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ASSESSMENT OF THE TRAFFIC-RELATED ELEMENTS BA, CR AND ZN DURING AND AFTER THE CONSTRUCTION OF A PERIPHERAL HIGHWAY USING TILLANDSIA USNEOIDES AS ATMOSPHERIC BIOMONITOR

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ABSTRACT

Tillandsia usneoides (L.) L. is an aerial epiphytic bromeliad that lives on trees or other kinds of inert substratum, absorbing water and nutrients directly from the environment. Due to this characteristic, this species also accumulates pollutants present in the atmosphere. In this study, *T. usneoides* was used as biomonitor aiming to verify if the construction of the western and southern parts of the peripheral highway Mario Covas (SP-21) in São Paulo city would alter the profile of atmospheric contamination by Ba, Cr and Zn in the region. These elements are often associated with traffic and can indicate contaminated urban areas. This knowledge is of great interest to the city, which has one of the biggest vehicle fleets in the world, with more than seven million circulating motor vehicles and serious environmental problems due to air pollution. Neutron Activation Analysis was employed as analytical technique. Samples of *T. usneoides* were irradiated at the IEA-R1 nuclear reactor at IPEN-CNEN/SP, and the induced activity was measured by high resolution gamma-ray spectrometry. Increasing concentrations of Ba, Cr and Zn were observed in the biomonitor after the inauguration of the highway, indicating that these elements originated from vehicular emissions.

1. INTRODUCTION

São Paulo city has one of the biggest vehicle fleets in the world, with more than seven million circulating motor vehicles in the city, which are the main source of air pollution. The peripheral highway Mario Covas (SP-21) was planned in order to remove cars and trucks that cross the expanded city center on their way to other cities and mainly to the southern sea coast of São Paulo State, where one of the most important Brazilian Ports (Santos) is settled. However, it was constructed in peripheral and less urbanized regions of São Paulo city, which were less affected by air pollutant impacts before its construction and opening for routine vehicular traffic. Although Zn, Ba and Cr are naturally occurring metals, they are often associated with anthropogenic activities and are then appropriate indicators of contaminated urban areas. Zn is emitted by exhaustion of petroleum refining plants, incinerators, extraction and manufacturing industrial processes, and other sources. Zn is also released by the

combustion of gasoline and dieselpowered vehicles, fluid leakage, tires, vehicle paint, and component detachment [1]. A study in the city of Stockholm had calculated a Zn emission of 17 t/year from street furniture, tires, and buildings [2,3].
Sources of Cr in urban areas are mainly the metallurgic and galvanic industries as it is employed as an alloy constituent to impart corrosion resistance. Dyes and paints can also contain Cr. Motor vehicle exhaust, waste incineration, and combustion of oil and coal are additional emission sources of Cr to the atmosphere [3].
The major sources of Ba compounds emitted into the atmosphere are the industrial processes involved in the mining, refining and production of barium and barium-based chemicals, as well as the use of barium compounds as a fuel additive for the reduction of smoke emissions from diesel engines [4].
The biomonitoring approach using *Tillandsia usneoides* was successfully applied previously in the metropolitan region of São Paulo [5]. These authors performed five transplant experiments in ten sites in São Paulo, exposing the biomonitor for 56 days/experiment (between April 2002 and May 2003). The results showed that Zn and Ba presented high concentrations in exposure sites near to heavy traffic avenues (cars, buses and trucks) and may be associated to vehicular sources.
In this study, *Tillandsia usneoides* was used as biomonitor of Zn, Ba and Cr atmospheric pollution during different phases of the construction until the inauguration of the southern part that was linked to the previously existing western part of the Rodoanel Mario Covas (SP-21) highway.

2. MATERIALS AND METHODS

2.1. Study Site and Monitoring Strategy

The western and southern parts of the peripheral highway Mario Covas (SP-21) were constructed in order to link important highways that reach the expanded center of São Paulo city and thus to reduce the number of cars and trucks that usually cross the city coming from those highways This ring road will be referred as SP-21 highway from now on.
The biomonitoring study was conducted in the following five sites located around both parts of SP-21highway, which are more or less affected by vehicle circulation:
- Control Site, 23º40’05,5’’S e 46º49’28,1’’W (PR): The control site was a non urbanized area near the southern part of SP-21 highway and covered by a remnant of forest, where *Tillandsia usneoides* (L.) L. was abundant on trees inside and at the border of the forest. *Tillandsia* samples were collected in this site for exposure experiments performed in the other studied sites and for reference concentration values.
- New road, 23º40’21’’S e 46º49’33’’W (PN): It is next to a local road dedicated only to vehicle traffic used during the construction of the southern part of SP-21 highway. *Tillandsia usneoides* was abundant in some trees found in this site. This road was deactivated when the highway was opened for routine traffic, and the site was separated from the road by a high wall, of about 50m from the highway.
In the other sites, *T. usneoides* was not present, and active biomonitoring was employed, by transplanting samples from the control site.
- “Old Road”, 23º37’55,1’’S e 46º49’48,9’’W (PV), located about 5m from the intersection between the new southern part to the previously existing western part of the SP-21 highway (this part of the road was opened to vehicular traffic in April/2010).

- Marginal Pinheiros Avenue (MP): This avenue follows along both margins of one of the two main rivers that cross the city. *Tillandsia* samples from the control site were transplanted to trees next to the asphalt (PP) and about 4m (PA) from the asphalt. These sites were chosen to assess the changes in metal concentration due to the supposed decrease of the truck traffic after the inauguration of the western and southern part of SP-21 highway.
The biomonitoring study was performed from 2009 to 2011, thus comprising the period during the construction and inauguration of the southern part SP-21 highway, which were linked to the western part previously opened. Table 1 shows the sampling schedule.

Table 1. Sampling schedule

	Date
T0	Jan/2009
T1 (1st sampling)	Apr/2009
T2 (2nd sampling)	Jun/2009
T3 (3rd sampling)	Nov/2009
T4 (4^{th} sampling)	Mar/2010
T5 (5^{th} sampling)	Aug/2010
T6 (6^{th} sampling)	Nov/2010
T7 (7^{th} sampling)	Feb/2011

2.2. Analytical Procedure

Samples were dried at 40^{o} C and then ground using an agate mill in order to obtain a fine and homogeneous powder. Aliquots of 200 mg of each sample of T. *usneoides* and of three biological reference materials (SRM 1547 Peach Leaves, SRM 1515 Apple Leaves and Mix Polished Herbs/INCT - MPH – 2) were accurately weighed in polyethylene envelopes, previously cleaned with diluted nitric acid solution.
Samples and standards were irradiated for 16 hours at a thermal neutron flux of about 10^{13} n cm^{-2} s^{-1} at the IEA-R1 nuclear reactor of IPEN. The measurements of the induced gamma-ray activity were carried out using a GX20190 hyperpure Ge detector. The multichannel analyzer was an 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. 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.
The accuracy and precision of the results were verified by the analysis of the reference Material NIST SRM 1515 Apple Leaves. Measurement bias and coefficients of variation were better than 10% (Table 1).

Table 1. Ba, Cr and Zn concentrations in NIST SRM 1515 Apple Leaves (mg kg^{-1}) (n=6)

Element	This work	NIST values	Bias (%)	Coefficient of Variation
Ba	54±4	49±2	10.2	7.4
Cr	290±25	(300)	3.3	8.6
Zn	13.2±0.9	12.5±0.3	5.6	6.8

3. Results and Discussion

The results obtained for Zn, Ba and Cr concentrations in T. *usneoides* in the studied period are presented in Tables 2 to 4 and in Figures 1 to 3, respectively.

Table 2. Zn concentration in *Tillandsia usneoides* (L.) L. in the studied period (mg kg^{-1})

Period	Control Site PR	Old Road PV	New Road PN	MP - PA	MP - PP
T0	75	---	71	---	---
T1	46.2	139	45	90	64
T2	58	116	56.2	113	88
T3	48.3	433	55.5	152	177
T4	65	413	81	184	126
T5	38.2	1109	84	138	124
T6	43.1	773	124	187	135
T7	46.3	663	89	175	162

(---) not determined

Table 3. Ba concentration in *Tillandsia usneoides* (L.) L. in the studied period (mg kg^{-1})

Period	Control Site PR	Old Road PV	New Road PN	MP - PA	MP - PP
T0	36	---	51	---	---
T1	22	59	35	33	29
T2	22	41	59	42	43
T3	23	102	60	79	84
T4	41	66	77	82	54
T5	25	158	45	81	94
T6	22	72	42	97	82
T7	24	137	36	81	98

(---) not determined

Table 4. Cr concentration in *Tillandsia usneoides* (L.) L. in the studied period (mg kg^{-1})

Period	Control Site PR	Old Road PV	New Road PN	MP - PA	MP - PP
T0	1.93	---	3.11	---	
T1	0.76	4.8	2.66	1.96	1.82
T2	1.34	3.1	3.14	2.62	3.09
T3	3.21	24	5.5	25.8	8.8
T4	11.8	14.7	5.5	31.6	15.4
T5	5.7	58	17.2	18.3	16.5
T6	6.8	38	11.9	14	35
T7	5.9	26	6.8	14.5	33

(---) not determined

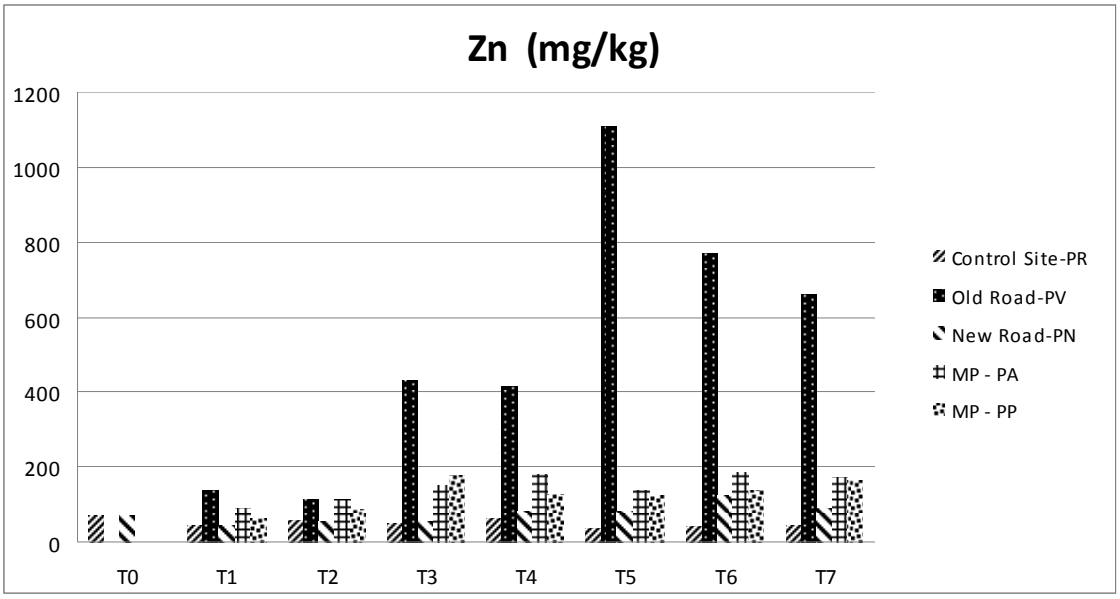

Figure 1: Zn concentration in *Tillandsia usneoides* (L.) L. in the studied period

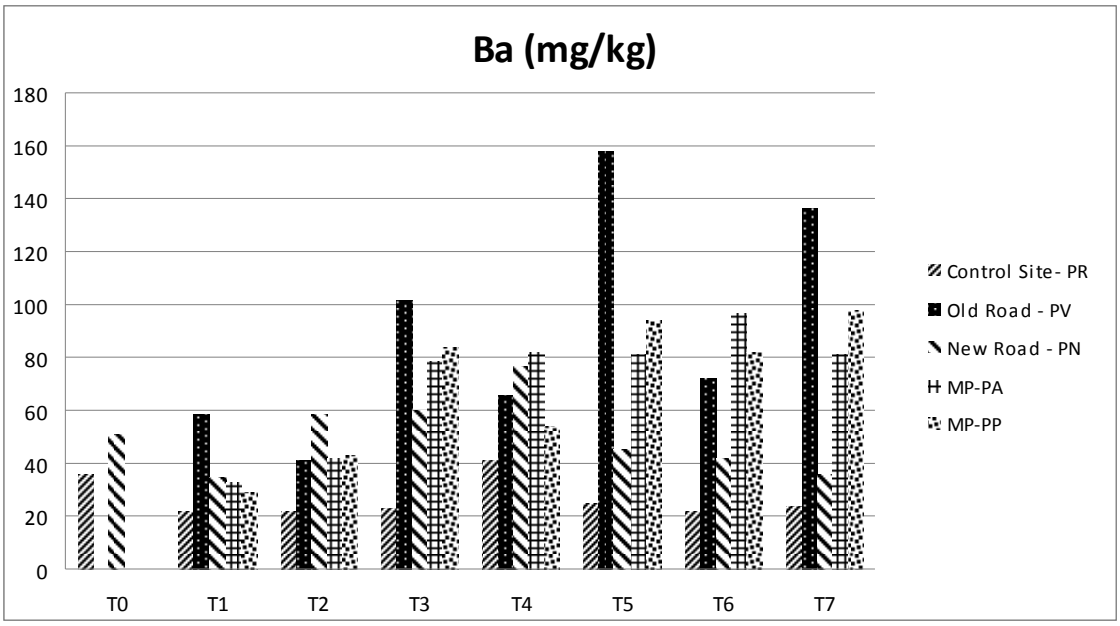

Figure 2: Ba concentration in *Tillandsia usneoides* (L.) L. in the studied period

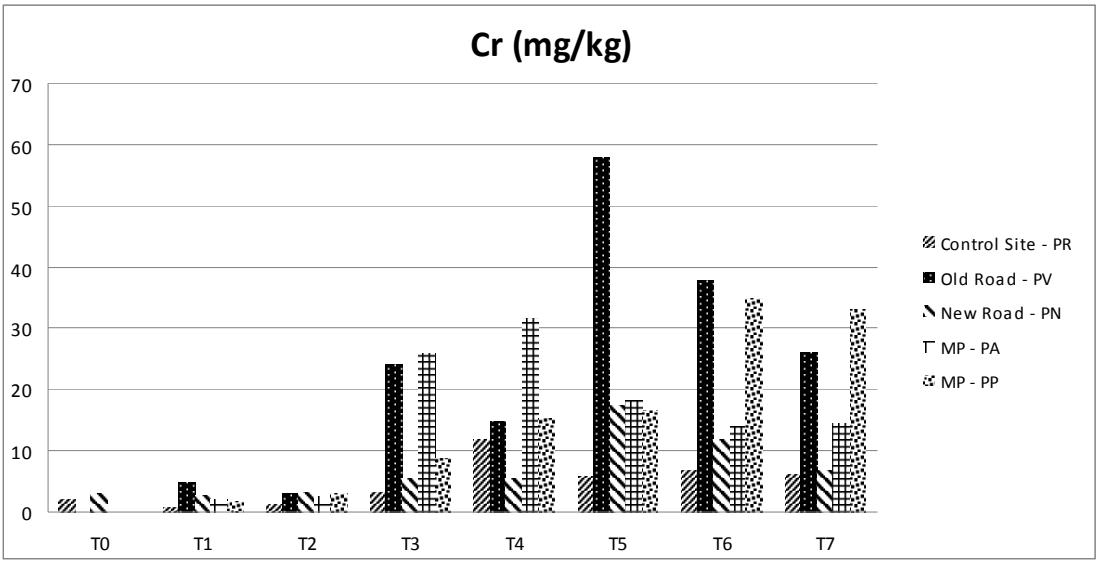

Figure 3: Cr concentration in *Tillandsia usneoides* (L.) L. in the studied period

It can be seen in Tables 2 to 4 and in Figs. 1 to 3 that the concentrations obtained for Zn, Ba, and Cr at the control site (PR) were lower than those obtained at the other studied sites and remained in similar levels during all the experimental period. This fact confirms the potentiality of *Tillandsia usnsoides* as bioaccumulator of these metals. The results show that higher concentrations were obtained in the sites with more vehicle circulation, which may indicate vehicular exhausts origin. It is also remarkable that barium, zinc and chromium presented similar behavior, with higher concentrations at the Old Road (PV) site from the 3rd sampling period on, reaching maximum values in the 5th sampling performed in August/2010,

when the intersection southern and western parts of the SP-21 highway was already opened to routine traffic (since April 2010). This site presents higher vehicle circulation in relation to the other sites. The highest concentration was observed in the period of March-August 2010. According to DERSA [6], the governmental department of traffic of São Paulo, in the first 30 days after the inauguration, 1.356.423 vehicles (70% of those were cars and 30% trucks) circulated in this road during the first 30 days after the inauguration. This fact corroborates the assumption that these elements were traffic related in the region.

On the other hand, an increase in the concentration of Ba, Cr and Zn at Marginal Pinheiros Avenue (PA and PP) was observed after the inauguration of the intersection southern and western parts of SP-21 highway (after T5), contrary to the expectations. A possible explanation for this fact is that the cars and trucks coming from that part of the SP-21 highway still crossed important avenues of São Paulo city, such as Marginal Pinheiros, even after the inauguration of the new part of the road. In addition, these results may also indicate that car exhausts are increasingly important sources of these metals to the urban atmosphere.

3. CONCLUSIONS

The bromeliad *Tillandsia usneoides* (L.) L. showed to be a good biomonitor to assess Ba, Cr and Zn atmospheric pollution. There is little information about atmospheric metal pollution in São Paulo, and biomonitoring can be a good alternative for conventional instrumentation due to advantages such as allowing the monitoring of large areas and low cost.

Neutron Activation Analysis demonstrated to be an efficient technique for Ba, Cr and Zn determination in plant samples, showing, one more time, the applicability of this nuclear analytical technique in environmental studies.

The results obtained showed an increase in Ba, Cr and Zn concentrations in the *Tillandsia* samples after the inauguration of the extension of SP-21 highway (April 2010), indicating that they are originated from vehicular emissions.

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