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A STUDY ON TEMPORAL VARIATION OF ELEMENTAL COMPOSITION IN TREE BARKS USED AS AIR POLLUTION INDICATORS

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ABSTRACT

The study of air pollution using biological matrices has shown that tree barks may be used as biomonitor due to accumulation of aerosol particles on its porous surface. The bark elemental composition can provide information on pollution sources as well as characterize the aerial pollutants from a wide geographical region. The aim of this study was to investigate the variation in elemental composition in barks with time of exposure. Tree barks from Tipuana (*Tipuana tipu*) and Sibipiruna (*Caesalpinia peltophoroides*) species were collected in February 2013 and July 2014 in the city of São Paulo. For analysis, the barks were cleaned, grated, ground and analyzed by neutron activation analysis (NAA). Aliquots of samples and synthetic standards of elements were irradiated with thermal neutron flux at the IEA-R1 nuclear research reactor and after a suitable decay time, the induced gamma activities were analyzed by gamma spectrometry. The elements As, Br, Ca, Co, Cr, Cs, Fe, K, La, Rb, Sb, Sc and Zn were determined and the results indicated variability in the concentrations depending on the element, sampling period and also on tree species, indicating that there are not very well defined temporal trends. The quality control of the analytical results evaluated by analyzing INCT Virginia Tobacco Leaves certified reference material (CRM) presented values of |z-score| < 2, indicating that the procedure of NAA applied is suitable for the analyses.

1. INTRODUCTION

The effects caused by atmospheric pollution in human health have become an issue of great importance that needs careful investigations concerning the measurements of pollutant levels. Different types of biomonitors as plants, lichens, mosses and bryophytes have been used as an additional support for the monitoring of air pollution. Many studies have shown that tree bark is an interesting alternative biomonitor because of its easy and low cost sampling and treatment, wide geographical distribution of the same arboreal species and also the barks can be collected directly from the trunk or transplanted to different locations [1 - 2]. All these advantages allow identifying emission sources to characterize the pollutants from a wide area [3].

However, there is great concern about the reliability of the results obtained when tree barks are used as biomonitor because the pollutant accumulation depends on several factors such as

tree bark porosity, exposure time, wind direction and arboreal species. This study presents results of element accumulation variation in tree barks with time of exposure.

Schulz et al [4] determined sulfate, nitrate, calcium, lead, benzo[a]pyrene and α-HCH in Scot pine barks in order to evaluate its temporal variation. They found a decrease in concentrations in most of these compounds in the barks due to substantial infra-structural changes in eastern Germany that started in 1991. The reduction of acid compounds emissions was also observed by Suchara [5] depending on the H^+ concentrations in bark extracts. He demonstrated that in comparison with 1990 the acidity in the extracts had decreased by 10 – 15% in 1995 and by 70% in 2005.

Concerning elements in tree bark, Catinon et al [6] pointed out that bark superficial deposit should not be considered as a simple cumulative archive but a source of information about recent atmospheric pollution pressures when compared to the bulk of suber integrated particle. Odabasi et al. [7] showed that tree rings could be used as a tool to investigate the historical trends of atmospheric persistent organic pollutants (POPs) in a region.

The objective of this study was to investigate the variation of elemental composition in tree barks from the same trees collected in different years by neutron activation analysis (NAA). The two tree species chosen for this study were Sibipiruna (*Caesalpinia peltophoroides*) and Tipuana (*Tipuana tipu*) the most abundant species in the São Paulo City, SP, Brazil.

2. MATERIALS AND METHODS

2.1. Sample Collection and Treatment

Barks were collected from three trees of each Tipuana and Sibipiruna species in two different periods, February 2013 and July 2014 at the same sampling site of the Campus of São Paulo University, São Paulo. Detachable barks free of lichens and mosses were removed around the trunk with diameter varying from 32 to 56 cm for Sibipiruna and 53 to 60 cm for Tipuana. The collection was made at a height of 1.5 m from the ground and the barks were stored into paper bags. For analysis, 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).

2.2. Synthetic Element Standards Preparation

Synthetic standards of elements were prepared by pipetting 50 μL standard solutions prepared using certified solutions provided by Spex Certiprep Chemical, USA onto sheets of Whatman No. 40 filter paper. The calibration of all pipettes and volumetric flasks were verified before 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 (1000.0), Co (0.150), Cr (2.0), Cs (0.60), Fe (360), K (500.0), La (1.0), Rb (10.0), Sb (0.6), Sc (0.10) and Zn (36.0).

2.3. Neutron Activation Analysis Procedure

The NAA procedure consisted of irradiating about 180 mg of the sample in clean polyethylene bags 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 GX2020 coupled to a Digital Spectrum Processor 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. Counting 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 [8] using the measurements obtained for radionuclides: ^{76}As, ^{82}Br, ^{47}Ca, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{59}Fe, ^{42}K, ^{140}La, ^{86}Rb, ^{124}Sb, ^{46}Sc and ^{65}Zn.

2.4. Quality Control of the Results

The quality control of the analytical results was evaluated by analyzing the certified reference material (CRM) CTA-VTL-2 Virginia Tobacco Leaves provided by the Institute of Nuclear Chemistry and Technology, Poland. This reference material was analyzed by applying the same experimental conditions used for tree bark analyses and was evaluated on a dry weight basis, as recommended in the certificate. The accuracy, the results of CRM obtained was evaluated by calculating the standardized difference or Z-score values [9].

3. RESULTS AND DISCUSSION

3.1. Ratio Between Element Concentrations Obtained in Samples Collected in 2013 and 2014

In order to evaluate the variation of element accumulation in barks collected in 2013 and 2014, the ratio of element concentrations was calculated using the relation:

$$R_i = \frac{C_{i\,2014}}{C_{i\,2013}} \quad (1)$$

Were R_i is the ratio value of the element, $C_{i\ 2014}$ and $C_{i\ 2013}$ are the concentrations of the element obtained in 2014 and 2013 respectively.

The ratio values (R_i) and mean ratios (R) obtained for three trees of Sibipiruna are presented in Tables 1 and 2 respectively.

Table 1: Ratio values between elemental concentrations obtained in Sibipiruna tree barks and mean ratios calculated

Elements	Tree 1 (R_i)[a]	Tree 2 (R_i)	Tree 3 (R_i)	R ± SD
As	0.70 ± 0.02	1.79 ± 0.06	2.14 ± 0.05	1.54 ± 0.75
Br	0.473 ± 0.004	0.392 ± 0.005	1.16 ± 0.01	0.67 ± 0.42
Ca	1.12 ± 0.05	0.92 ± 0.05	0.65 ± 0.02	0.90 ± 0.24
Co	0.91 ± 0.01	1.18 ± 0.02	1.61 ± 0.02	1.23 ± 0.35
Cr	0.593 ± 0.007	1.00 ± 0.02	1.71 ± 0.03	1.10 ± 0.56
Cs	0.57 ± 0.01	1.56 ± 0.06	1.65 ± 0.08	1.26 ± 0.60
Fe	0.625 ± 0.004	1.41 ± 0.01	2.26 ± 0.02	1.43 ± 0.82
K	0.987 ± 0.007	1.098 ± 0.005	3.70 ± 0.03	1.9 ± 1.5
La	0.879 ± 0.004	1.534 ± 0.007	2.23 ± 0.01	1.55 ± 0.67
Rb	0.70 ± 0.02	1.15 ± 0.04	1.55 ± 0.04	1.12 ± 0.44
Sb	0.78 ± 0.02	0.99 ± 0.03	1.66 ± 0.04	1.14 ± 0.46
Sc	0.644 ± 0.003	1.70 ± 0.01	2.20 ± 0.12	1.52 ± 0.79
Zn	0.809 ± 0.004	0.939 ± 0.006	1.410 ± 0.007	1.05 ± 0.32

a. R_i = ratio value of the element concentration
b. R ± SD = Mean ratios and standard deviation obtained from three tree barks

Table 2: Ratio values between elemental concentrations obtained in Tipuana tree barks and mean ratios calculated

Elements	Tree 1 (R_i)	Tree 2 (R_i)	Tree 3 (R_i)	R ± SD
As	0.78 ± 0.02	0.26 ± 0.01	0.94 ± 0.03	0.66 ± 0.36
Br	0.802 ± 0.004	0.818 ± 0.005	0.831 ± 0.005	0.82 ± 0.01
Ca	0.96 ± 0.05	1.24 ± 0.06	1.02 ± 0.04	1.07 ± 0.14
Co	0.86 ± 0.02	0.60 ± 0.01	1.01 ± 0.01	0.82 ± 0.21
Cr	0.706 ± 0.009	0.303 ± 0.003	0.89 ± 0.01	0.63 ± 0.30
Cs	0.93 ± 0.04	0.44 ± 0.01	0.84 ± 0.02	0.74 ± 0.26
Fe	0.781 ± 0.006	0.313 ± 0.002	0.935 ± 0.007	0.68 ± 0.32
K	1.010 ± 0.009	0.785 ± 0.005	0.89 ± 0.01	0.89 ± 0.11
La	1.004 ± 0.004	0.444 ± 0.002	0.795 ± 0.004	0.75 ± 0.28
Rb	1.00 ± 0.02	0.58 ± 0.01	1.04 ± 0.03	0.86 ± 0.24
Sb	0.81 ± 0.02	0.379 ± 0.007	0.84 ± 0.02	0.68 ± 0.26
Sc	0.791 ± 0.004	0.348 ± 0.002	0.907 ± 0.005	0.68 ± 0.29
Zn	0.905 ± 0.005	0.610 ± 0.003	1.069 ± 0.005	0.86 ± 0.23

The standard deviations of the mean ratios R obtained for both arboreal species show wide variability in the concentrations for most elements. These variations indicate the element accumulations in barks depend on the several factors which makes difficult to evaluate temporal variation of elemental concentrations in bark. Santitoro et al [10] observed that rainfall does not appear responsible for the decrease in trace metal contents. Besides, Baptista et al. [1] observed that longest exposure periods hardly ever correspond to the highest accumulation of elements in tree barks.

3.2. Quality Control of the Results

Experimental results obtained for CRM Virginia Tobacco Leaves are presented in Table 3 along with the values of the certificates and the standardized difference or Z-score values. The |Z-score| values obtained were lower than 2 indicating that the results are satisfactory and in agreement with the certified values. The results are given with the respective expanded uncertainties corresponding to 95% confidence level.

Table 3: Elemental concentrations in the certified reference material CTA-VTL-2 Virginia Tobacco Leaves

Elements	This study[a]	Values of the certificate [11]	Z-score
As, ng g^{-1}	887 ± 219	969 ± 72	-0.57
Br, µg g^{-1}	16.5 ± 2.9	14.3 ± 1.4	1.27
Ca, mg g^{-1}	35.8 ± 2.2	36 ± 0.15	-0.17
Co, ng g^{-1}	425 ± 73	429 ± 26	-0.05
Cr, µg g^{-1}	2.09 ± 0.44	1.87 ± 0.16	0.73
Cs, ng g^{-1}	527 ± 51	515 ± 46	0.12
Fe, µg g^{-1}	1116 ± 79	1083 ± 33	0.53
K, mg g^{-1}	10.7 ± 1.4	10.30 ± 0.40	1.03
La, ng g^{-1}	1012 ± 133	1010 ± 100	0.02
Rb, µg g^{-1}	48.5 ± 2.1	48.6 ± 2.3	-0.03
Sb, ng g^{-1}	309 ± 43	312 ± 25	-0.05
Sc, ng g^{-1}	315 ± 30	(268)[b]	-
Zn, µg g^{-1}	44.2 ± 1.3	43.3 ± 2.1	0.22

a. Arithmetic mean and standard deviation from 7 determinations.
b. Number in parenthesis indicates informative values.

4. CONCLUSIONS

The findings obtained showed variability in the element accumulations between samples collected in 2013 and 2014. These data indicates fluctuations in the elemental composition of Tipuana and Sibipiruna tree barks.

These preliminary results indicated the need to study in details the temporal trend of the element accumulation in tree barks whose data are quite scarce.

The results obtained in the CRM Virginia Tobacco Leaves indicated that NAA procedure used was suitable for the analysis.

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