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Pb ISOTOPIC COMPOSITION OF THE ATMOSPHERE OF THE SÃO PAULO CITY, BRAZIL, AND ISOTOPIC CHARACTERIZATION OF SOME POLLUTANT SOURCES

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INTRODUCTION

Lead isotopes are known to be good tools for surveying lead origin in atmospheric samples (Chow et al., 1975).

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 atmosphere comes from various sources, such as leaded gasoline, industrial emissions and coal combustion. Thus, lead isotope ratios different from those of the mother rock in the region are often observed in the atmosphere (Tatsumoto and Patterson, 1963). Lead 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 Artic and Antarctica (Sturges and Barrie, 1989).

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

The main purpose of the present work is to characterize the Pb isotope composition in the atmosphere in São Paulo city, and suggest the possible pollutant sources. For our study lead isotopes were measured in different samples: aerosols and rainwater which would yield the Pb isotope 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 isotopic composition we also analyzed rock and K-feldspar samples. Lead concentrations were only determined on aerosols and rainwater samples

STUDIED AREA

The study area is located in the city of São Paulo (latitude 23°32′S, longitude 46°38′W), 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 (Orsini et al., 1986).

SAMPLING

The sampling was done on Campus of the University of São Paulo, 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 volume of the air passing through the filter was measured with a massfluxometer for a vacuum pump operating with a flux from 16 L/min. 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 (ca. 6 cm) K-feldspar crystals, croping out on campus was also collected.

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 also using a plastic spatula. Filters containing particles from industrial emission were provided to us by local companies.

ANALYTICAL PROCEDURES

Because this was the first work attempt to determine Pb isotopes on environmental samples at the Centro de Pesquisas Geocronológicas (CPGeo), USP, 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.

Filters containing particulate matter (PM_{10}) were prepared following a procedure adapted from Bollhöfer et al. (1999). The particulate matter was removed from the filter by ultrasonic agitation in 3 ml of 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 1 ml 6N HCl + 1 ml 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 1 ml 6N HCl, and after evaporation the residue was re-dissolved with 300 μl 0.7N HBr.

Rainwater was prepared according to a procedure described by Monna et al. (1997). The sample was evaporated at 80 °C and the residue was digested by a mixture of 2 ml 6N HF, 1ml 16N HNO_3, and 3 ml 6N HCl, during 48 hours at 110 °C. The solution was evaporated and the residue was warmed up in 6 ml 1N HBr for 24 hours at 110 °C. After the evaporation, the samples were diluted in 300 μl 0.7N HBr.

The whole rock sample was digested with a mixture of 3 ml 6N HF and 1ml 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 put back into the oven for ca. 12 hours. The solution was transferred to a Savillex® beaker, dried up and the residue was diluted with ca. 2 ml 0.7N HBr.

The fuels (gasoline and ethanol) were slowly evaporated at 23 °C, and the residue was digested in 1 ml 6N HCl + 1 ml 7N HNO_3 at 110 °C for 24 hours. This solution was evaporated and the residue was diluted in 300 μl 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 2 ml 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 3 ml HF + 1 ml 7N HNO_3 for one week. The solution was evaporated to dryness, and the residue was dissolved in 6 ml 6N HCl for 12 hours, and after evaporation the residue was again diluted in 1 ml 0,7N HBr (second leach). The same procedure was used for soot samples.

Particulate matter from filters containing industrial emissions was removed with 3ml 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 300 μl 0.7N HBr.

Lead was separated from interfering elements using standard anion exchange chromatographic methods in HBr medium. Pb was loaded onto Re filaments using the silica gel and phosphoric acid method (Cameron et al., 1969).

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 equipped with five Faraday cups using simultaneous multicollection in static mode. The data have been normalized to National Bureau of Standards SRM 981 common Pb standard. Analytical precision was generally better than 0.1% for the isotopic ratios.

The Pb analytical blanks varied from 200 to 140 pg, and represent less than 0.5% of the Pb concentration in the samples.

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 correspond 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 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 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.

Previous work done by Rosman et al. (1994) measured Pb isotopes in snow samples from Antarctica, where they observed a significant anthropogenic component. The Pb sources were attributed to emissions from cities in South America such Buenos Aires, Rio de Janeiro or Santiago, but the lack of Pb isotopic data from these regions did not allow them to confirm the hypothesis. However, Bollhöfer and Rosman (2000) determined lead isotopic compositions and concentrations in aerosol samples collected between 1994 and 1999 in more than 70 different sites from the South Hemisphere including cities from Chile, Colombia, Argentina, Brazil, and Ecuador, and based on their set of isotopic data, which roughly follow the same interval defined by our data, they suggested that countries from South America, specially Argentina, Chile and Brazil could be responsible for emitting the Pb found in Antarctica. However, comparing the Pb concentrations measured in the early 90's in these countries, Brazilian Pb concentrations are the lowest ones suggesting that it cannot be a significant source of Pb that contaminated the Antarctica, as proposed by Rosman et al (1994). Furthermore, we suggest that a larger and systematic set of data from other South American countries is necessary to better constrain the Pb pollutant sources that reached Antartica.

CONCLUSIONS

The atmosphere in São Paulo city presents low anthropogenic 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 around 0.78. However, this source has not been identified.

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 suggests that they all contribute to the anthropogenic Pb pollution found in the São Paulo atmosphere.

The data obtained from the gutter sweepings do not follow the trend defined by the PM_{10} samples evidencing that they could have been transported from other regions.

In addition, we conclude that despite the Pb isotopic composition data from São Paulo city being similar to those measured in Antarctica, the Pb concentrations measured in Brazil are lower as compared with other countries in South America. This suggests that Brazilian contribution would not be significant to the anthropogenic contamination detected in Antarctica during the early 90's. However, a larger set of data is necessary to better constrain the origin of Pb pollutant sources that reached Antarctica.

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REFERENCES

Bollhöfer, A. and Rosman, K.J.R. 2000 Isotopic source signatures for atmospheric lead: the Southern Hemisphere. Geochimica et Cosmochimica Acta, 19: 3251-3262.

Bollhöfer, A., Chisholm, W. and Rosman, K.J.R. 1999 Sampling aerosols for lead isotopes on a global scale. Analytica Chimica Acta, 390: 227-235.

Cameron, A. E., Smith, D. M. and Walker, R. L. 1969 Mass spectrometry of nanogram-size samples of Pb. Analytical Chemistry, 41(3):525-526.

Chow, T. J., Snyder, C. B., and Earl, J. L. 1975 Isotope ratios of lead as pollutant source indicators. In: Isotope Ratios Pollution Source Behavior Indicator, Proceedings of the Symposium, 1974. IAEA-SM-191/4, Vienna, Austria, p. 95-108.

Monna, F., Lancelot, J., Croudace, I.W., Cundy, A.B. and Lewis, J.T. 1997 Pb isotopic composition of airborne particulate material from France and the Southern United Kingdom: Implications for Pb pollution sources in urban areas. Environment Science Technology, 31: 2277-2286.

Orsini, C., Tabacniks, M., Artaxo, P., Andrade, M.F. and Kerr, A.S. 1986 Characteristics of fine and course particles of natural and urban aerosols of Brazil. Atmospheric Environment, 20: 2259-2269.

Rosman, K.J.R., Chisholm, W., Bouton, C.F. Candelone, J. P. and Patterson, C.C. 1994 Anthropogenic lead isotopes in Antarctica. Geophysical Research Letters, 21(24):2669-2672.

Sturges, W.T. and Barrie, L. A.,1989 Stable lead isotope ratios in Artic aerosols: evidence for the origem of artic air pollution. Atmospheric Environment, (23):2513-2519.

Tatsumoto, M. and Patterson, C.C., 1963 Concentrations of common lead in some Atlantic and Mediterranean waters and in snow. Nature, 199: 350-352.