The use of an epiphyte (*Tillandsia usneoides* L.) as bioindicator of heavy metal pollution in São Paulo, Brazil

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Abstract

In the present work, *Tillandsia usneoides* L., an epiphytic bromeliad, was used as bioindicator of atmospheric metal pollution in São Paulo, Brazil, the biggest city in South America. *Tillandsia* samples were collected from an unpolluted area and were exposed bimonthly at ten sites of the city with different pollution levels and at a control site. Seven trace metals (Ni, Co, Cu, Cd, Pb, V, and Sb) were analysed in the plants by inductively coupled plasma mass spectrometry (ICP-MS) thereafter. The results indicated that Co, Ni, Cd, and V can be attributed to industrial sources while Cu can be associated to both vehicular and industrial sources. Sb is suggested to be influenced mainly by vehicular sources. For Pb, no evident sources could be identified so far as it was spread evenly along the monitoring sites.

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Introduction

Biomonitoring of air pollution with plants has been a common practice for many decades. In general, bioindicators can be defined as organisms that can be used for the identification and qualitative determination of human-generated environmental factors, while biomonitors are organisms mainly used for the quantitative determination of contaminants. Bioindicators can be classified as being sensitive or accumulative. Bioaccumulation is the result of the equilibrium process of biota compound intake/discharge from and into the surrounding environment [1].

Spanish moss (*Tillandsia usneoides* L.) and many other species of this genus have been used recently as bioaccumulators, indicators, and monitors of airborne elements [2–4]. Air quality studies have shown that geographic variations in mineral concentrations in plants of *T. usneoides* L. were often correlated with the proximity to aerosol sources, e.g., the ocean, roads, mines, power plants, soils, and urban centres [5].

The city of São Paulo is one of the biggest cities in the world. The metropolitan region of São Paulo (MRSP) has a population of about 18 million people, with about 8000 km^2, with severe environmental problems due to the atmospheric emissions of about 2000 highly pollutant industries and emissions from about 7.8 million motor vehicles [6]. Serious environmental and health problems have specially been observed in the region due to particulate matter (PM_{10}) with varied composition [7].

In previous studies [8,9], samples of *T. usneoides*, taken from an unpolluted area, were exposed for 8 weeks at different sites of the city of São Paulo, in order to evaluate the potentiality of this species as a bioindicator of atmospheric metal pollution in São Paulo. Instrumental neutron activation analysis (INAA) was used to analyse trace elements in the plants. This analytical technique allowed the determination of 21 elements, such as As, Ba, Cr, and Zn, and notable correlations of Zn and Ba to vehicular sources and of Cr to industrial emissions sources could be identified. However, in spite of the multi-elemental analysis characteristics of INAA, this analytical technique is not suitable for the determination of Pb, Ni, and Cd, which are also relevant elements in pollution studies. Thus, in the present study, seven trace metals (Co, Ni, Cu, Cd, Pb, V, and Sb) were analysed in the *T. usneoides* samples by inductively coupled plasma mass spectrometry (ICP-MS), providing a more complete description of the atmospheric metal pollution in São Paulo.

Sampling and exposure sites

T. usneoides samples were sampled at a small farm with natural vegetation, located in the city of Mogi das Cruzes, about 70 km to the north-east of São Paulo city. The area has low industrialization and traffic influence and consequently low impact of PM_{10} and metal pollution. All samples were collected in the same area in order to guarantee same origin conditions during the experiments.

In this study, ten monitoring sites next to automatic monitoring stations operated by the government agency of air quality control (CETESB) were chosen in MRSP to transplant the samples of *T. usneoides* (Fig. 1). Seven sites were situated in the city of São Paulo and three in the extended city (Santo André, São Caetano, and Mauá), having different levels of PM_{10} and metal pollution. Four exposure sites were located in the downtown area, representing a car shift region, where 20% of the total number of vehicles are not allowed to run one day of the week, by the number of the license plate (PI, DP, CC, and IB; Fig. 1). The transplantation of plants was also performed at Mogi das Cruzes, which served as the control site. Each exposed sample was composed of 5 g of plants, tied by Teflon strings to a gyrator apparatus (six samples per apparatus, 1.5 m above the soil), which turned

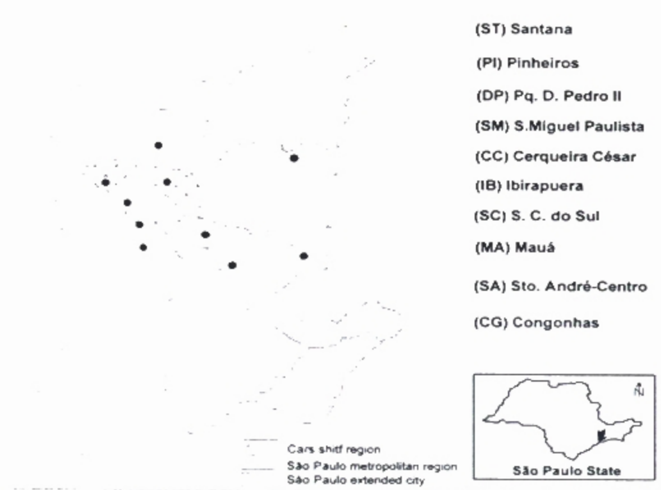


Fig. 1. Exposure sites of *Tillandsia usneoides* plants in the metropolitan region of São Paulo. Car shift region: area where 20% of the total number of vehicles are not allowed to run one day of the week by the number of the license plate

with the wind so that homogenous contact with air contaminants was guaranteed. The samples were submitted to exposure for 8 weeks and, after exposure time, were substituted by new samples allowing to performing eight transplantation experiments (A = April–May/2002; B = June–July/2002; C = November/2002–January/2003; D = February–April/2003; E = April–May/2003; F = June–July/2003; G = September–October/2003; H = November/2003–January/2004).

Experimental

T. usneoides samples were freeze-dried without washing and homogenized using an agate vibratory micro-mill. At the IHI Zittau laboratories, the *Tillandsia* samples were digested by microwave-assisted dissolution using nitric acid and hydrogen peroxide (MLS microwave oven; PTFE reaction vessels). The measurements were done by ICP-MS, using a Perkin–Elmer–Elan DRC. To evaluate the accuracy of the data, three biological reference materials were analysed: peach leaves (NIST SRM 1547), tea (GBW 08505), and white cabbage (BCR 679). The results obtained presented accuracy better than 15% in relation to the certified and recommended values.

Results and discussion

Figures 2A–G show the enrichment of the element concentrations in *T. usneoides* exposed at the monitoring sites in relation to the concentrations measured in plants from the control site during the different monitoring periods. This relation, in percentage, was calculated by:

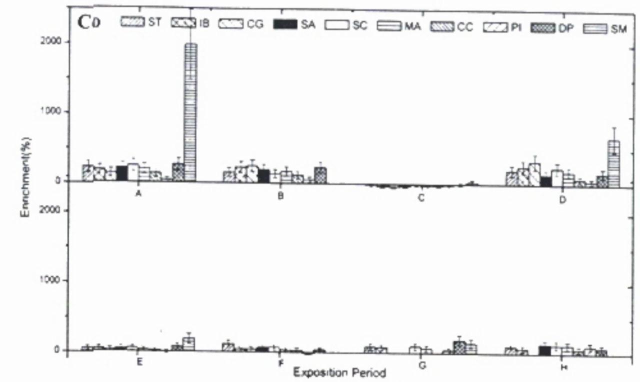
$$RC_E = (CE_A - CE_C / CE_C) \times 100 \quad (1)$$

where:

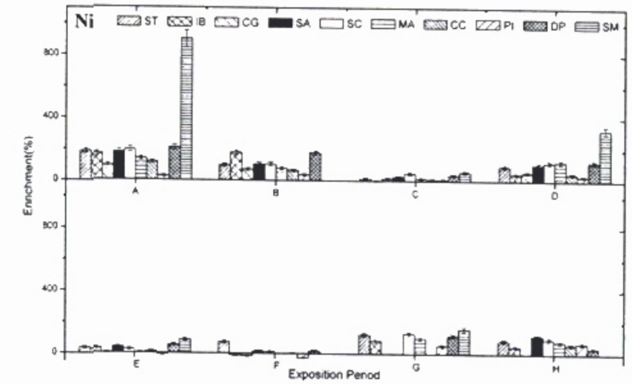
RC_E = Enrichment (%) of the concentration of the element E
CE_A = Concentration of the element E in the sample
CE_C = Concentration of the element E in the control sample

For Co and Ni, there was a significant enrichment in São Miguel Paulista (SM), compared to the other sites (Figs. 2A and B). In this area, there is a metal processing plant, which produces about 16,000 t $year^{-1}$ of Ni and 600 t $year^{-1}$ of Co, which may indicate that Co and Ni contents of *T. usneoides* are related to emissions from the mentioned metal plant.

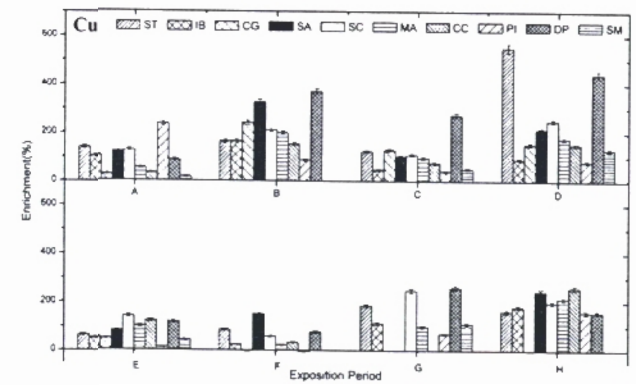
(A)



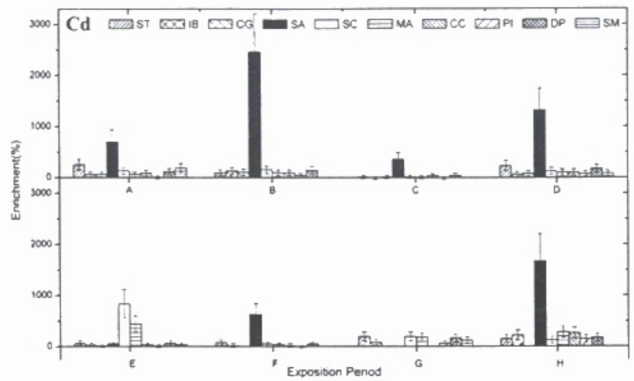
(B)



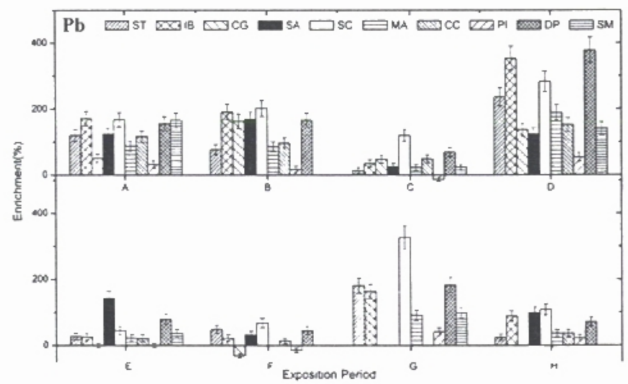
(C)



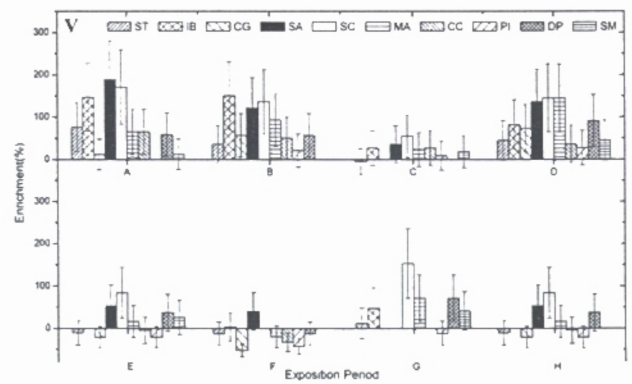
(D)



(E)



(F)



(G)

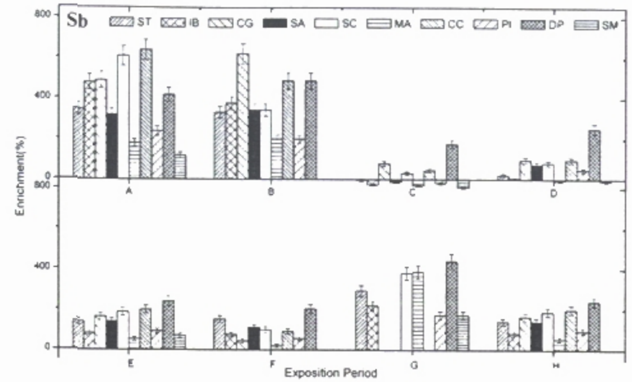


Fig. 2. Enrichment of the elements (%) in *T. usneoides* in relation to the exposure sites and exposure periods. (A) Co; (B) Ni; (C) Cu; (D) Cd; (E) Pb; (F) V; (G) Sb. Exposure period: A = Apr–May/2002; B = June–July/2002; C = Nov/2002–Jan/2003; D = Feb–Apr/2003; E = Apr–May/2003. F = June–July/2003; G = Sept–Oct/2003; H = Nov/2003–Jan/2004. Stations: ST = Santana; IB = Ibirapuera; CG = Congonhas; SA = Santo André; SC = São Caetano; MA = Mauá; CC = Cerqueira César; PI = Pinheiros; DP = Parque D. Pedro; SM = São Miguel

For a better understanding of the behaviour of the other elements analysed, a cluster analysis was applied by using Statistica software and the dendrogram obtained from the data analysis is presented in Figure 3.

The dendrogram shows that V and Cd are in one group. Vanadium is considered a toxic element and is associated with industrialized areas [10].

This element has increased during recent years in urban environments due to industrial dusts. In this study, in fact, high levels of vanadium were observed in Santo André (SA), São Caetano (SC), and Mauá (MA), which are highly industrialized (Fig. 2F). The highest enrichments of Cd were also observed in the same sites (Fig. 2D), and may be associated with the industrial emissions.

T. usneoides showed high concentration of copper in Parque D. Pedro (DP), downtown, near big avenues with high volume of traffic, and in SA (Fig. 2C), with high density of metallurgic industries, indicating industrial and vehicular sources probably caused by the abrasion of car brakes.

Antimony was highly concentrated in plants exposed in DP, and is suggested to be mainly associated with vehicular sources.

Pb (Fig. 2E) is still widespread in spite of lead-free gasoline in Brazil being available since 1983. However, fuel containing lead continues to be

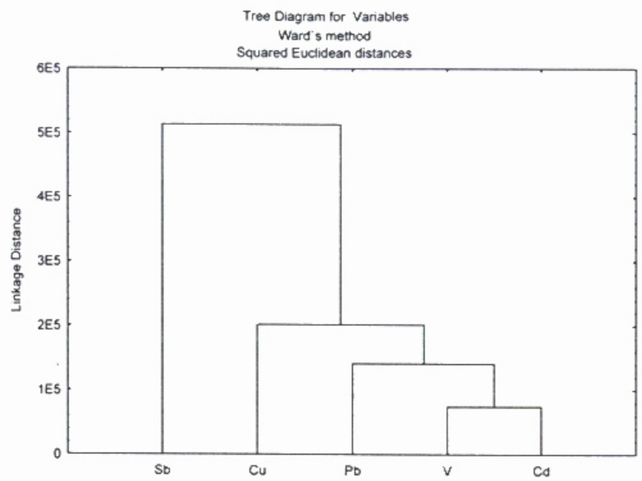


Fig. 3. Dendrogram obtained from the data of Pb, Cd, Cu, V, and Sb

used in aircraft and helicopters (São Paulo has intense helicopter traffic), which may explain this behaviour.

Conclusions

Traffic-related elements such as Cu and Sb presented high concentrations in exposure sites near heavy traffic avenues (cars, buses, and trucks) and may be associated to vehicular sources. For Cd, V, Co, and Ni, the highest contents were related to industrial zones and can be associated to the presence of anthropogenic emission sources.

Acknowledgements

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