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Pb isotopic signatures of the atmosphere of the São Paulo city, Brazil

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Abstract: Lead isotopic compositions of the atmosphere of the São Paulo city, Brazil, were determined from particulate matter (PM_{10}) collected on teflon filters, and rainwater samples at the São Paulo University for the period between August/1999 and September/2000. The PM_{10} $^{207}Pb/^{206}Pb$ ratios range from 0.786 to 0.875, and $^{208}Pb/^{206}Pb$ from 1.934 to 2.119, defining an array on the Pb diagram. Lead concentrations range from 3.02 to 254.52 ng/m^3. Rainwater samples displayed the same isotopic ratios measured on PM_{10} collected the same day, thus indicating that aerosols are scavenged by rain. Analyses of possible pollutants sources such as gasoline and ethanol, soot from vehicle exhaust pipes, and particulate material from industrial emissions, collected on fiberglass filters, mostly yielded isotopic compositions falling into an interval defined by 84% of the PM_{10} samples ($^{207}Pb/^{206}Pb$ = 0.840-0.870). However, 15% of the PM_{10} samples are more radiogenic, indicating a significant, unidentified radiogenic source ($^{207}Pb/^{206}Pb$ < 0.780), evident mainly in samples collected during weekends and from November/1999 to April/2000. We suggest that most of the anthropogenic Pb found in the São Paulo atmosphere comes from industrial emissions, since the amount of Pb present in vehicular fuels is negligible.

1. INTRODUCTION

Lead isotopes are known to be good tools for tracing the origin of the lead in atmospheric samples, because Pb emitted into the environment retains the isotopic composition of the ore from which it was derived [1]. Consequently, it is possible to identify sources of Pb pollution in the atmosphere by examining the Pb isotopic ratios [1, 2]. Lead has four naturally occurring stable isotopes: ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{204}Pb. The first three isotopes are end products of radioactive decay chains from ^{238}U, ^{235}U and ^{232}Th, respectively, and the last one is non-radiogenic. Therefore, their abundance and the ratios among the four isotopes gradually change with time. Lead in the environment comes from various sources, such as leaded gasoline, industrial emissions and coal combustion, and it is emitted to the atmosphere in fine particles, which can be transported within air masses for very long distances, e.g. from mid latitude regions to the Arctic and Antarctica [3].

Lead isotopes have been used to trace the pollutant sources in many cities of the world. However, a systematic study using this methodology was not available for any Brazilian city.

The main purpose of the present work is to characterize the Pb isotopic composition of the atmosphere in São Paulo city, and suggest the possible pollutant sources.

2. STUDIED AREA

The study area is located in the city of São Paulo, Brazil, one of the largest urban areas in the world. It is located ca. 60 km from the coast, over a plateau with an average altitude of 700 meters above sea level. Its average annual precipitation is about 1,930 mm, and the average temperature is 15-22 °C. São Paulo Metropolitan area has an unfavorable meteorology for dispersion of pollutants during the wintertime [4].

3. SAMPLING

For our study we collected aerosols and rainwater samples which would yield the Pb isotopic composition of the atmosphere. Samples of gasoline and ethanol, gutter sweepings, soot from vehicle exhaust pipes, and filters containing particulate material from industrial emissions were also analyzed, since they were considered potential pollutant sources of the atmosphere. In order to obtain the local geogenic Pb ratios we also analyzed rock samples.

The sampling was done at the University of São Paulo Campus, situated in the western part of the city. The aerosol samples were collected using a diaphragm pump connected via 2-3 m of PVC tubing to a plastic monitor fitted with a precleaned teflon filter, with a porosity of 1.0 μm and diameter of 47 mm. The particulate material collected had a diameter smaller than or equal to 10 μm (PM_{10}). The sampling period was from August 1999 to September 2000. During this time 136 samples were collected. Air samples were collected during 7 to 20 days per month, and the filters were changed each 24 hours.

Rainwater sampling was done using a teflon funnel connected to a teflon bottle set up at about 50 centimeters high from the ground. At the beginning of the rain, the plastic cover of the funnel was removed and rainwater was collected straight into a decontaminated teflon bottle. After the rain the bottle was taken to the laboratory for analysis.

A gneissic rock of granitic composition, displaying large K-feldspar crystals, cropping out on campus was also collected. This rock would represent the geogenic Pb of the studied area.

Samples from gasoline and ethanol were obtained straight from the pump into previously decontaminated glass recipients. Soot from vehicular exhaust pipes was collected from cars fueled with gasoline and ethanol, using a plastic spatula. In addition, gutter sweepings from the streets and parking lots were collected using a plastic spatula. Filters containing particles from industrial emission were provided to us by local companies.

4. ANALYTICAL PROCEDURES

All analytical procedures were developed in our laboratory or adapted from the literature. Sample preparation was carried out under Class 100 laminar air flow clean benches in a clean room. Details of the analytical procedures were described by Aily [5]

Filters containing particulate matter (PM_{10}) were prepared following a procedure adapted from Bollhöfer *et al.* [6]. The particulate matter was removed from the filter by ultrasonic agitation in 0.7N HBr. The solution was transferred to a Savillex® beaker and the filter was warmed up with 0.7N HBr on the hot plate for two hours; this solution was added to the first one. A mixture of 6N HCl + 7N HNO_3 was added to the filter and warmed up on the hot plate for 24 hours. This solution was added to the previous one and then evaporated to dryness. The residue was dissolved with 6N HCl, and after evaporation the residue was re-dissolved with 0.7N HBr.

Rainwater was prepared according to a procedure described by Monna *et al.* [7]. The sample was evaporated at 80 °C and the residue was digested by a mixture of concentrated HF + 16N HNO_3 and 6N HCl, during 48 hours at 110 °C. The solution was evaporated and the residue was warmed up in 1N HBr for 24 hours at 110 °C. After the evaporation, the samples were diluted in 0.7N HBr.

The whole rock sample was digested with a mixture of concentrated HF + 7N HNO_3 in a Parr® bomb, at 150 °C, in an oven for five days. The solution was dried up and 6 ml 6N HCl was added to the residue. Afterwards the sample was returned into the oven for ca. 12 hours. The solution was transferred to a Savillex® beaker, dried up and the residue was diluted with 0.7N HBr.

The fuels (gasoline and ethanol) were slowly evaporated at 23 °C, and the residue was digested in 6N HCl + 7N HNO_3 at 110 °C for 24 hours. This solution was evaporated and the residue was diluted in 0.7N HBr.

The gutter (curbside) sweeping samples were homogenized, sieved and the fraction finer than 35 mesh was taken for analysis. This was done using a dual leaching procedure. The first leach was perfomed with 3N HBr; the sample was warmed up during 4 hours at 80 °C. The sample was then centrifuged and the clear solution was isolated (first leach). The residue was first digested with 50% aqua

regia (overnight), and later with concentrated HF + 7N HNO_3 for one week. The solution was evaporated to dryness, and the residue was dissolved in 6N HCl for 12 hours, and after evaporation the residue was again diluted in 0,7N HBr (second leach). The same procedure was used for soot samples.

Particulate matter from filters containing industrial emissions was removed with 7N HNO_3 for 12 hours at 85 °C. Care was taken to avoid partial decomposition of the filter (made of fiber glass) that may introduce a significant blank contribution. The solution was evaporated and the residue was dissolved in 0.7N HBr.

All the above solutions were submitted to Pb purification using standard anion exchange chromatographic methods in HBr medium as described by Babinski *et al.* [8]. Pb was loaded onto Re filaments using the silica gel and phosphoric acid.

Lead concentrations were measured using isotopic dilution technique with ^{208}Pb tracer. Lead isotopic ratios were measured by thermal ionization mass spectrometry (TIMS) on a VG 354 mass spectrometer. The data have been normalized to SRM 981 common Pb standard. Analytical precision was generally better than 0.1% for the isotopic ratios. Pb procedural blanks varied from 140 to 200 pg.

5. RESULTS AND DISCUSSION

Ninety two aerosol samples were analyzed showing $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios ranging from 0.786 to 0.875 and 1.934 to 2.119, respectively, defining a linear trend on the $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ diagram. Most of the samples (84%) presented $^{207}Pb/^{206}Pb$ ratios in the interval of 0.840 – 0.870; 15% of the samples showed more radiogenic ratios ($^{207}Pb/^{206}Pb$ lower than 0.84). It was observed that most of the radiogenic samples were collected during weekends and from November to April (warm and wet season). The concentrations ranged from 3.02 to 254.52 ng/m^3; the higher concentrations were observed in samples collected during wintertime (average of 60.56 ± 43.38 ng/m^3), characterized by dry weather and unfavorable conditions for dispersion of the pollutants. The lower concentrations (average of 36.14 ± 37.80 ng/m^3) were obtained from samples collected in the summertime, which corresponds to the rainy season.

The Pb isotopic ratios measured on seven rainwater samples collected in different months showed a good correlation with those obtained for the air samples collected in the same periods. This indicates that a large part of the local aerosols is scavenged during the rainy episode. The lead concentrations in rainwater varied from 0.83 μg/L to 4.99 μg/L.

The local geogenic lead determined on gneissic rock and K-feldspars is non-radiogenic and showed $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ values varying from 0.909 to 0.932 and 2.190 to 2.205, respectively.

Gasoline samples showed $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios ranging from 0.839 to 0.872 and 2.068 to 2.114, respectively. The Pb concentrations varied from 0.56 to 2.27 μg/L. The Pb ratios obtained for ethanol sample fall in the same general interval obtained for the gasoline samples, but showing a narrower range. Concentration however is higher (38.5 μg/L). The difference in concentrations determined for ethanol and gasoline can be explained based on the analytical procedure. A significant amount of residue was formed after the evaporation of the gasoline samples, and thus the lead could have remained in the solid phase. In any case, the extremely low concentrations reflect existing legal restrictions effective in Brazil since the 80's on addition of Pb to gasoline.

The samples of soot from exhaust pipes of vehicles presented $^{207}Pb/^{206}Pb$ in the interval of 0.852 to 0.890, and $^{208}Pb/^{206}Pb$ between 2.093 and 2.162. These values are similar to those obtained for the fuel samples.

The gutter (curbside) sweepings showed $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios from 0.838 to 0.945 and 2.065 to 2.233, respectively. These ratios do not follow the trend defined by the other samples, suggesting that this material can come from other regions, transported by wind or aggregated to vehicles.

Three samples of industrial emissions exhibited $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios of 0.781 to 0.861, and 1.940 to 2.112. In a large city like São Paulo it is difficult to identify the Pb isotopic fingerprints due to multiplicity of existing industrial emissions. However, the isotopic ratios identified in the present work for all the potential pollutant sources fit into the same interval defined by PM_{10} samples.

Few Pb isotopic data for São Paulo city are available in the literature. Bollhöfer and Rosman [9] determined Pb isotopic ratios and concentrations in aerosol samples collected between 1994 and 1999 in more than 70 different sites from the South Hemisphere. Despite the differences during sampling (their ratios represent average values of ca. 60 day sampling) the isotopic ratios determined on aerosols collected during 1997–1998 [9] fall in the main interval defined by our samples. However, they were not able to detect the radiogenic ratios which, during our study, were observed in the atmosphere for short periods of time (1 to 2 days).

6. CONCLUSIONS

The atmosphere in São Paulo city presents Pb concentration ranging from 3.02 to 254.52 ng/m^3; the higher concentrations (60.56 ± 43.38 ng/m^3) were observed in the wintertime, and the lower ones (36.14 ± 37.80 ng/m^3) during the summer.

The particulate matter (PM_{10}) samples showed $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios ranging from 0.786 to 0.875 and 1.934 to 2.119, respectively. These data defined an array on the $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ diagram that could represent a mixing line formed by different Pb sources. Most of the samples (84%) presented $^{207}Pb/^{206}Pb$ values between 0.840 and 0.870, that corresponds the same isotopic composition interval determined for most of the pollutant sources, whose extreme values could define the upper end member of the mixing line. Also the non-radiogenic Pb isotopic compositions, observed from the geogenic source, could represent this end-member. However, no significant contribution from this source has been observed on the PM_{10} samples. More radiogenic ($^{207}Pb/^{206}Pb < 0.84$) aerosol samples (15% of the samples) were collected during the weekends and in the period from November to April (warm and wet season), and they indicate the presence of a radiogenic source, which would be the low end-member of the array, with $^{207}Pb/^{206}Pb$ ratios lower than 0.78. However, this source has not been identified during this study.

All the potential sources analyzed in this study (fuels, soot from vehicular exhaust pipes, industrial emissions) follow the same trend defined by the isotopic compositions obtained on PM_{10} samples. This indicates that they all contribute, at different rates, to the anthropogenic Pb pollution found in the São Paulo atmosphere. However, we suggest that most of the Pb comes from industrial emissions since the amount of Pb present in vehicle fuels is negligible.

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References

[1] Chow T. J., Earl J. L., *Science* **176** (1972) 510-511.
[2] Sturges W.T., Barrie L. A., *Nature* **329** (1987) 144-146.
[3] Sturges W.T., Barrie L. A., *Atmos. Environ.* **23** (1989) 2513-2519.
[4] Orsini C., Tabacniks M., Artaxo P., Andrade M.F., Kerr A.S., *Atmos. Environ.* **20** (1986) 2259-2269.
[5] Aily C. *MSc Thesis* (2001) University of São Paulo, Brazil.
[6] Bollhöfer A., Chisholm W., Rosman, K.J.R., *Anal. Chim. Acta* **390** (1999) 227-235.
[7] Monna F., Lancelot J., Croudace I.W., Cundy A.B., Lewis, J.T., *Environ. Sci. Technol.* **31** (1997) 2277-2286.
[8] Babinski M., Van Schmus W.R., Chemale Jr. F., *Chem. Geol.* **160** (1999) 175-199.
[9] Bollhöfer A., Rosman K.J.R., *Geochim. Cosmochim. Acta* **64** (2000) 3251-3262.