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The use of *Tillandsia usneoides* L. as bioindicator of air pollution in São Paulo, Brazil

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Epiphytic bromeliad *Tillandsia usneoides* was used as a biomonitor of metal atmospheric pollution in the city of São Paulo, Brazil. The samples were collected from an unpolluted area and were exposed for 8 weeks in 10 sites of the city and in a control site. The data obtained showed that the control site presented lower concentration for most elements analyzed and the highest concentrations of Na, Cl, Br, K. The highest concentrations of Zn, Cu and V were observed in stations submitted to industrial and vehicular sources. The results obtained for rare earth elements, Al, Fe, Mg, Mn, Rb and Sc indicate mineral dust origin. The elements Ba, As and Sb presented higher values in stations near streets with heavy traffic.

Introduction

Epiphytic plants are efficient air pollution biomonitors, because they have no contact with soil, taking out nutrients from the atmosphere. Their tissue content largely reflects atmospheric contamination. In general, they are excellent accumulator biomonitors.

Tillandsia usneoides L. is an aerial epiphytic bromeliad that lives on trees or other kinds of inert subtracts, absorbing water and nutrients directly from the environment. Due to its morphological and physiological characteristics this species accumulates the pollutants present in the atmosphere. This species is well adapted to dry and hot regions, and has been used as a bioindicator in tropical areas. Because of its characteristics, some authors, including ARNDT and SCHWEIZER[1] and MARKERT et al.[2] have suggested the universal use of *T. usneoides* as a metal accumulator.

In Brazil, *Tillandsia usneoides* was demonstrated to be a suitable biomonitor for atmospheric mercury contamination, in a chlor-alkali plant.[3] More recently, AMADO FILHO et al.[4] confirmed the Hg accumulation by *Tillandsia usneoides*, exposing this species to a Hg-air-contaminated area during 15 days. A concentration of 2702±318 $\mu g \cdot g^{-1}$ was determined in exposed plants. By using scanning electron microscopy (SEM), these authors observed that Hg was highly absorbed by the scales, steam and leaves surfaces and less absorbed by epidermal cells of *T. usneoides*. According to these authors, the characteristics of *T. usneoides* morphology confer great capability of holding Hg.

In a previous study,[5] the potential usefulness of this species as an active accumulator biomonitor of metal atmospheric pollution was observed. In the present work, *T. usneoides* collected from an unpolluted site was exposed in ten different sites of São Paulo city (Brazil) and in a control site. After this period, samples were analyzed by neutron activation analysis.

Experimental

Exposure sites

There are serious air pollution problems in São Paulo city, which represents an important industrialized and economic center of Brazil, having a population of around 18 million people. According to Köppen system, its climate is Cwa type, characterized by hot and wet summer (mean hottest month temperature higher than 22 °C), dry winter (mean coldest month temperature below 18 °C) and mean annual rainfall around 1300 mm.[6] The city is subjected to frequent thermal inversions. According to the Environmental Protection Agency of the State of São Paulo (CETESB), the government air quality control agency, daily emissions from about 5.5 million motor vehicles are the main sources of air pollution in the city. The quantity of suspended matter released into the atmosphere of the extended city, which consists of the city of São Paulo and the cities that surround it, is estimated in 64,100 tons.[7]

The government air quality control agency CETESB operates in São Paulo an automatic network with 23 monitoring stations. In this study, ten exposure sites were chosen to transplant the samples of *Tillandsia usneoides*, being seven in the city of São Paulo and three in the extended city (Santo André, São Caetano e Mauá), having different levels of pollution. These sites were chosen because of information about other air quality parameters provided by CETESB about these areas. The unpolluted area chosen to collect the *Tillandsia usneoides* was a small farm in Mogi das Cruzes, located about 70 km from São Paulo, with a low industry and traffic influence, making it adequate for transplantation experiments. The control site was a vegetation house with filtered air and controlled temperature and humidity at the Botanic Institute of São Paulo.

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Transplantation

Active biomonitoring, which consists of transferring plants collected from unpolluted sites to the area to be monitored, was employed. This methodological approach is adopted because, in polluted or urban sites, the vegetation is frequently absent. Each sample for exposure was composed of 5 g of plants, tied by teflon strings to a gyrator apparatus (6 samples per apparatus), which turned with the wind so that homogenous contact with air contaminants was guaranteed. The samples of *Tillandsia usneoides* were submitted to exposure for 8 weeks and, after the exposure time, the samples were separately frozen without washing and stored at –20 °C until analyses.

The *T. usneoides* plants in the polluted and control sites remained green during the monitoring period, even showing some growth. Regarding it, the species is well suited to active monitoring studies in urban environments, such as São Paulo city.

Analytical procedure

Samples were dried at 40 °C in a ventilated oven until reaching constant weight and were grinded in a blender with Ti knifes. After this procedure, the samples were ground and homogenized manually in agate mortars. Two hundred mg of the samples were accurately weighed in polyethylene envelopes, previously cleaned with diluted nitric acid solution.

Standards of the elements of interest were prepared by mixing appropriate aliquots of solutions of these elements made from spectroscopically pure reagents or from SPEX standard solutions. Aliquots of these solutions were pipetted onto 1 cm^2 pieces of Whatman No. 40 filter paper, evaporated to dryness under an infrared lamp, and sealed in polyethylene envelopes, similar to those used in the preparation of the samples. About 200 mg of the biological standard reference material Orchard Leaves (NIST SRM 1571) and of the geological reference material Soil-7 (IAEA) were weighed and prepared similarly to the sample.

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For the determination of Al, Ti, V, Cl, Mg and Mn, samples and standards were irradiated for 5 minutes at a thermal neutron flux of $4\cdot10^{11}$ $n\cdot cm^{-2}\cdot s^{-1}$, at the IEA-R1m nuclear reactor of Instituto de Pesquisas Energéticas e Nucleares. For the other analyzed elements (As, Ba, Br, Co, Cr, Fe, K, Mo, Na, Rb, Sb, Sc, Th, Zn, and the rare earths La, Ce, Nd, Sm ,Eu, Tb and Yb), samples and standards were irradiated for 16 hours at a thermal neutron flux of $1\cdot10^{13}$ $n\cdot cm^{-2}\cdot s^{-1}$. The measurements of the induced gamma-ray activity were carried out using a GMX20190 hyperpure Ge detector. The multichannel analyzer was a 8192 channel Canberra S-100 plug-in-card in a PC computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of ^{60}Co. For the 5 minute irradiation, decay and counting times were each 3 minutes. Two series of measurements were performed after the 16 hour irradiation; the first was done from 5th–7th days after irradiation and the second one after 15–20 days of decay. Counting times ranged from 3 to 10 hours. The gamma-ray spectra were processed by using an in-house gamma-ray software VISPECT,[8] which locates peak position and calculates the energies and net areas.

Results and discussion

The homogeneity of the samples was previously verified,[5] by analyzing separately two aliquots of the same sample of *Tillandsia usneoides.* The reproducibility was better than 10% for the elements Mg, Mn, Na, V, Cl and Al. The accuracy and precision of the method was previously observed by analyzing biological reference material Orchard Leaves NIST SRM 1571.[5] The method showed accuracy and precision better than 15% for most elements.

In Table 1, the results obtained for trace element concentrations in samples of *Tillandsia usneoides* in the sites studied are presented. Station 01 is the control site, a vegetation house with filtered air and controlled temperature and humidity at the Botanic Institute of São Paulo, Station 02 (Santana) is located in the northern part of the city, in a military area, far from industrial and vehicular sources. Station 03 (Ibirapuera) is inside a park in the southern region of the city. Station 04 (Congonhas), station 08 (Cerqueira César), station 09 (Pinheiros), in the western part of the city, and station 10 (Parque D. Pedro II), downtown, are highly polluted sites in São Paulo city, situated in avenues exposed to air pollutants released by heavy traffic of passenger cars, buses and trucks. Station 05 (Sto. André), 06 (São Caetano), 07 (Mauá) and 11 (São Miguel) are industrial cities around São Paulo. The results are the mean of the analyses of the samples exposed in the same device, and the errors represent one standard deviation. The data obtained showed that the control site presented lower concentration for most elements analyzed and the highest concentrations of Na, Cl, Br, K. The highest concentrations of Zn, Cu and V were observed in stations 05 and 10 (Fig. 1). These metals are used in lubricating oils and the high values observed may be associated to industrial and vehicular sources in these sites, as far as the region of Santo André has about 200 steel companies and, according to CETESB, station 10 presented acceptable levels of NO_2, in 2000, in only 46.9% of days (in 152 days).[7] The emission of NO_2 is mainly related to automotive vehicles emissions. On the other hand, Co showed a spot of concentration in station

11 (São Miguel), which might be associated to a metal industry located at about 5 km from the monitoring site (Fig. 1). This fact will be further verified in temporal and seasonal monitoring. The results obtained for rare earth elements, Al, Fe, Mg, Mn, Rb and Sc indicate mineral dust origin. The elements Ba, As and Sb presented higher values than those found in control site in stations 04, 08 and 10 (Fig. 2), what may be attributed to diesel engines (vehicular sources) once these stations present high levels of SO_2 and NO_2.[7]

There is few information about atmospheric metal pollution in the city of São Paulo, as far as CETESB gives only data of the gaseous emissions (SO_2, CO, O_3 and NO_2) and particulate matter. The use of *Tillandsia usneoides* in monitoring sites of CETESB may provide new and useful information about atmospheric pollution of elements such as As, Ba, Co, Cr, Cu, Sb, V and Zn in urban and industrial sites of São Paulo city and its correlation with other pollution parameters.

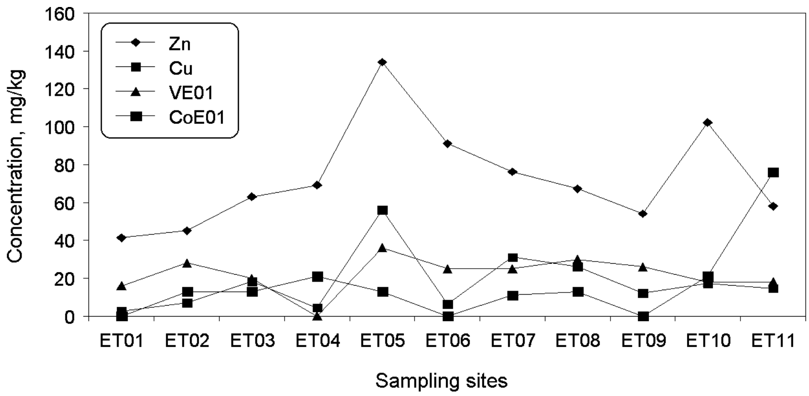

Fig. 1. Concentration of Zn, Cu, V and Co in the exposure sites

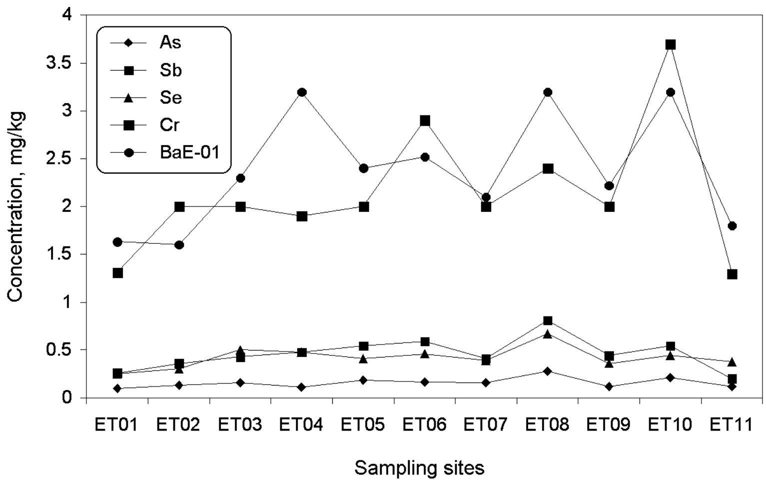

Fig. 2. Concentration of As, Sb, Se, Cr and Ba in the exposure sites

Table 1. Values of elemental concentrations (in $\mu g \cdot g^{-1}$) obtained in *Tillandsia usneoides* exposed for 8 weeks in different sites of São Paulo

Element	St01 (Control Site)	St02[a] (Santana)	St03[b] (Ibirapuera)	St04[c] (Congonhas)	St05[d] (Sto. André)	St06[d] (S. Caetano)	St07[d] (Mauá)	St08[c] (Cerq. César)	St09[c] (Pinheiros)	St10[c] (Pq.D. Pedro)	St11[d] (S. Miguel)
Al	900 ± 11	1135 ± 14	1118 ± 12	1160 ± 15	1326 ± 14	1103 ± 14	981 ± 13	1403 ± 19	1232 ± 13	706 ± 8	955 ± 14
As	0.10 ± 0.05	0.13 ± 0.01	0.16 ± 0.01	0.11 ± 0.01	0.18 ± 0.01	0.16 ± 0.01	0.16 ± 0.01	0.28 ± 0.02	0.12 ± 0.04	0.21 ± 0.01	0.12 ± 0.01
Ba	16 ± 1	16 ± 2	23 ± 1	32 ± 2	24 ± 2	25 ± 1	21 ± 2	32 ± 2	22 ± 1	32 ± 2	18 ± 1
Br	10.1 ± 0.1	6.8 ± 0.1	8.9 ± 0.1	7.7 ± 0.1	8.8 ± 0.1	8.8 ± 0.1	9.5 ± 0.1	10.2 ± 0.1	10.4 ± 0.1	7.5 ± 0.1	7.2 ± 0.1
Ca	3303 ± 40	2241 ± 47	3548 ± 75	3808 ± 70	3783 ± 90	3612 ± 41	3738 ± 69	3589 ± 85	3111 ± 50	3724 ± 75	4332 ± 76
Ce	1.4 ± 0.1	1.4 ± 0.1	1.9 ± 0.2	1.5 ± 0.1	2.1 ± 0.2	1.4 ± 0.1	1.8 ± 0.2	2.5 ± 0.3	2.0 ± 0.1	1.35 ± 0.11	1.37 ± 0.12
Cl	1484 ± 68	1130 ± 52	1179 ± 61	958 ± 42	1309 ± 53	1104 ± 45	1679 ± 71	1068 ± 46	1102 ± 51	1576 ± 65	1307 ± 57
Co	0.61 ± 0.03	1.3 ± 0.1	1.3 ± 0.1	2.1 ± 0.2	1.3 ± 0.1	1.1 ± 0.1	1.1 ± 0.1	1.3 ± 0.1	0.75 ± 0.03	2.1 ± 0.2	7.6 ± 0.9
Cr	1.3 ± 0.1	2.0 ± 0.1	2.0 ± 0.1	1.9 ± 0.1	2.0 ± 0.1	2.9 ± 0.1	2.0 ± 0.1	2.1 ± 0.1	2.0 ± 0.1	3.7 ± 0.2	1.3 ± 0.1
Cu	2.7 ± 0.3	7.1 ± 0.9	18.2 ± 0.5	4.3 ± 0.5	56 ± 7	6.4 ± 0.7	31 ± 6	26 ± 7	12 ± 4	17 ± 4	15 ± 3
Eu, $ng \cdot g^{-1}$	16 ± 1	19 ± 1	21 ± 1	20 ± 1	23 ± 2	24 ± 6	23 ± 1	28 ± 1	25 ± 6	0.019 ± 0.001	0.015± 0.001
Fe	650 ± 12	820 ± 30	979 ± 42	782 ± 28	1073 ± 46	1058 ± 19	1025 ± 43	1189 ± 50	925 ± 17	804 ± 29	683 ± 25
K	5850 ± 8	2646 ± 68	5007 ± 259	5631 ± 112	5722 ± 316	4366 ± 87	5572 ± 280	4084 ± 260	3767 ± 58	5209 ± 122	5567 ± 118
La	0.90 ± 0.04	0.89 ± 0.06	1.2 ± 0.1	0.92 ± 0.01	1.36 ± 0.01	1.44 ± 0.01	1.20 ± 0.01	1.51 ± 0.01	1.32 ± 0.07	0.86 ± 0.08	0.98 ± 0.08
Mg	2324 ± 103	1640 ± 72	1855 ± 148	2214 ± 89	1915 ± 173	1877 ± 88	2286 ± 166	2386 ± 193	1885 ± 194	1886 ± 75	2304 ± 176
Mn	244 ± 8	137 ± 5	171 ± 5	187 ± 6	142 ± 4	135 ± 5	233 ± 7	161 ± 5	153 ± 5	234 ± 8	187 ± 6
Na	421 ± 15	222 ± 34	326 ± 10	277 ± 14	355 ± 11	285 ± 13	380 ± 11	240 ± 7	295 ± 13	334 ± 42	226 ± 9
Nd	0.66 ± 0.04	0.54 ± 0.05	0.94 ± 0.08	0.79 ± 0.01	1.2 ± 0.1	0.85 ± 0.02	1.0 ± 0.1	1.1 ± 0.1	0.95 ± 0.06	0.68 ± 0.05	0.68 ± 0.0.8
Rb	37 ± 2	14 ± 1	29 ± 2	30 ± 1	31 ± 2	24 ± 1	36 ± 2	24 ± 1	21 ± 1	29 ± 1	24 ± 1
Sb	0.26 ± 0.02	0.36 ± 0.02	0.43 ± 0.05	0.48 ± 0.05	0.54 ± 0.06	0.59 ± 0.02	0.41 ± 0.04	0.81 ± 0.07	0.44 ± 0.02	0.54 ± 0.04	0.20 ± 0.02
Sc	0.13 ± 0.01	0.12 ± 0.01	0.17 ± 0.01	0.10 ± 0.01	0.17 ± 0.01	0.19 ± 0.01	0.14 ± 0.01	0.18 ± 0.01	0.18 ± 0.01	0.09 ± 0.01	0.11 ± 0.01
Se	0.25 ± 0.02	0.30 ± 0.03	0.50 ± 0.05	0.28 ± 0.02	0.53 ± 0.04	0.46 ± 0.01	0.39 ± 0.02	0.67 ± 0.02	0.36 ± 0.01	0.44 ± 0.04	0.38 ± 0.03
Sm, $ng \cdot g^{-1}$	83 ± 2	83 ± 2	110 ± 7	85 ± 4	126 ± 1	115 ± 3	101 ± 5	147 ± 9	127 ± 3	0.077 ± 0.005	0.084± 0.004
V	1.6 ± 0.1	2.8 ± 0.1	2.0 ± 0.1	2.87 ± 0.16	3.6 ± 0.1	2.5 ± 0.1	2.5 ± 0.2	3.0 ± 0.2	2.6 ± 0.1	1.8 ± 0.1	2.87 ± 0.16
Yb, $ng \cdot g^{-1}$	30 ± 2	23 ± 2	39 ± 3	20 ± 2	31 ± 3	38 ± 1	24 ± 2	32 ± 3	34 ± 2	13 ± 2	27 ± 2
Zn	41 ± 1	58 ± 1	63 ± 2	69 ± 2	134 ± 4	91 ± 1	76 ± 2	67 ± 2	54 ± 1	102 ± 3	58 ± 2

[a] Military area, far from industrial and vehicular sources.
[b] Inside a park in the southern region of the city.
[c] Highly polluted sites situated in avenues with heavy traffic of passenger cars, buses and trucks.
[d] Industrial cities around São Paulo.

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