CHANGES IN THE ATMOSPHERE OF THE SÃO PAULO CITY, BRAZIL, FROM 1999 TO 2001: AN ISOTOPIC APPROACH

ABSTRACT

Recent studies have shown the feasibility of using lead (Pb) isotopes for tracing the origin of this heavy metal in many environments such as soils, sediments, and atmospheric particles. We have determined Pb concentrations as well as Pb isotopic compositions in PM_{10} aerosol samples collected during the 2001 year to identify and quantify the Pb pollution in the atmosphere of the São Paulo city, Brazil. These results were compared with data obtained on the PM_{10} samples collected during 1999 and 2000 in order to verify changes in the atmosphere during this time interval.

Our study showed that a slight increase in the Pb content took place during the 2001 year, especially in the wintertime (1999-2000 average = 60.6 ± 43.4 ng/m³ ;2001 average = 78.3 ± 87.4 ng/m³). Some changes were also observed on the Pb isotopic compositions. The samples collected during the 1999-2000 period showed $^{206}Pb/^{207}Pb$ ratios ranging from 1.143 and 1.272, and the more radiogenic ratios ($^{206}Pb/^{207}Pb$ > 1.1905) were only observed during the rainy season (November to April). In the 2001 year, the range is larger ($^{206}Pb/^{207}Pb$ from 1.154 to 1.320), and the Pb radiogenic ratios were observed in samples collected in all seasons. These data can indicate that although the main pollutant sources are the same (mainly industrial emissions with some contribution of vehicle emissions), an unidentified radiogenic source, which was previously detected, became more important in the atmosphere of São Paulo city during the 2001 year.

INTRODUCTION

High concentration of pollutants can be found in the air of large cities. Among different elements present in the particulate matter, the occurrence of lead (Pb) in the fine particles (PM_{10}; < 10 mm in diameter) in the atmosphere is a cause of major concern due to its effect on public health. Because of that the source and the extent of Pb pollution have been more intensively investigated in the last few years (see Bollhöffer and Rosman, 2000, 2001a, 2001b) using a different approach, which is based on Pb isotopes.

Pb isotopic ratios have been used to determine and identify the sources of contamination. This is possible because the Pb isotope ratios are not affected by physical and/or chemical fractionation processes in the surface environments (Bollhöffer and Rosman, 2000; Duzgoren-Aydin et al., 2004), and work as a fingerprint of the pollutant source.

Here we apply the Pb isotope geochemistry on particulate matter from the São Paulo city in order to identify the different sources of Pb emitted to the atmosphere during the 1999-2000 (Aily, 2001) and 2001 periods, as well as to verify possible changes that could have taken place during this time interval.

SAMPLING AND ANALYTICAL PROCEDURES

The PM_{10} aerosol samples were collected from January to December of 2001 at the campus of the University of São Paulo, at the same location of the 1999-2000 sampling. The particulate matter (PM10) was collected in teflon filters which were changed each 24 hours. Only six samples per month were analyzed following procedures previously described (Aily, 2001; Aily et al., 2001; Babinski et al., 2003). 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 multi-collection 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

We collected aerosols (PM_{10}) samples for 10 consecutive days each month from January to December, 2001 and analyzed six samples per month. The Pb concentrations measured on 72 aerosol samples range from 16.5 to 377.3 ng/m^3, but only 14% of the samples presented Pb concentrations higher than 100 ng/m^3. The higher concentrations were observed during the wintertime (78.3 ± 87.4 ng/m^3), and the lower ones were measured on samples collected during the summer season (36.4 ± 14.7 ng/m^3). When these results are compared to those measured on samples collected in 1999-2000, we observe an increase in Pb concentrations, especially in the wintertime (1999-2000 average = 60.6 ± 43.4 ng/m^3).

The Pb isotopic compositions measured on aerosols show a large interval, with $^{206}Pb/^{207}Pb$ ratios varying from 1.154 to 1.320, and $^{208}Pb/^{206}Pb$ from 1.874 to 2.099. The largest intervals of Pb ratios were observed on samples collected in February ($^{206}Pb/^{207}Pb$ from 1.159 to 1.266), April ($^{206}Pb/^{207}Pb$ from 1.164 to 1.266), and June ($^{206}Pb/^{207}Pb$ from 1.164 to 1.320). The Pb isotopic values obtained in 2001 are more radiogenic compared to those observed in 1999-2000 samples, where only 16% of the samples presented $^{206}Pb/^{207}Pb$ ratios higher than 1.1905; in the 2001 year, 29% of the collected samples are more radiogenic ($^{206}Pb/^{207}Pb > 1.1905$). In addition, a different pattern is observed: most of the radiogenic samples from the 1999-2000 period were collected in weekends and in rainy days between November 1999 and April 2000. In contrast, during the 2001 year, only 3 out of 11 samples collected on weekends showed radiogenic ratios ($^{206}Pb/^{207}Pb > 1.1905$). We observed that Pb radiogenic ratios were detected on samples collected in all months, except in October, and on working days (mostly on Mondays and Wednesdays). Another difference detected on these two set of samples is that in 1999-2000 period the radiogenic samples generally presented low concentrations, while in 2001 samples the Pb concentrations increased and in some cases, the most radiogenic samples are the ones that have the highest Pb concentration (considering the set of samples analyzed in each month).

These results indicate that the Pb isotopic ratios measured in samples collected in 2001 present a larger interval ($^{206}Pb/^{207}Pb$ between 1.154 and 1.320) compared to that determined for samples collected in 1999-2000 period ($^{206}Pb/^{207}Pb$ between 1.143 and 1.272) as well as an increase in Pb concentrations. However, the interval of the Pb ratios fall in the same range previously determined for most of the sources (fuels, car exhausts, industrial emissions, soils, etc) that contribute to the Pb content found in the atmosphere of the São Paulo city (Aily, 2001; Aily et al., 2001; Babinski et al., 2003), and do not suggest any new source emission.

CONCLUSIONS

Comparing these results with those obtained on samples collected from August 1999 to September 2000, in the same location, we observed an increase in Pb concentration in the atmosphere particles since the values were lower during the earlier period (3.02 to 254,52 ng/m^3). Regarding the Pb isotopic compositions, which

can reflect the different sources of Pb that contribute to the atmosphere, the values are in the same range of that defined by earlier samples, but an increase in the number of samples with more radiogenic ratios ($^{206}Pb/^{207}Pb > 1.1905$) was observed (16% in 1999-2000; 29% in 2001). This variation can indicate that although the main pollutant sources are the same (mainly industrial emissions with some contribution of vehicle emissions), an unidentified radiogenic source became more important in the atmosphere of São Paulo city during the 2001 year.

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Authors Contact

Babinski, Marly; Ruiz, Izabel R.; Aily, Cristiane; Yoshida, Sergio S.

Centro de Pesquisas Geocronológicas, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, CEP 05508-060 São Paulo, SP, Brazil.

E-mail: babinski@usp.br; bilica@usp.br; aily@igc.usp.br; ssyoshida@yahoo.com.br