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Use of *Tipuana tipu* Tree Barks in Active Biomonitoring of Atmospheric Pollutants

G. Ishimaru[1] and M. Saiki[2]

[1]*gabrielishimaru@gmail.com,*
[2]*mitiko@ipen.br, Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, 05508-000, São Paulo, SP, Brasil*

1. Introduction

Biomonitors are organisms (part of an organism or a community of organisms) that contain quantitative aspects of environmental quality [1]. Monitoring air pollution through biomonitors, known as biomonitoring, is a technique that has been widely used due to its advantages of low-cost, ease of sampling and the possibility of evaluating a broad range of pollutants [2].

Biomonitoring can be passive or active. In passive biomonitoring, organisms that are naturally present in the ecosystem are collected to determine pollutants. In active biomonitoring, biomonitors are created in laboratories or collected in regions with low concentrations of pollutants and they are exposed in the study area in a standardized way for a delimited period, after exposure the reactions by the pollutants are recorded or the pollutants absorbed or retained by the organisms are analyzed [3, 4].

Various species are used in active biomonitoring of atmospheric pollution, such as lichen, mosses and leaves of vascular plants, mainly of the genus Tillandsia [5, 6]. The choice of a biomonitor species should fit the objective of the study, taking into account aspects such as the organism's ability to accumulate elements from atmospheric pollution, the availability and adaptability of the species in the region and knowledge of the specific characteristics of each organism [7].

Tree barks has been widely used in passive biomonitoring of air pollution due to its ability to retain pollutants and its ample availability [8]. However, studies on application of tree barks in active biomonitoring are very scarce. Consequently, it is of great importance to evaluate the performance of tree bark for using in active biomonitoring of air pollutants in regions where there is an absence of suitable biomonitor species.

The aim of this study was to evaluate the performance of tree barks in the active biomonitoring of atmospheric pollution by chemical elements. Barks from *Tipuana tipu* (Benth.) Kuntze tree species were exposed in different sites of urban area of São Paulo to examine its chemical elements accumulation.

Concerning the analytical methodologies applied for element mass fractions determinations in tree barks, several techniques have been applied [9, 10]. In this study, Neutron Activation Analysis (NAA) was applied because of its advantages in analyzing this type of matrix. NAA is a highly sensitive, precise and accurate analytical technique and very suitable for element determinations in environmental samples of tree barks due to its multielement character without sample dissolution.

2. Experimental

Bark samples of the Tipuana (*T. tipu*) species were obtained from branches of trees that fell with the rain in the campus of the University of São Paulo. These branches were sawn to obtain samples of specimens in cylindrical shapes with diameter of 8 cm and height of 10 cm. Each specimen was used to obtain a control sample and an exposed sample. To obtain these samples for the analyses, the outer faces of each specimen were divided into four parts.

Control sample was obtained first by removing the bark from two opposite faces of each specimen using a titanium grater. The specimen with two other opposite faces whose barks were not removed was used for active biomonitoring. It was placed in a plastic net bag and exposed during two months at a height of about 2 m from the topsoil. The specimens were exposed at 9 locations in the urban area of São Paulo.

The preparation of the barks samples for the analyses consisted of a cleaning using a nylon dental brush to remove the surface dust. After that, about 3 mm thickness of the bark external surface was removed with a titanium grater, followed by grinding of the samples in an agate-type ball mill (Fritsch, Pulverisette 0).

For NAA, synthetic element standards were prepared using standard solutions provided by Spex Certiprep Chemical, USA. Aliquots of single or multielement standard solutions were pipetted onto sheets of Whatman nº 40 filter paper. These filter sheets were placed in a desiccator to dry the aliquots at room temperature. After drying, these sheets were folded using tweezers and inserted into clean polyethylene bags, which were heat sealed.

About 150 mg of each tree bark sample weighed in clean polyethylene bag were irradiated at the IEA-R1 nuclear research reactor together with the synthetic element standards. Short irradiations of 20 s under a thermal flux of about 1.9×10^{12} n cm^{-2} s^{-1} were carried out for the determination of Mg, Mn, Na and V. Long irradiations of 16 h under a thermal neutron flux of about 4.5×10^{12} n cm^{-2} s^{-1} were performed for As, Br, Ca, Co, Cr, Cs, Fe, K, La, Rb, Sb, Sc and Zn determinations.

After adequate decay times, gamma-ray activities of samples and standards were measured by a hyperpure Ge detector coupled to a Digital Spectrum Analyzer DAS 1,000, both from Canberra. Spectral data were collected and processed using Canberra Genie 2,000 version 3.1 software. The radioisotopes of gamma-ray spectra were identified according to their half-lives and gamma-ray energies. The elements mass fractions were calculated by comparative method [11].

Certified reference materials INCT-MPH-2 Mixed Polish Herbs, provided from the Institute of Nuclear Chemistry and Technology of Warsana, Poland and IAEA-336 Lichen, provided from the International Atomic Energy Agency, Vienna, Austria, were analyzed using the same procedure for quality control purposes and the results presented good precision and accuracy.

Statistical parameters of arithmetic mean and standard deviation were calculated for the results obtained. Enrichment factors were calculated to evaluate the element retention capacities by the barks. The enrichment fator is given by the relation: $EF_x = F_{af}/F_{bf}$, where EF_x is the enrichment fator of the element x; F_{af} is the element mass fraction obtained after exposure and F_{bf} is the element mass fraction obtained before exposure (result of control sample). Tree barks specimens that presented EF_x higher than 1.0 were considered enriched by element x [12].

3. Results and Discussion

Results obtained indicated that NAA allowed the determination of the elements As, Br, Ca, Co, Cr, Cs, Fe, K, La, Mg, Mn, Na, Rb, Sb, Sc, V and Zn. Mean values of element mass fractions determined in control samples and exposed samples in nine locations, with their respective standard deviations and the minimum and maximum values are shown in Table I. Results obtained for control samples show that there were variations of the element mass fractions among the specimens used for exposure. This variation is probably due to the specimens used were from tree branches that were exposed to different levels of pollution. So, these results indicate the need to analyze each specimen (control sample) to be exposed.

Table I: Arithmetic means and ranges of elements mass fractions in *Tipuana tipu* barks

Elements	Control samples		Exposed samples	
	$\bar{F} \pm SD$ (n = 9)	Min – Max	$\bar{F} \pm SD$ (n = 9)	Min – Max
As, µg kg^{-1}	186 ± 42	139 – 253	298 ± 93	127 – 380
Br, mg kg^{-1}	3.8 ± 2.6	0.8 – 8.0	4.6 ± 2.2	2.2 – 8.2
Ca, %	3.2 ± 0.5	2.6 – 4.1	3.0 ± 0.4	2.6 – 3.6
Co, µg kg^{-1}	393 ± 160	462 – 587	506 ± 208	425 – 840
Cr, mg kg^{-1}	3.7 ± 1.1	2.0 – 5.7	5.7 ± 2.3	2.6 – 10.7
Cs, µg kg^{-1}	170 ± 55	87 – 250	227 ± 69	146 – 340
Fe, mg kg^{-1}	1190 ± 328	654 – 1637	1604 ± 376	947 – 1989
K, mg kg^{-1}	1695 ± 548	1123 – 2705	2566 ± 741	1856 – 3874
La, mg kg^{-1}	2.4 ± 0.7	1.4 – 3.2	3.0 ± 0.8	1.8 – 4.2
Mg, mg kg^{-1}	1885 ± 378	1371 – 2730	2337 ± 802	1657 – 4262
Mn, mg kg^{-1}	50.7 ± 8.5	40.4 – 60.8	57.4 ± 11.0	46.1 – 73.7
Na, mg kg^{-1}	173 ± 41	96 – 212	238 ± 43	177 – 292
Rb, mg kg$^{-1,}$	6.3 ± 2.6	3.6 – 10.8	9.2 ± 3.6	5.6 – 15.7
Sb, mg kg^{-1}	1.4 ± 0.4	0.9 – 1.8	1.9 ± 0.4	1.0 – 2.4
Sc, µg kg^{-1}	239 ± 64	130 – 312	323 ± 75	209 – 408
V, mg kg^{-1}	2.32 ± 0.68	1.21 – 3.18	2.95 ± 0.73	1.71 – 3.93
Zn, mg kg^{-1}	96 ± 15	73 – 119	123 ± 19	80 – 140

$\bar{F} \pm SD$ = mean and standard deviation of element mass fractions; n = number of exposure points

Results of enrichment factors means of chemical elements in *T. tipu* barks were calculated and presented Fig. 1. Considering that for enrichment factors higher than 1 there is accumulation of elements, this Fig. 1 indicates that there was accumulation for most of all elements determined, except Ca. The elements As, Cr, K and Rb presented the highest mean enrichment factor values. These results indicate that the *T. tipu* tree barks are suitable for the bioaccumulation of elements and, consequently, they can be used in active biomonitoring of air pollution.

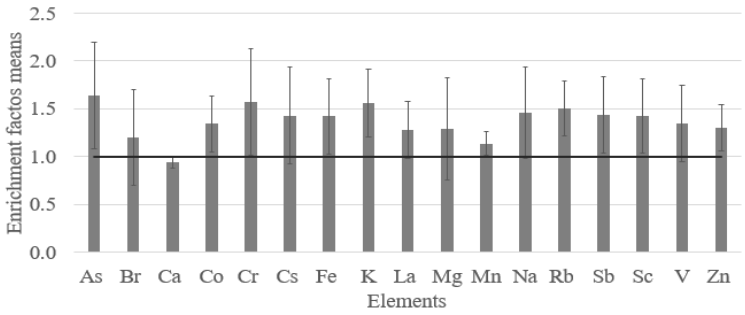

Figure 1: Means of enrichment factors for chemical elements determined in *Tipuana tipu* barks.

4. Conclusions

From the results obtained, it can be concluded that NAA method used is suitable for determining several elements of interest from an environmental point of view in tree bark samples. The bark of the *T. tipu* tree was also very suitable for the accumulation of aerial particulate matter due to its high porosity. In addition, these tree barks after exposure were intact, indicating the possibility of exposure for more than two months. Preliminary results obtained indicated the viability of using *T. tipu* barks in active biomonitoring of air pollutants. The exposed bark samples presented higher element mass fractions than control samples. Enrichment factors indicated that there was accumulation of several elements with the exception of Ca.

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