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EVALUATION OF GROWTH TREE RINGS OF TIPUANA TIPU AS BIOMONITORING OF ENVIRONMENTAL POLLUTION BY SYNCHROTRON RADIATION TOTAL REFLECTION X-RAY FLUORESCENCE

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ABSTRACT

Nowadays many studies use the bioindicators, plants or animals capable to present qualitative and/or quantitative answers, when exposed to pollutant substances. Trees record and incorporate in their log, developed year after year, the impressions of the environment, becoming possible the study of the different environmental changes, including contamination, that have occurred over the life of these trees. The selected species, Tipuana tipu, of the Leguminosae family, is native of Argentina and Bolivia and was introduced in Brazil as an ornamental plant. It is one of the most common trees in the urban landscaping in Sao Paulo city. The present project has as main objective the determination of the content of potentially toxic elements in samples of growth the tree rings of Tipuana tipu, previously dated, collected in strategically locations of São Paulo, using Synchrotron Radiation Total Reflection X-Ray Fluorescence. Samples were also collected in the Piracicaba (SP), local of little access and small flow traffic. The SR-TXRF analysis was carried out in the X-ray Fluorescence Beamline at the Brazilian Synchrotron Light Source Laboratory, located in Campinas city, São Paulo State, Brazil. Some trace elements present concentrations higher than considered as normal in some periods. In this paper the highest value for Pb was 123.54 $\mu g.g^{-1}$ considered as threshold value was observed for the period 1998 to 2000 for University of São Paulo, Butantã site. For the same period excessive level was also observed for samples collected in Piracicaba city. In São Paulo city, sample collected in the campus of University of São Paulo (Butantã), showed the highest toxicity, with concentration above the tolerable limit for Ti, Cr and Cu. For the samples collected in Piracicaba city the concentrations of Cr, Ni, Cu, and Pb exceeding the toxicity limits.

1. INTRODUCTION

Nowadays, many studies use the bioindicators, plants or animals which are able to present qualitative and/or quantitative responses when exposed to pollutants (Wyttenbach et. al.,1990).

The difference between bioindicadores and biomonitores occurs due the type of answers that they can supply. While the bioindicadores supply information on the quality of the environment or its modifications, the answers of the biomonitores make possible to quantify such modifications (Mota-Filho, 2007).

The trees record and incorporate in their wood developed year after year, the impressions of the abiotic environment, making possible the study of different environmental changes, including pollution, occurring during their lives.

The possibility of dating the growth rings of wood trees, combined with the application of the registered information on their structure for environmental and historical studies initiated the science called dendrochronology (Tomazello Filho, et. al., 2001).

The species selected for this study was the *Tipuana tipu (*Brazolin, et. al., 2010). The goal of this work was the determination of potentially toxic elements in samples of tree rings growth of *Tipuana tipu* species, previously dated, collected in the regions of Lapa, Pompéia, Sumaré, Butantã in the city of São Paulo and in the campus of University of São Paulo, Piracicaba city, using Synchrotron Radiation Total Reflection X-Ray Fluorescence (SR-TXRF).

2. INSTRUMENTAL

2.1. Characterization of the sampling

Samples used in this study were collected in São Paulo's urban area and Piracicaba at University of São Paulo Campus (ESALQ/USP). Sampling included five sites in São Paulo, where the trees were used as ornamental plant, and one site in University of São Paulo, Piracicaba Campus (ESALQ).

In the city of São Paulo, Lapa, Butantã, Sumaré and Pompéia were regions chosen, due to the intense and old urbanization, with old trees, and could be resulted in the history of the pollution by metals. Sampling points of the Agriculture School "Luiz de Queiroz" (ESALQ) were selected for comparing, as this area is urbanized but far from vehicular traffic.

Table 1 presented the addresses of the trees sampled, the cut date or fall, and the cutting procedure, i.e., the way which was removed from its place of origin.

Table 1: Characterization of the sampling of *Tipuana* trees in São Paulo and Piracicaba cities

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Address/region	Cutting Date	Cutting Procedure
Rua Valença, 169, Sumaré	22/09/2006	scheduled cutting
Av. Mercedes, 830, Lapa	09/02/2007	tree fall
Av. Pompéia, s/n, Pompéia	26/02/2007	tree fall
Campus do IPT, Butantã	03/08/2008	scheduled cutting
Campus da ESALQ, Piracicaba	25/09/2009	(*)

(*) Sampling performed by a non destructive method.

Some trees were falling due to rotting of roots and also to their large size and undue bias, while others were removed by the Municipal Prefecture of São Paulo, due to intense heartwood rot on their lap, rotting roots, large size, bad slope and risk of falling.

For the species located in the campus of Agriculture School "Luiz de Queiroz" (ESALQ/USP) removal of the rings was performed by non-destructive method, which consists in removing the wooden cylinders with the introduction of the Pressler probe with 5 mm in diameter in the trunk of the tree (Tomazello Filho, et al., 2001).

Characterization and dating of the growth rings for all samples were performed in the Laboratory of Anatomy, Identification and X-ray Densitometry in Wood, Department of Forest Sciences at the Agriculture School "Luiz de Queiroz" (ESALQ/USP), Piracicaba, SP. Growth rings were demarcated on the intervals of 3 years, due to the small thickness of each growth ring and for a reduction in the number of samples to be analyzed.

2.2. Sample Preparation

After dating the tree rings growth, they were submitted to an extraction procedure with concentrated nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) (Moreira et al., 2005). An analytical blank was prepared in order to eliminate possible contaminants in the reagents employed. All samples and standards were prepared in triplicate.

2.3. Measurements

The SR-TXRF analysis was carried out in the X-ray Fluorescence Beamline at the Brazilian Synchrotron Light Source Laboratory, located in Campinas city, São Paulo State, Brazil. The standards and wood samples were measured for 100 s employing a white beam (2 to 24 keV), 2 mm width and 1 mm height, operating under total reflection conditions. The X-ray detection was performed by a Si (Li) detector (FWHM: 165 eV at 5.9 keV).

For system calibration multielemental standard solutions, in different concentrations, containing Al, Si, K, Ca, Ti, Cr, Fe, Ni, Zn, Ga, Se, Sr and Mo for K series and Mo, Cd, Ba, Sb, Pt, Tl and Pb for L series were prepared by an adequate dilution of stock solutions. Gallium was added as internal standard in all standard solutions and samples (Moreira and Fazza, 2008).

3. RESULTS AND DISCUSSION

3.1. Calibration of the system

The fluorescent intensities were obtained from fitting the spectra with Quantitative X-Ray Analysis System (QXAS). Experimental relative sensitivities were calculated for K (Equation (1)) and L series (Eq. (2)).

$$S_R = \exp(-0.0233\ Z^2 + 1.4726\ Z - 23.2540) \qquad R^2 = 0.9967 \qquad (1)$$

$$S_R = \exp(-0.0056\ Z^2 + 0.8291\ Z - 31.9152) \qquad R^2 = 0.9992 \qquad (2)$$

3.2 Detection Limits

Table 2 shows the detection limits obtained for growth tree rings.

Table 2: Detection limits (μg.g^{-1}) for growth tree rings, determined by SR-TXRF.

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Element	Ti	Cr	Co	Ni	Cu	Pb
Detection Limit (μg.g^{-1})	0.018	0.009	0.004	0.005	0.005	0.043

3.3. SR-TXRF validation procedure

To validate the methodology a standard reference material Drinking Water Pollutants (DWP) was analyzed. This standard contains polluting elements in drinking water and, the measured and certified values, were showed in the Table 3.

Table 3: Comparison of measured and certified values for Drinking Water Pollutants standard reference material.

Element	**Measured Value (mg L^{-1})**	**Certified Value (mg L^{-1})**	**Error (%)**
Cr	10.54±0.28	10.00±0.50	5.4
As	9.93±0.14	10.00±0.50	0.7
Se	4.53±0.07	5.00±0.25	9.3
Cd	4.96±0.16	5.00±0.25	0.7
Ba	100.87±0.33	100.00±5.00	0.9
Pb	10.41±0.07	10.00±0.50	4.1

n=10 (ten lectures) α=0.05 (95% confidence level)

3.4. Quantitative Analysis of Wood Samples

In Figure 1 can be observed that the concentrations of chromium in the growth rings exceeded the toxicity threshold (10 μg g^{-1}) for all samples collected in the city of Piracicaba. Chromium levels were also high in growth rings for samples collected on the Campus of University of São Paulo, Butantã region, in the city of São Paulo. For the tree located on Mercedes Avenue (Lapa) just one growth ring showed concentrations above the threshold value for the period 1986 to 1988. For growth rings of Pompéia Avenue (Pompéia) and Valença Street (Sumaré) were not observed values that could compromise the species.

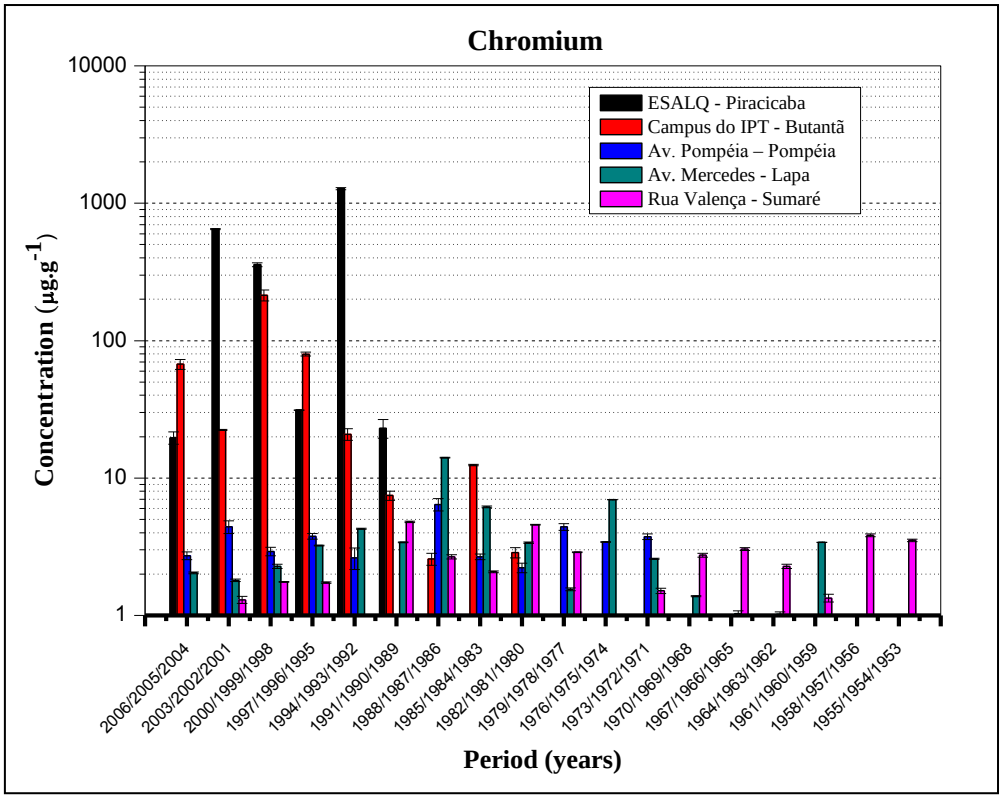

Figure 1: Concentrations of chromium in the growth tree rings of *Tipuana tipu*.

On the other hand, the behavior of nickel (Figure 2) and copper (Figure 3) was similar to the element chromium. The levels above the threshold of toxicity (30 µg g^{-1}) were observed for some samples collected in Piracicaba city and at University of São Paulo, Butantã. For samples collected in Pompéia, Lapa and Sumaré villages the contents of Ni and Cu were well below those observed for Piracicaba and for the University of São Paulo (Butantã) sites.

Growth tree rings of the *Copaifera langsdoffii* had been collected in the Horto Florestal of the city of Bauru, SP, place contaminated for dejections of a battery industry. The growth rings had been identified and detected and the period sample corresponds to 1966 up to 2004. Tree rings had been joined in three years. Using the SR-TXRF it was observed that the concentrations of Cr varied of 4 the 890 µg g^{-1}, whereas the contents of Cu varied of 21 the 815 µg g^{-1}. In relation to Ni the maximum value observed was 87 µg g^{-1} and for Pb the minimum value was of 3 µg g^{-1} and the maximum of 128 µg g^{-1} (Faria, 2007).

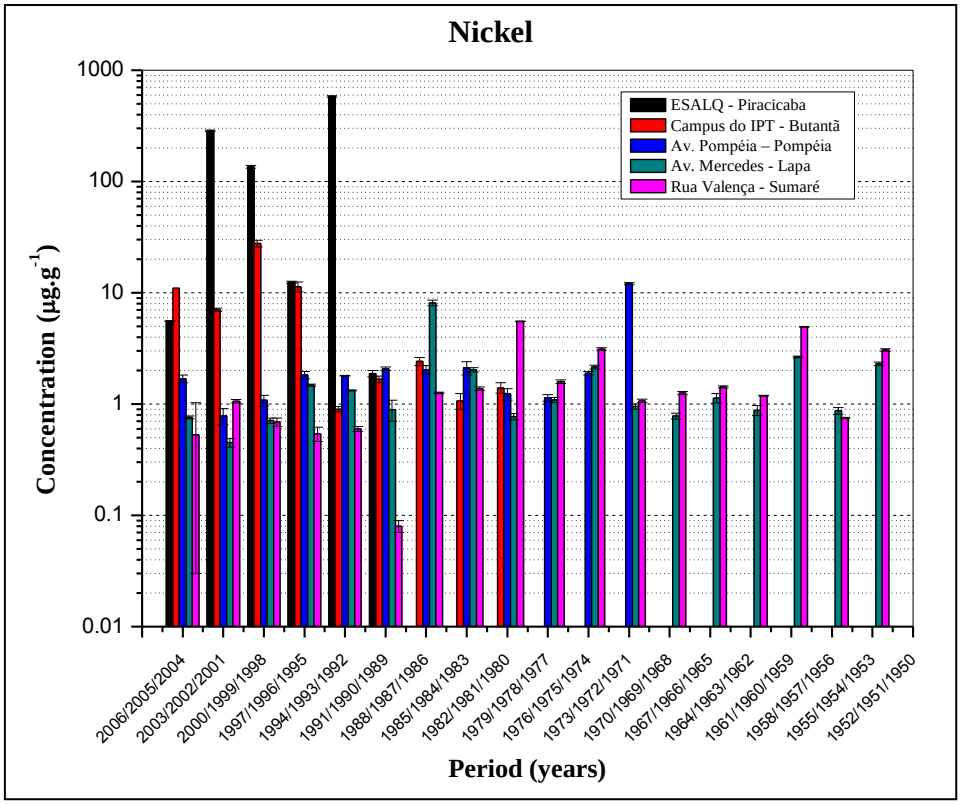

Figure 2: Concentrations of nickel in the growth tree rings of *Tipuana tipu*.

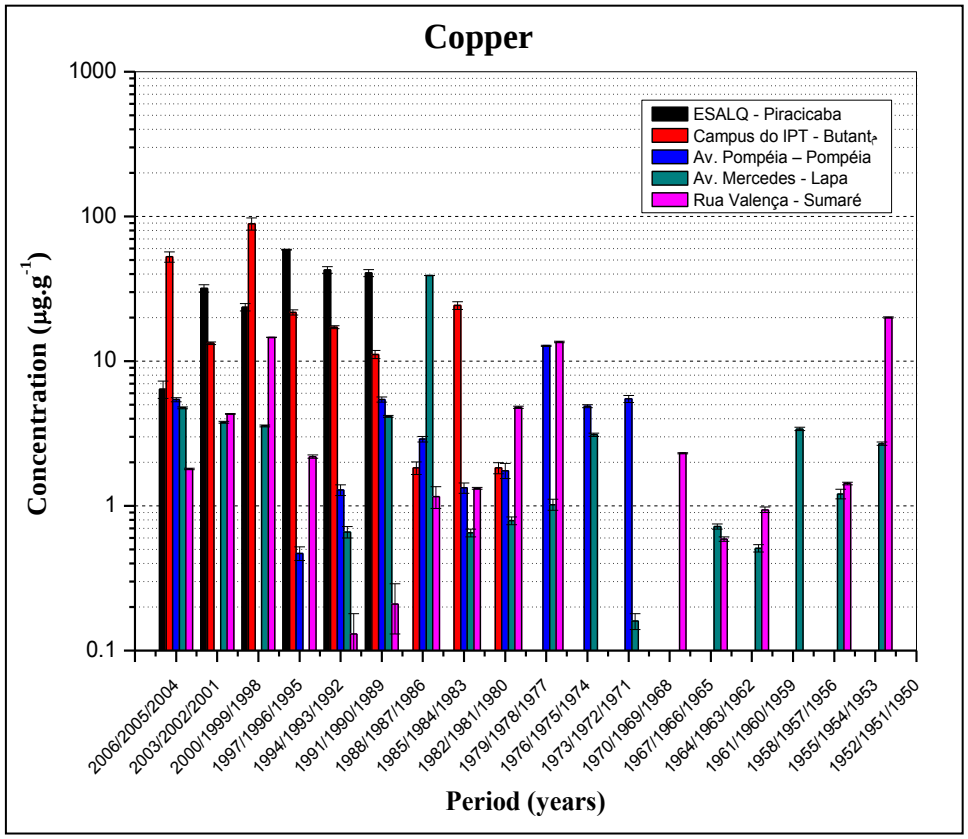

Figure 3: Concentrations of cooper in the growth tree rings of *Tipuana tipu*.

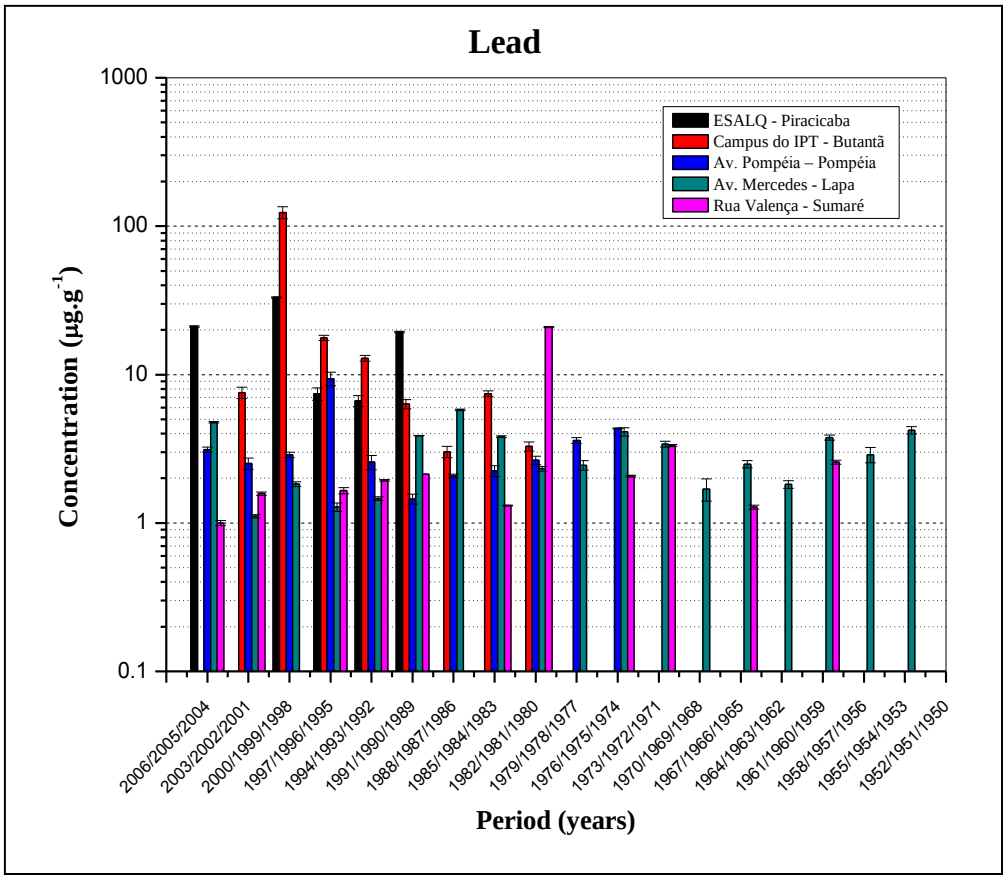

Figure 4: Concentrations of chromium in the growth tree rings of *Tipuana tipu.*

Levels higher than 30 µg g^{-1} of Pb are considered excessive or toxic and 43 µg g^{-1} is the threshold value indicating death of trees while 10 µg g^{-1} or less is the normal concentration in plants (Allen, 1989).

Vives et al., 2006, found in *Caesalpinia peltophoroides* growth tree rings Pb concentrations varying from 9.89 and 46.54 µg g^{-1}. The threshold value was observed between 1971 and 1973 and toxic levels occurred between 1974 and 1979.

In this paper the highest value for Pb was 123.54 µg g^{-1} considered as threshold value founded and it is observed for the period 1998 to 2000 for University of São Paulo, Butantã site. For the same period level considered excessive was also observed for Piracicaba city (Figure 4).

4. CONCLUSION

With the dating of the rings and the detection of the elements it was possible to carry out a study of the pollution of areas sampled, not only in the collection period, but throughout the life of the *Tipuana tipu* until the time of sample collection, showing the feasibility of the use of tree rings as bio-monitoring of the environments.

Among the analyzed trees, samples collected on ESALQ Campus, Piracicaba city and on the Campus of University of São Paulo, Butantã, showed the higher concentrations for most elements.

A difficulty founded in this study was the absence of national or international legislation that would establish limit values for the elements considered potentially toxic to plants.

An interesting alternative for future studies would be the soil analysis near the location sampled, as it would facilitate the understanding of the process of metal incorporation by the plants.

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