
334 of buildings, and presence of cement mixing plants, located four km to the north and six km west of USP.  
335 Samples were collected close to the plant located in the northern part and near of the São Paulo station, and a  
336 commercial cement sample. This potential source of resuspended particulate matter in São Paulo shows  
337  $^{206}\text{Pb}/^{207}\text{Pb}$  signatures between 1.1964 and 1.1994 and  $^{208}\text{Pb}/^{206}\text{Pb}$  between 2.0365 and 2.0436; [Pb] in coarse and  
338 fine fractions are  $20.31$  and  $11.18 \mu\text{g}\cdot\text{g}^{-1}$ , respectively.

339 A phosphogypsum sample collected in Cubatão shows  $^{206}\text{Pb}/^{207}\text{Pb}$  values between 1.1870 and 1.1878  
340 and  $^{208}\text{Pb}/^{206}\text{Pb}$  between 2.1236 and 2.1285. Dust from parking lots in the industrial plants and roads show  
341  $^{206}\text{Pb}/^{207}\text{Pb}$  values between 1.1742 and 1.2155 and  $^{208}\text{Pb}/^{206}\text{Pb}$  between 2.0331 and 2.0808. The surface soil has  
342  $^{206}\text{Pb}/^{207}\text{Pb}$  values ranging from 1.1816 to 1.1891 and road dust close to fertilizer plants show  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios  
343 between 1.1742 and 1.1801 (Supplementary Table S2). The isotopic signatures identified in these sources are  
344 much less radiogenic than the compositions measured in aerosols collected in Cubatão. This indicates that a  
345 source having a more radiogenic Pb ratios, which has not been identified, predominates in the Cubatão aerosols  
346 signature, and is different from the fertilizer plants emissions investigated in this study.

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348

## 349 **4. Discussion**

### 350 *4.1. Sources of atmospheric lead around USP sampling station*

351 The isotopic compositions of aerosols from São Paulo are plotted on a  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  diagram  
352 along with data from sources and aerosols collected on Juquitiba, São Lourenço and Cubatão (Fig. 9,  
353 Supplementary Table S2). This allow us to identify the contributions of these sources to the São Paulo  
354 atmosphere composition. Lead ratios from São Paulo aerosol plot along a trend, where the end members are

355 represented by geogenic and anthropogenic lead signatures. The more thorogenic ratios were determined on  
356 geogenic lead end member which is represented by rocks and minerals collected at USP (Aily, 2001). Their  
357 ratios are distinct from those determined on SP aerosols suggesting this end member does not contribute  
358 significantly to the aerosols of São Paulo. The anthropogenic lead sources can be separated in three end  
359 members, namely: end member 1 - vehicular, smelting and alcohol fuel; end member 2 - aerosols from Cubatão  
360 industrial area; and end member 3 - industrial emissions from São Paulo (Aily, 2001).  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios from  
361 São Paulo aerosols are ranging from 1.1491 to 1.2527, and  $^{208}\text{Pb}/^{206}\text{Pb}$  from 1.9169 to 2.1115, defined by the  
362 blue field in Fig. 9. Although these lead ratios show a large spread in the diagram, the average of  $^{206}\text{Pb}/^{207}\text{Pb}$  and  
363  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios ( $1.1840 \pm 0.0187$ , and  $2.0567 \pm 0.0331$ , respectively) are very similar to those from end  
364 member 1, suggesting that fuels and traffic are the most important pollutant sources of the São Paulo  
365 atmosphere, and will be discussed below.

366

#### 367 4.1.2. Traffic sources

368 Gasoline has a wide range of isotope composition (Fig. 9, Supplementary Table S3), and the ratios are  
369 similar to the isotopic composition of aerosols collected in São Paulo (Fig. 9). Gioia et al. (2005) determined  
370 lead isotopic compositions of different fuels in Brazil and found typical range from 1.1438 to 1.1529  
371 ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) and from 2.114 to 2.102 ( $^{208}\text{Pb}/^{206}\text{Pb}$ ) for alcohol, from 1.1651 to 1.1938 ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) and from  
372 2.096 to 2.050 ( $^{208}\text{Pb}/^{206}\text{Pb}$ ) for regular gasoline, from 1.1825 to 1.1913 ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) and from 2.0943 to 2.0680  
373 ( $^{208}\text{Pb}/^{206}\text{Pb}$ ) for premium gasoline, and from 1.1939 to 1.1989 ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) and from 2.063 to 2.082  
374 ( $^{208}\text{Pb}/^{206}\text{Pb}$ ) for diesel. Our data show that the isotopic signature of gasoline fuel fits better with those measured  
375 on São Paulo aerosols, suggesting that it represents one of the main source of lead in the atmosphere. However,  
376 the most significant Pb isotopic compositions was obtained in gasoline and diesel vehicular exhaust pipes, which  
377 Pb ratios show that vehicular exhaust has significant influence from gasoline ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.1635$  to  $1.1752$ ,  
378 and  $^{208}\text{Pb}/^{206}\text{Pb} = 2.0894$  to  $2.0751$ ) and diesel ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.1569$  to  $1.1814$ , and  $^{208}\text{Pb}/^{206}\text{Pb} = 2.0613$  to  
379  $2.0916$ ) emissions and are correlated with USP aerosol Pb isotopic compositions (Supplementary Table S3).

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

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

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

391 *4.1.3 Industrial emission sources at cubatão*

392 One of the end-members of the ternary mixing diagram (Fig. 9) can be correlated to aerosols from the  
393 industrial area in Cubatão (Gioia et al. 2010). Radiogenic anthropogenic sources have  $^{206}\text{Pb}/^{207}\text{Pb}$  signatures  
394 ranging between 1.1854 and 1.3279, and they are quite distinct from natural aerosols (1.1870-1.1878). The  
395 industrial emissions analysed at Mogi Valley (Cubatão) are most similar to dust collected from parking areas in  
396 the industrial plants and roads in Cubatão (1.1742-1.2155). The surface soil has a lead isotopic composition  
397 (1.1816-1.1891) close to the composition of road dust collected near the fertilizer plants (1.1742-1.1801). The  
398 aerosols collected in Cubatão have more radiogenic lead composition, suggesting the source is not derived from  
399 the local fertilizer plants and an unknown other source.

400

401 *4.1.4 Dust resuspension from urban construction*

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

407

408 *4.2. Evidence for significant air mass transport from Cubatão to São Paulo*

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

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

426 In contrast, our data do not show air mass transport towards SW because the [Pb] determined on the São  
427 Lourenço and Juquitiba stations are low. The two forested areas, São Lourenço da Serra and Juquitiba, were  
428 selected to characterize the background lead isotopic signature of aerosols in the region. The lead isotopic  
429 composition of aerosols in Juquitiba is close to those found for aerosols collected at USP, representing soil dust  
430 resuspension, possibly from rural tracks (Figs. 7 and 8). The highest  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio determined on Juquitiba is  
431 18.67 (Table 2), which is similar to the isotopic composition of the natural atmospheric lead (Kylander et al.,  
432 2010).

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

437

438

## 439 5. Conclusions

440 1) The phasing out of leaded gasoline and its replacement with ethanol in Brazil, which started in 1989, brought  
441 about 10-fold decreases in [Pb] in São Paulo city. Between the 1970's and the summer of 2005, these values  
442 decreased from  $1 \mu\text{g}\cdot\text{m}^{-3}$  to  $0.042 \mu\text{g}\cdot\text{m}^{-3}$  in 24h  $\text{PM}_{10}$  fraction, respectively. Pb concentrations showed to be  
443 significant, even during the Brazilian summer when pollutant dispersion and removal is higher. The [Pb] in  
444 the USP area are lower than the revised lead level of the primary and secondary (health-based) standard of  
445  $0.15 \mu\text{g}\cdot\text{m}^{-3}$ , measured as total suspended particles (TSP), which is explained by favourable meteorological  
446 conditions to particulate matter dispersion during hot days and high precipitation occurrences, which  
447 characterize the summer period. This study demonstrates that although [Pb] are not as high as in the 1970's,  
448 they are significant, especially the increase in fine fractions ( $0.055 \mu\text{g}\cdot\text{m}^{-3}$ ). This points to a serious public  
449 health hazard, of an intensely urbanized city, which is heavily populated and contains and is surrounded by  
450 many industrial areas.

451 2) The sources of atmospheric lead sampled in São Paulo city are diverse. The analytical techniques applied to  
452 characterize sources and aerosols in São Paul, i.e. isotope dilution thermal ionization mass spectrometry (ID-  
453 TIMS), particle induced X-ray emission (PIXE) and multivariate analysis (Factor Analysis) suggest a  
454 predominance of vehicular traffic emissions (fuel combustion, brake wear, tyre wear, road surface abrasion,  
455 and resuspension of road dust) and admixing from cement from urban construction and local cement mixing  
456 plants. The main evidence is lead isotopic compositions from vehicular exhaust and tunnel dust, which mostly  
457 characterize emissions from light vehicles.

458 3) Industrial emissions from Cubatão have a distinguished radiogenic Pb isotopic compositions ( $^{206}\text{Pb}/^{207}\text{Pb} >$   
459 1.20). On cloudy and rainy days, more radiogenic lead is detected in aerosols collected at USP (São Paulo  
460 city), suggesting an important contribution via air mass transport, to Metropolitan Area of São Paulo (MASP)

461 from the eastern industrial area, via SE winds. Our data are the first evidence of a distinct impact of industrial  
462 emissions in the megacity of São Paulo.

463 4) The remote sampling station at Jquitiba, a nature reservoir located west of the MASP, shows that a chemical  
464 composition of the aerosol samples is distinct and different from those of the industrial sources investigated  
465 in Cubatão and the emissions from São Paulo. The low [Pb] average of  $0.597 \pm 0.5 \text{ ng.m}^{-3}$  indicates that the  
466 Jquitiba area is indeed shielded from the influence of the megacity and the industrial areas.

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