2017 International Nuclear Atlantic Conference - INAC 2017
Belo Horizonte, MG, Brazil, October 22-27, 2017
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN

Agência Brasileira do ISBN
ISBN 978-85-99141-07-6
9 788599 141076

AIR POLLUTION ASSESSMENT USING TREE BARKS AS BIOMONITORS

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ABSTRACT

In the last decades tree barks have become a very common bioindicator of air pollution because of its several advantages over other bioindicators. In the present study, tree barks were collected from different sites of Metropolitan Region of São Paulo (MRSP) and from two control sites far away from MRSP. The barks were analyzed by neutron activation analysis (NAA) for determinations of As, Br, Ca, Cl, Co, Cr, Cs, Fe, K, La, Mg, Mn, Ni, Rb, Sb, Sc, V and Zn and for Cd, Cu and Pb by graphite furnace absorption spectrometry (GF AAS). Results obtained for samples collected in different sampling sites in the MRSP presented wide variability due to the different pollutants levels that each tree was exposed to. High concentrations of Cd, Pb, Sb and Zn were obtained in tree barks sampled close to high vehicular traffic. The principal components analysis (PCA) applied a identify four possible emission sources, soil resuspension plus vehicular emission, industrial, marine aerosols as well as the tree bark structure itself. The enrichment factor (EF) results indicated that all the elements originated from anthropic sources, with the exception of Cs. The cluster analyses indicated no significant differences between MRSP and control sites were observed with regards to characteristics of element emissions, probably due to the control sites are located also in urban areas. The results of certified reference material analyses indicated that NAA and GF AAS provided reliable data for element concentrations with standardized differences, |Z score| < 2.

1. INTRODUCTION

The air quality assessment has become a matter of great importance since several studies have related air pollution with adverse effects on human health and the environment. The atmospheric pollutants are usually measured from instrumental physicochemical methods by automatic monitoring networks. The installation and maintenance of these monitoring networks involves high cost and the results obtained are representative within a small area, making this method impractical in regions with few financial resources. As an alternative to instrumental methods, the use of biomonitors has been extensively studied for the determination of atmospheric pollutants.

Biomonitors are live organisms that their chemical analyses allow to obtain quantifiable information of the environmental quality from where they were collected [1]. The analyses of biomonitors such as some species of plants, lichens, mosses, bryophytes and non-lichenized fungi have proved to be important tools for the evaluation of air pollution [2].

The use of tree barks has become of great interest for air pollution biomonitoring due to its several advantages over other biomonitors, such as its wide availability in extensive areas, resistance to environmental variations, easy sample collection and treatment and the bark structural porosity that allows accumulate aerosol particles. In urban and industrial areas the analysis of tree barks can be an excellent complement to conventional monitoring to establish and maintain a large-scale monitoring system, or to evaluate dispersion models of pollutants.

In this study, tree barks were used as a biomonitor to study the atmospheric pollution of chemical elements in different regions of Metropolitan Region of São Paulo (MRSP), Brazil. The continuous evaluation of the atmospheric pollution of the MRSP is performed by 30 automatic monitors stations scattered throughout the metropolis. However, their measurements do not characterize element composition of the particulate matter.

Several air pollution studies have been carried out in MRSP using biomonitors, such as plants of species *Tradescantia pallida* [3 – 4], lichens [5 – 6] and bromeliads of *Tillandsia usneoides* L. species [7 – 8]. Studies using tree barks have also been performed in RMSP to verify the correlations of its element concentrations with vehicular traffic [9], mortality rate due to respiratory disease [10] and genotoxic effects in plants [3 – 4].

As MRSP presents a very complex air pollution profile with different emission characteristics characteristics, it is of great importance to study its atmospheric pollution of chemical elements for identification of emissions sources.

2. MATERIALS AND METHODS

2.1. Sampling Regions

The sampling regions selection was based on the Sibipiruna and Tipuana tree species availability at a distance of 500 m from the surrounding air quality monitoring station of the Environmental Company of the State of São Paulo (CETESB) located in the MRSP and in control regions. The tree barks were collected at six different sites in the MRSP and in two small cities (Marília and Presidente Prudente) considered as control regions located in the interior of the São Paulo state as shown in Fig. 1. In each study region tree barks were collected at different sampling points (area where trees were located up to 30 m apart).

It was difficult to select a region to be considered as a control since the Tipuana and Sibipiruna tree species were not found outside urban areas. The control region was selected based on the particulate matter (PM_{10}) means concentration obtained from the period of January 2010 to December 2015 [11].

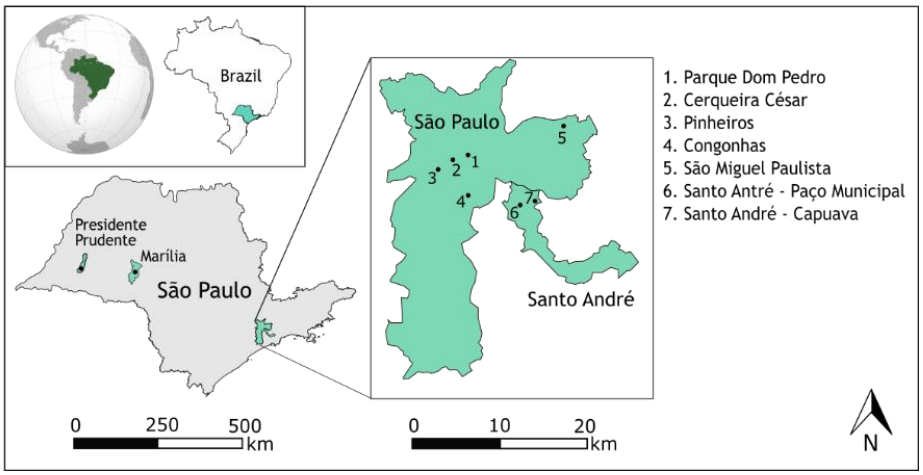

Figure 1: Location of tree barks sampling regions in the MRSP and control regions.

2.2. Collection and Treatment of the sample

The bark sample collection was carried out at a height of 1.5 m from the top soil using a stainless steel knife. For the analyses, the bark surface layer was cleaned with a nylon brush and then 2 mm of the surface was grated using a Ti grater. This sample was ground using an agate-type ball mill (Fritsch, Pulverisette 0).

When there were more than one tree of the same species at the same sampling point, composed samples were prepared to obtain a representative sample. For the preparation of this composed sample, the same amount (180 – 200 mg) of each simple samples was mixed together and homogenized. In this study, 75 individual tree bark samples were collected which was prepared 25 composed samples and 11 simple samples.

2.3. Neutron Activation Analysis Procedure

2.3.1. Synthetic element standards preparation

Synthetic standards of elements were prepared by using diluted standard solutions that were prepared using certified solutions provided by Spex Certiprep Chemical, USA. This diluted solution was pipetted onto a sheets of Whatman No. 40 filter paper. The calibration of all pipettes and volumetric flasks were verified before their use. These filter sheets were dried at room temperature inside a desiccator and then placed into clean polyethylene bags and sealed. In these standards, the quantities of each element, in μg (in parentheses) were the following: As (1.5), Br (5.0), Ca (499), Cl (500), Co (0.15), Cr (2.0), Cs (0.60), Fe (360), K (501), La (0.60), Mg (499), Mn (4.0), Ni (502), Rb (10.0), Sb (0.60), Sc (0.08), V (24.0) and Zn (36.4).

2.3.2. Long-term irradiation procedure

The NAA using long-term irradiation procedure was applied for As, Br, Ca, Co, Cr, Cs, Fe, K, La, Ni, Rb, Sb, Sc and Zn determinations. For this, about 180 mg of each sample weighed in a polyethylene bags were irradiated with synthetic standards of elements at the IEA-R1

nuclear research reactor for sixteen hours under a thermal neutron flux of about 5 x 10^{12} n cm^{-2} s^{-1}. After adequate decay times, the irradiated samples and standards were measured by a high pure Ge detector Model GX2019 coupled to a Digital Spectrum Analyzer DSA 1000, both from Canberra. The resolution (FWHM) of the system was 0.9 keV for 122 keV gamma ray peak of ^{57}Co and 1.87 keV for 1332 keV gamma ray of ^{60}Co. Couting times from 5,400 to 50,000 seconds were used based on the half-lives or activities of the radioisotopes considered. Spectra were collected and processed using Canberra Genie 2000 Version 3.1 software. All samples and standards were measured at least twice for different decay times. The radionuclides measured were identified according to their half-lives and gamma-ray energies. The concentrations of elements were calculated by comparative method [12] using the measurements obtained for radionuclides: ^{76}As, ^{82}Br, ^{47}Ca, ^{58}Co (for Ni determination), ^{60}Co, ^{51}Cr, ^{134}Cs, ^{59}Fe, ^{42}K, ^{140}La, ^{86}Rb, ^{124}Sb, ^{46}Sc and ^{65}Zn.

2.3.3. Short-term irradiation procedure

For NAA using short-term irradiation the samples and synthetic standards of elements were irradiated in the IEA-R1 nuclear reactor for 25 s under a thermal neutron flux of about 1.9 x 10^{12} n cm^{-2} s^{-1}. The end time of irradiation and the start and end times of the counting were recorded using a chronometer. The counting times of 300 and 600 s were used depending on the half-lives or activities of the radioisotopes. The measurements were performed at the same system used for long-term irradiation counting. The radioisotopes measured were ^{38}Cl, ^{27}Mg, ^{56}Mn and ^{52}V.

2.4. Graphite Furnace Absorption Spectrometry Procedure

The GF AAS procedure was performed for Cd, Cu and Pb determinations. For this, about 200 mg of each sample were digested in 10 mL of concentrated HNO_3 and 1 mL of 30 volume H_2O_2 overnight and then in a digester block at 90°C for 3 h. At the end of this acid digestion, the volumes of these solutions were completed to 25.3 mL. The sample solutions were analyzed at the GF AAS equipment model AAnalyst 800 from Perking Elmer. The lamps used for the Cd, Cu and Pb determinations were EDL (228.8 nm), LCO (324.8 nm) and EDL (283.3 nm), respectively. For the construction of the calibration curves, Cd, Cu and Pb solutions were previously prepared from certified solutions of the Spex CertiPrep USA. The HNO_3 solution was used as a diluent and the chemical modifier was a composed solution of $NH_4H_2PO_4$ 0.5% (w/v) and $Mg(NO_3)_2$ 0.03% (w/v). The absorbance analytical signal was determined from the area of the absorption peak and on the straight-line equations obtained from the calibration curves.

2.5. Quality Control of the Results

The quality control of the analytical results was evaluated by analyzing the certified reference materials (CRM) CTA-VTL-2 Virginia Tobacco Leaves, INCT-MPH-2 Mixed Polish Herbs and INCT-OBTL-5 Oriental Basma Tobacco Leaves, all provided by the Institute of Nuclear Chemistry and Technology, Poland. The CRMs were analyzed by applying the same experimental conditions used for tree barks analyses and the concentrations were evaluated on a dry weight basis, as recommended in the certificate. The accuracy of the results of CRMs obtained in the CRMs analyses was evaluated by calculating the standardized difference or z-score values [13].

3. RESULTS AND DISCUSSION

3.1. Results of Tree Bark Analyses

3.1.1. Element concentrations in tree barks

In the Fig. 2 to 4 are shown the mean concentrations of the determined elements for each sampling region. These results present a wide variability in the contents of some elements in the barks collected. This variability is related to the emission characteristics of the sampling points. In general, the barks collected at points of intense vehicular traffic had higher levels of As, Cd, Pb, Sb and Zn.

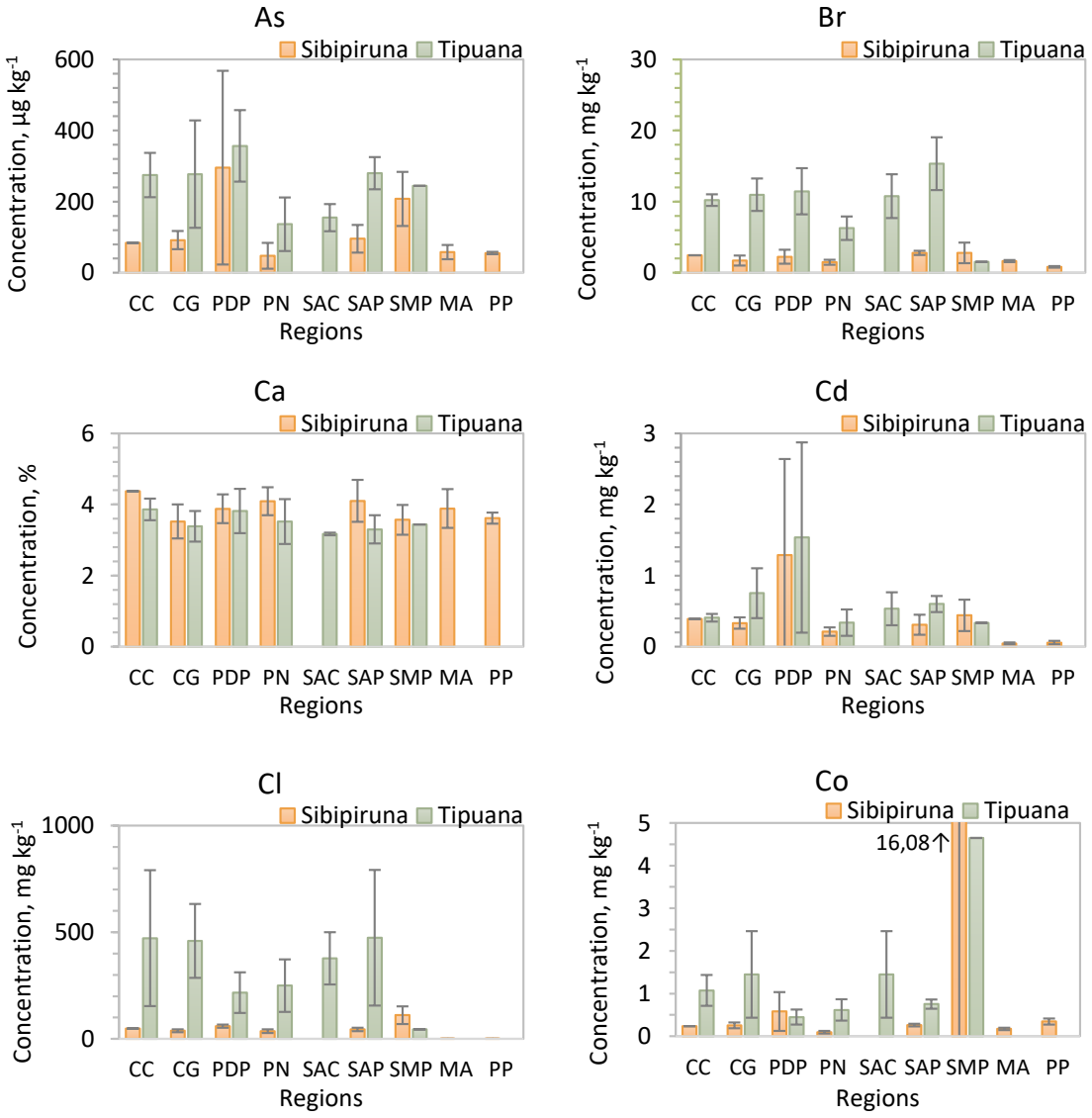

Figure 2: Concentrations of As, Br, Ca, Cd, Cl and Co in barks of Sibipiruna and Tipuana collected in Cerqueira César (CC), Congonhas (CG), Parque Dom Pedro II (PDP), Pinheiros (PN), Santo André – Capuava (SAC), Santo André – Paço Municipal (SAP), São Miguel Paulista (SMP), Marília (MA) and Presidente Prudente (PP).

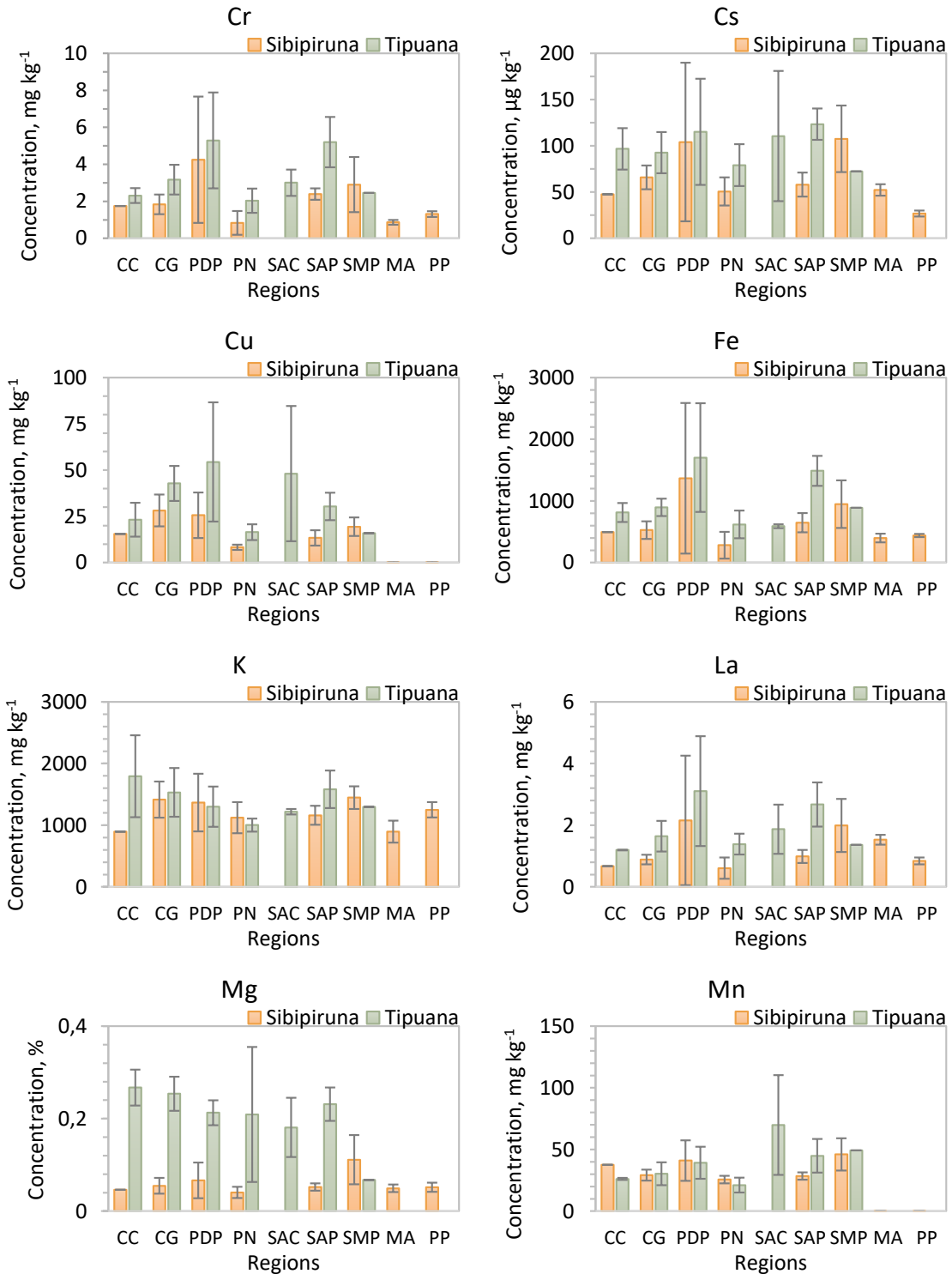

Figure 3: Concentrations of Cr, Cs, Cu, Fe, K, La, Mg and Mn in barks of Sibipiruna and Tipuana collected in Cerqueira César (CC), Congonhas (CG), Parque Dom Pedro II (PDP), Pinheiros (PN), Santo André – Capuava (SAC), Santo André – Paço Municipal (SAP), São Miguel Paulista (SMP), Marília (MA) and Presidente Prudente (PP).

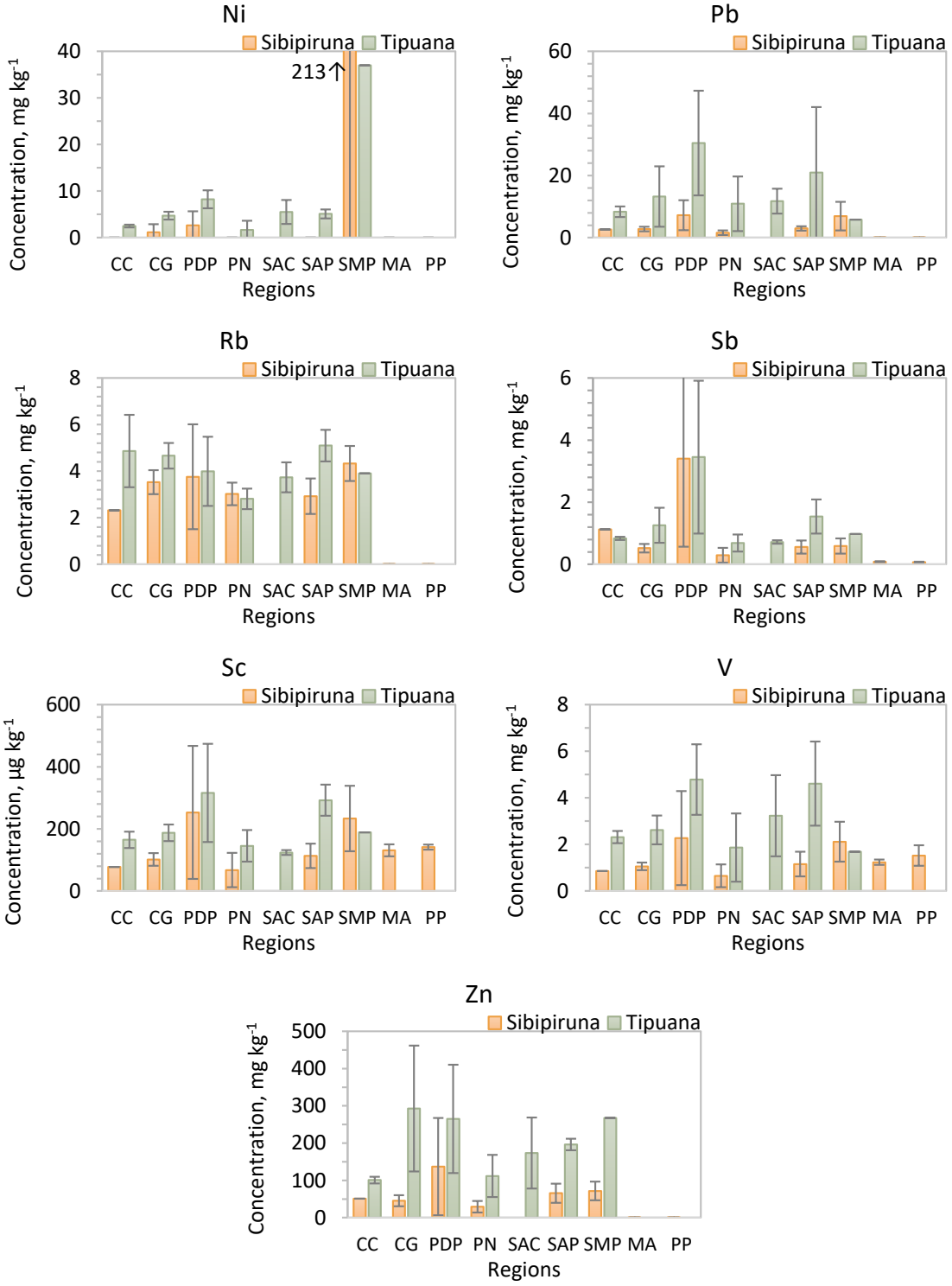

Figure 4: Concentrations of Ni, Pb, Rb, Sb, Sc, V and Zn in barks of Sibipiruna and Tipuana collected in Cerqueira César (CC), Congonhas (CG), Parque Dom Pedro II (PDP), Pinheiros (PN), Santo André – Capuava (SAC), Santo André – Paço Municipal (SAP), São Miguel Paulista (SMP), Marília (MA) and Presidente Prudente (PP).

The elements Co and Ni presented high mean concentrations in the São Miguel Paulista, the sampling points with highest concentrations of theses elements was located in the surroundings of a metallurgical industry in this region. This may explain the high results variability in this region. The mean concentrations of As, Cd, Fe and Sb were highest in the Parque Dom Pedro II in relation to the other RMSP regions, indicating that the intense vehicular traffic of this region may be causing the increase of these element concentrations in the resuspended particulate matter. The results obtained from the samples collected in the control regions of Marília and Presidente Prudente presented mean concentrations of Cd, Cl, Cs, Cu, Mn, Pb, Rb, Sb and Zn lower than the results obtained in the RMSP. This may be an indication that these elements are also related to vehicular traffic but with low intensity in control regions.

3.1.2. Principal component analysis (PCA) of the element results obtained in tree barks

The PCA of results obtained in tree barks was applied using the STATISTICA 6.0 software in order to obtain a reduction of the data and to visualize the patterns of similarity between the elements determined in the tree barks. Using the Kaiser method, the results were reduced by the first four components, which represent 80.97% of the results variance accumulate. The graphs of the extracted components are shown in Fig. 5.

The first principal component (CP 1) is composed by As, Cd, Cr, Cs, Fe, La, Sb, Sc and V which represents 53.57% of the data variance that may be related to particulate matter from soil ressuspension, as well as vehicular emissions. In the CP 2 the elements Co and Ni explain 11.09% of the variance of the results obtained, whose their origin may be related to the emission of the metallurgical industry located in the region of São Miguel Paulista. The elements that make up CP 3 are Br, Cl and Mg, that together they represent 9.72% of the data variance, composed by elements of marine aerosol, since the Brazilian coast is 60 km away from the São Paulo city. The CP 4 represents 6.58% of the data variance and is composed by the elements Rb and K, and related to the structure of the tree bark and to the soil composition.

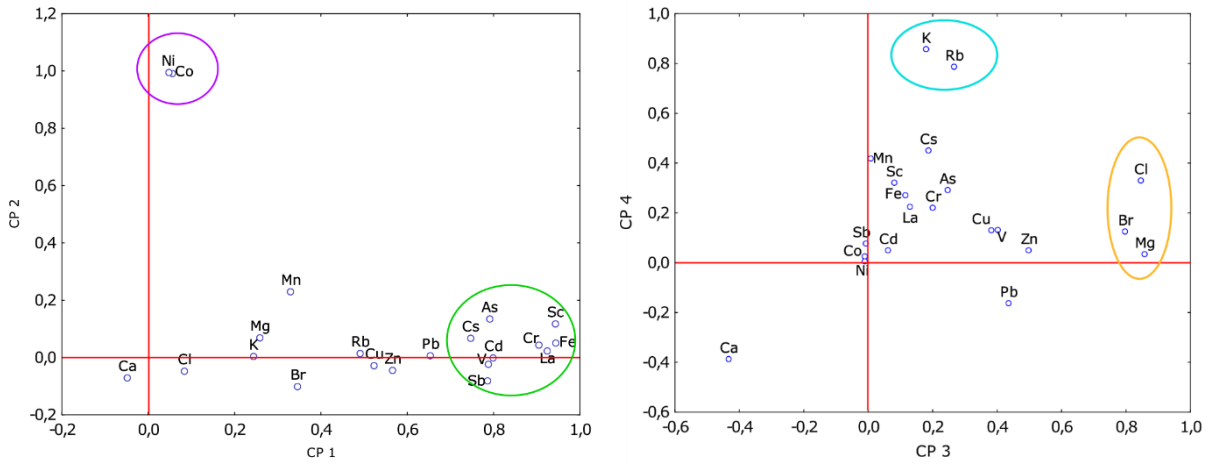

Figure 5: Graph of the four main components (CP1, CP2, CP3 and CP4) from the PCA applied in the tree bark results.

3.1.3. Cluster analysis of the results

The cluster analysis was applied using the STATISTICA 6.0 software for the hierarchy of the sampling regions for their atmospheric emission characteristics and the resulting dendrogram is shown in Fig. 6. It can be concluded that the regions selected as control did not differ from the regions located in the MRSP in its profile of atmospheric emissions. This result may be due to the sampling points of the control regions are located within urban areas.

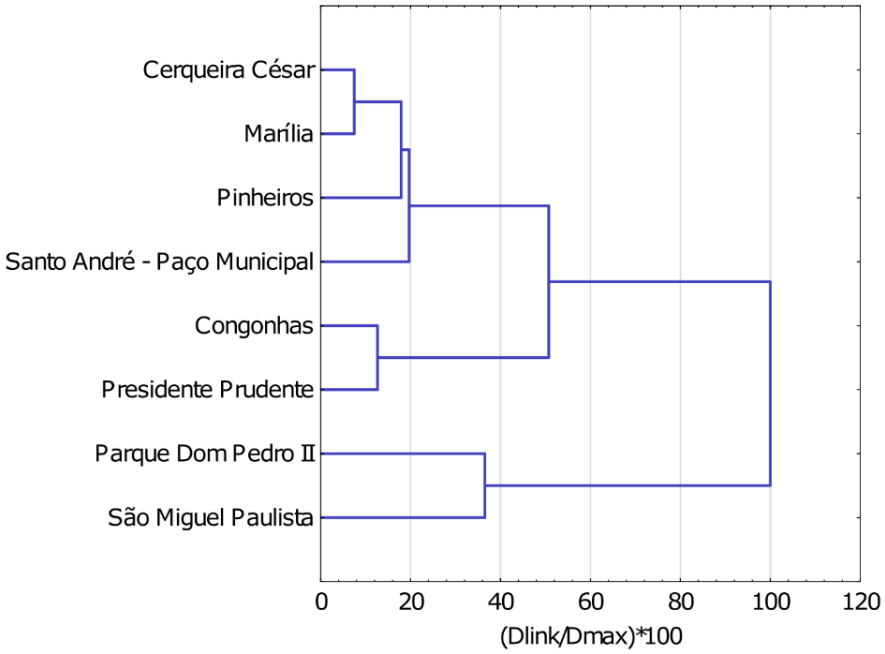

Figure 6: Dendrogram obtained by cluster analysis for the different sample regions.

3.1.4. Determinations of Enrichment Factor (EF)

The EF was calculated according to Guéguen et al. [14] to evaluate the levels of contamination by chemical elements in the different sampling regions. The concentration of Sc in the upper continental crust (UCC) was used as reference [15] and the results obtained are presented in Table 1.

The elements As, Cd, Cr, Cu, Sb, Pb and Zn presented higher EFs values in the MRSP than those of Presidente Prudente and Marília. This indicates that there is a greater anthropogenic contribution to the enrichment of these elements in the city of São Paulo in relation to the control regions, due to differences in the intensities of vehicle emissions. In São Miguel Paulista the EF was over than 41, indicating that the emissions of the metallurgical industry increased considerably the contents of this element in the particulate material in this region.

Table 1: Enrichment factors (EF) obtained using concentrations of the elements in the bark of the Sibipiruna in different regions.

Elements	CC[a]	CG[b]	PDP[c]	PN[d]	SAP[e]	SMP[f]	MA[g]	PP[h]
As	**3.8**	**3.2**	**4.1**	**2.5**	**3.0**	**3.1**	**1.5**	**1.4**
Br	**138.8**	**73.8**	**38.9**	**96.2**	**108.5**	**52.3**	**54.5**	**25.4**
Ca	**134.1**	**82.6**	**36.5**	**144.2**	**86.1**	**36.4**	**70.4**	**60.9**
Cd	**346.5**	**225.4**	**349.9**	**217.8**	**187.2**	**129.7**	**24.1**	**28.2**
Cl	**6.8**	**4.1**	**2.6**	**5.9**	**4.3**	**5.2**	**1.2**	**2.6**
Co	**1.8**	**1.5**	**1.4**	**1.7**	**1.4**	**41.6**	0.8	**1.5**
Cr	**4.5**	**3.6**	**3.4**	**2.5**	**4.2**	**2.5**	**1.3**	**1.9**
Cs	0.7	0.8	0.5	0.9	0.6	0.6	0.5	0.2
Cu	**97.6**	**136.0**	**49.6**	**60.3**	**57.7**	**40.7**	**36.5**	**22.0**
Fe	**1.4**	**1.2**	**1.2**	0.9	**1.3**	0.9	0.7	0.7
K	**2.8**	**3.4**	**1.3**	**4.1**	**2.5**	**1.5**	**1.7**	**2.2**
La	**1.9**	**1.9**	**1.8**	**2.0**	**1.9**	**1.8**	**2.5**	**1.3**
Mg	**3.1**	**2.8**	**1.4**	**3.1**	**2.4**	**2.5**	**1.9**	**1.9**
Mn	**6.4**	**3.8**	**2.2**	**5.1**	**3.3**	**2.6**	**3.6**	**2.7**
Pb	**14.1**	**11.4**	**11.7**	**9.7**	**10.8**	**12.3**	**2.1**	**1.1**
Rb	**1.9**	**2.2**	0.9	2.9	**1.6**	**1.2**	0.9	**1.5**
Sb	**326.9**	**116.4**	**303.8**	**98.3**	**111.2**	**57.3**	**15.0**	**11.1**
V	**1.5**	**1.4**	**1.2**	**1.3**	**1.3**	**1.2**	**1.2**	**1.4**
Zn	**89.0**	**60.2**	**72.8**	**58.7**	**78.0**	**41.3**	**22.9**	**14.0**

a. Cerqueira César; b. Congonhas; c. Parque Dom Pedro II, d. Pinheiros; e. Santo André – Paço Municipal; f. São Miguel Paulista; g. Marília; h. Presidente Prudente.

3.2. Quality Control of the Results

The quality control of the results was evaluated by calculating Z score in the results obtained in the MRCs analysis. The |Z-score| values presented in Fig. 7 are lower than 2, indicating that the results are satisfactory and in agreement with the certified values.

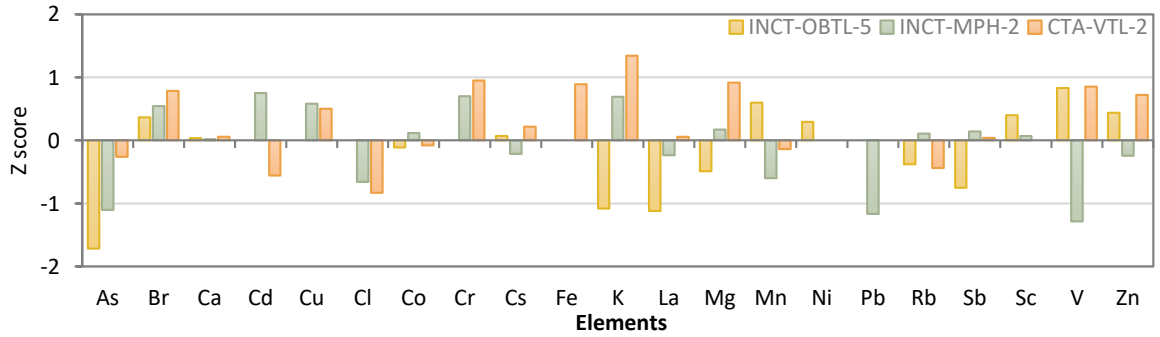

Figure 7: Z score values obtained for MRCs INCT-MPH-2 Mixed Polish Herbs, CTA-VTL-2 Virginia Tobacco Leaves and INCT-OBTL-5 Oriental Basma Tobacco Leaves analyzed by NAA and GF AAS.

3. CONCLUSIONS

The findings of this study allowed to conclude that tree barks can be used in the evaluation of aerial pollution of chemical elements. The results showed wide variability of element concentrations due to differences in the emission characteristics of each sampling site and the results provided the identification of possible emission sources.

From the PCA results four different sources with respect to the origins of the elements were obtained. These sources were soil ressuspension plus vehicular emissions, industrial pollutants, marine aerosol and the tree bark structure itself.

The cluster analysis applied in the results showed that the control regions did not differ from those of MRSP, indicating that the emission profiles of both are similar, however, the calculated enrichment factors indicated that the control regions presented lower anthropogenic contribution in the composition of the airborne particulate matter.

The Z score values obtained from the CRMs analysis indicated that NAA and GF AAS procedures used were adequate for tree bark analysis.

ACKNOWLEDGMENTS

The authors thank Brazilian agencies CNPq and FAPESP for financial support. Eliane C. Santos is grateful to CAPES for the fellowship.

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