



Comparative study between the bromeliad *Tillandsia usneoides* and the *Tipuana tipu* tree barks for use in active biomonitoring of atmospheric pollution

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1. Introduction

Biomonitoring is a Nature-Based Solution (NbS) for assessing and monitoring environmental contamination, utilizing natural resources effectively and providing benefits for both human well-being and biodiversity [1, 2]. This technique employs living organisms to obtain quantitative information about biosphere characteristics, including concentrations of pollutants accumulated by species [3, 4]. Several organisms have been utilized in biomonitoring studies such as lichenized fungi, mosses, plant leaves, and tree barks [5, 6, 7].

The selection of a biomonitor should consider its ability to accumulate pollutants and its adaptability to the study region [3]. Comparative studies among biomonitoring species have been conducted to assist in selecting the most suitable candidates [8, 9, 10].

Besides, there are two main kinds of biomonitoring: active and passive. Active biomonitoring involves the transplantation of selected species to the study site for subsequently analyzed. Conversely, passive biomonitoring entails the collection of organisms already inhabiting the site to determine pollutant levels [4].

Tillandsia usneoides, a bromeliad species, is frequently employed in active biomonitoring of air pollution. However, its suitability hinges on its adaptation to environmental conditions of the study site [6, 11].

Tree bark serves as a valuable medium in biomonitoring studies, offering insights into air and soil pollution levels while being readily accessible. The application of tree bark in active biomonitoring is still limited. However, it can be argued that the efficacy of tree bark can be enhanced in this type of biomonitoring, as it remains unaffected by soil pollutants absorbed by tree roots. Concerns regarding bark acclimatization in study areas are alleviated by the absence of metabolic processes in the outer layer of the bark, which effectively retains atmospheric pollutants. [7, 12].

The aim of this study was to compare the *Tillandsia usneoides* bromeliad and *Tipuana Tipu* tree barks for application in the active biomonitoring, due to their frequent analyses in air pollution biomonitoring studies in the State of São Paulo, Brazil.

2. Methodology

T. usneoides bromeliad sample was acquired from Boiatche Bromeliary, in Brasília, DF, Brazil. Control sample of this species was taken from various parts of the bromeliad tuft to obtain a representative sample and it was stored in a paper envelope for subsequent treatment and analysis. Samples for exposure were prepared similarly to this control sample, with approximately 10 g of bromeliad placed in plastic mesh packaging.

Tree bark samples were obtained from branches of *Tipuana* trees in the Campus of the University of São Paulo. These branches were sawn to obtain cylindrical specimens with diameter of 8 cm and height of 10 cm. Each of this specimen was used to obtain a control sample and an exposed sample. The outer faces of each specimen were divided into four parts. Control sample was obtained 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.

Both *T. usneoides* and *T. tipu* barks samples were exposed at the same locations approximately 2 m above the ground, suspended by nylon threads in tree branches. The samples were exposed in points of different levels of pollution in the São Paulo city and after two-month exposure period, the samples were collected and stored in paper envelopes for subsequent treatment and analysis.

For preparation of the *T. usneoides* samples were cut into fragments smaller than 0.5 cm using titanium-coated scissors, placed in clean polypropylene pots, and kept refrigerated. These samples were lyophilized. The lyophilized samples were then ground using a planetary ball mill (Retsch, PM200). In the case of bark tree the sample was cleaned using a nylon dental brush to remove the surface dust. Approximately 3 mm of the bark's external surface was removed with a titanium grater, followed by grinding of the sample in an agate-type ball mill (Fritsch, Pulverisette 0).

For Neutron Activation Analysis (NAA), synthetic element standards prepared using standard solutions and about 150 mg of each tree bark or *T. usneoides* sample were irradiated at the IEA-R1 nuclear research reactor. Short irradiations of 20 s under a thermal flux of about $1.9 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ were carried out for the determination of Cl, Mg, Mn, Na and V. Long irradiations of 16 h under a thermal neutron flux of about $4.5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ 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. Radioisotopes in the gamma-ray spectra were identified based on their half-lives and gamma-ray energies. The mass fractions of elements were calculated by comparative method [13]. Certified reference materials were analyzed using the same procedure for quality control, and results with good precision and accuracy were obtained.

Enrichment factors were calculated to assess the element retention capacities by the biomonitors. The enrichment factor (EF_x) is defined as the ratio between the element mass fraction obtained after exposure and this element mass fraction obtained before exposure (result of control sample). Samples with EF_x values exceeding 1.0 were considered enriched by element [10].

3. Results and Discussion

Table 1 presents the arithmetic mean and median values of the Enrichment Factors (EFs) calculated for *T. usneoides* and *Tipuana tipu* barks for nine exposure points for the determined elements. The results indicate that there was accumulation for most elements in both biomonitor species with the exception of K and Mg for *T. usneoides* and Ca for *T. tipu* barks.

Table 1. Arithmetic mean and median values of element enrichment factors for *T. usneoides* bromeliad and *T. tipu* barks.

Elements	<i>T. usneoides</i>		<i>T. tipu</i> barks	
	EF \pm SD (n = 9)	Median	EF \pm SD (n = 9)	Median
As	2.27 \pm 0.44	2.35	1.64 \pm 0.56	1.49
Br	2.36 \pm 0.85	2.24	1.26 \pm 0.47	1.19
Ca	1.24 \pm 0.24	1.28	0.94 \pm 0.06	0.96
Cl	3.51 \pm 1.64	2.77	2.87 \pm 1.75	2.54
Co	2.62 \pm 0.45	2.87	1.34 \pm 0.29	1.40
Cr	4.74 \pm 1.53	4.36	1.57 \pm 0.56	1.57
Cs	1.40 \pm 0.26	1.39	1.43 \pm 0.50	1.21
Fe	3.10 \pm 0.84	3.08	1.42 \pm 0.40	1.43
K	0.91 \pm 0.09	0.95	1.56 \pm 0.35	1.55
La	3.17 \pm 0.81	3.11	1.28 \pm 0.29	1.30
Mg	0.98 \pm 0.10	0.99	1.29 \pm 0.53	1.16
Mn	1.35 \pm 0.28	1.37	1.14 \pm 0.12	1.14
Na	5.98 \pm 2.38	6.37	1.46 \pm 0.48	1.44
Rb	1.18 \pm 0.37	1.24	1.50 \pm 0.29	1.45
Sb	3.16 \pm 1.86	2.48	1.43 \pm 0.40	1.42
Sc	3.85 \pm 0.80	3.87	1.42 \pm 0.39	1.43
V	3.81 \pm 0.51	4.02	1.34 \pm 0.40	1.35
Zn	2.25 \pm 0.67	2.10	1.30 \pm 0.24	1.29

EF \pm SD (n) = Mean and standard deviation of the enrichment factor for samples analyzed from n exposure points

The highest arithmetic mean and median of EF values obtained for most elements in *T. usneoides* indicate its greater capacity to accumulate elements, particularly trace elements as Cr, Sc, V, La, and Sb, which can be sourced from atmospheric pollution related to vehicle emissions or soil suspension.

The difference in the enrichment factors values can be attributed to variations in the element accumulation characteristics between the two biomonitor species. *T. usneoides* absorbs elements directly, primarily through moisture or dew water uptake. In contrast, tree bark adsorbs and retains elements, potentially leading to leaching, i.e., the release of retained elements due to rainfall.

4. Conclusions

The results obtained in this study indicated that the same elements can be quantified in both biomonitor species by using neutron activation analysis. The enrichment factor values demonstrated that there is element accumulation in both species of *T. usneoides* and *T. tipu* barks. The variation in mean enrichment factor values between these two species suggests distinct mechanisms of pollutant retention. These findings indicated possibility of selecting suitable species for an active atmospheric pollution biomonitoring.

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