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PRELIMINARY STUDY OF QUARESMEIRA (*TIBOUCHINA GRANULOSA* (DESR.) CONG.) AS BIOMONITOR IN THE CITY OF SÃO PAULO

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Biomonitoring has recently received considerable attention by scientific community, becoming a powerful tool to assess pollution and evaluate of environmental quality. With the increasing of industrialization and human activities, many pollutants such trace elements have been released into the atmosphere through the introduction of harmful particles to the environment. The *quaresmeira* plant *Tibouchina granulosa* (Desr.) Cong. is native specie from the Atlantic rainforests of Brazil, occurring from Bahia to Santa Catarina State. This study presents the preliminary results concerning the use *T. granulosa* as biomonitor for a region São Paulo, SP. There is a concern about these elements due to the adverse effects which can cause on human populations and plants. This preliminary study aimed to analyze the concentrations of metals (Ce, Cr, Cu, Pb, Pt, V, Zn) in dry deposition on leaves of *T. granulosa* in the São Paulo city (summer of 2011) using HR-ICP-MS technique. According to the results it could be identified a pattern of distribution of Ce, Cr, Cu, Pb, Pt, V and Zn concentrations. This pattern varies with the time of exposure of the leaves (different internode). Further data will be included in this model in order to confirm that plants from the genus *Tibouchina* Aubl. can be used in passive biomonitoring in urban areas.

Key word: Biomonitor, quaresmeira, pollution.

1. INTRODUCTION

The industrial and urban development has caused worldwide an increasing emission air pollutant [1]. The increase in concentrations these substances, their deposition on soil, plant and material factors are responsible for damage to human health, reduced agricultural

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production, damage forests, deterioration buildings and works of art, in general, cause imbalances in ecosystems [1, 2].

In metropolitan areas the problem of degradation of air quality has constituted one of the most serious threats to the quality of life of its inhabitants. In the Metropolitan Region of São Paulo (MRSP), one of the largest urban areas in the world, the sources of contamination of atmospheric air are related to industrial processes and intense fleet of light and heavy vehicles. However, in recent years the burning of the vehicular fleet has been considered the main source of air pollutants [2, 3]. The RMSP showed a vehicular fleet in December 2010 of 6,954,750 vehicles in the capital and 21,554,110 vehicles in State [4].

Vehicles are also responsible for other forms of pollution as the excess particulate material in the atmosphere. The atmospheric concentration of particulate matter (PM) is an important indicator of environmental pollution regional assessment [5].

Physical and chemical compositions of MP depend on the location, time of year and length of stay in the atmosphere. MP is composed of coarse and fine particles, whereas large particles in suspension (PM_{10}) have an aerodynamic diameter between 2.5 and 10 μm your life is from minutes to hours, and its course varies from less than 1 km to 10 km [6].

Fine particles have an aerodynamic diameter less than 2.5 µm ($PM_{2.5}$). Differing from MP_{10} in origin and chemical property.

$PM_{2.5}$ are formed from gas and condensation of vapors during high temperature combustion, and are formed of various combinations of compounds of sulfate, nitrate, carbon, ammonia, hydrogen ion, organic compounds, metals (lead, cadmium, vanadium, nickel, copper, zinc, manganese and iron), water and particles bound [6]. Its permanency in the atmosphere takes long time (approximately two weeks). These particles can be transported over long distances and thus have an impact regional covering a large urban area [5].

The accumulation of pollutants in biomonitors can demonstrate specific or nonspecific effects in response to exposure to a particular element or compound, or a number of substances [7, 8].

The use of plant leaves as biomonitors is known and widely reported in the literature [9, 10]. However different species growing in the same habitat may display different levels of metals.

According Markert (1998), the leaves that have trichomes showed higher accumulation of metals than leaves without trichomes. And the use of trees in biomonitoring can provide the degree of environmental pollution; indicate the sources of emissions of pollutants and to evaluate for a long period the deposition of several elements. Besides sampling techniques do not interfere with the vitality of trees, only a small amount of leaves is removed, as consequence it is possible to repeat the sampling, the tree identification is not a problem with flowering [11].

This work is the first assessment to use tree *Tibouchina granulosa* (Desr.) Cong. (Melastomataceae) (known as *quaresmeira*) as biomonitor. Quaresmeira is native specie from the Atlantic rainforests of Brazil, occurring from Bahia to Santa Catarina State. The tree can

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grow up to 12 m tall and has great potential to be used as an ornamental plant. Its flowering occurs twice a year and the flowers have shades ranging from pink to purple so it is recommended for landscaping projects [12].

2. OBJETIVES

This preliminary study aimed to analyze the concentrations of metals (Ce, Cr, Cu, Pb, Pt, V, Zn) in dry deposition on leaves of *T. granulosa* in the São Paulo city, and analyzed by scanning electron microscopy the particulate matter.

3. MATERIALS AND METHODS

3.1. Study area and sample collection

The study area was located on Jabaquara Avenue (São Paulo-SP) with geographic coordinates 23°37'08.57" S and 46° 38'22.18" W. This area is characterized by high emissions of air pollutants. The tree had 4.5 m height. The branches, up to 0.25 m in length, were collected up to 3 m height facing the side of the avenue using a tree pruning knife. Each branch was five nodes. Each node presented two leaves. Five lives from the branch were used to quantify the PM by scanning electron microscopy technique. Others five were used to chemical analysis.

3.2. Protocol analysis

3.2.1. Scanning Electron Microscopy (SEM)

The PM analyses were carried out by Scanning Electron Microscope, SEM, (TM3000 TableTop, Hitachi) with 15kV acceleration capability, magnification range 15x to 30000x, resolution 30nm and with high-sensitive semiconductor Backscattered Electrons (BSE) detector.

The leaves were dried in an oven (FANEM 320F) for eight days. They were separated systematically in samples of the upper (A), median (M) and basal (B). For each leaf two samples were analyzed 1 x 1 cm/region, considering the adaxial (AD) and abaxial (AB). The samples were mounted on stubs with double sided carbon tape. The photomicrographs were capture at magnifications of 600x. The analysis of the images and particle characterization was performed automatically with the software ImageJ 1.44p with Java 1.6.0. [15].

3.2.2. Processing of dry deposition

Dry deposition was analyzed by using high resolution inductively coupled plasma mass spectrometer HR-ICP-MS (Element, Finnigan MAT). The selected area for the analysis was 1 mm² on each surface of the leaf. Particles were removed of the leaves with purified water Milli Q produced (Millipore, France) in an ultrasonic cleaning bath (Mod. Thorton T14, Inpec Eletronic) for 1 hour.

The remaining solution was lead to total dryness in a heating plate (Quimis). The residual material was leached in acid media HNO_3/HCl 1:3 v/v.

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The final solution was centrifuged (FANEM - Mod 206 BL) for 10 min. The supernatant was transferred to conical tube and diluted to 10 fold with Milli Q water.

The calibration curves were performed using solutions containing 50.0 ng mL^{-1} of each element (Ce, Cr, Cu, Pb, Pt, V and Zn) prepared from a CLMS-2 (Multi-element Solution 2) and CLMS-3 (Multi-element Solution 3) standard solutions (SPEX CertiPrep). A 10.0 ng mL^{-1} Indium solution was used to optimize the instrumental parameters and as internal standard. Analytical grade acids (Suprapur, Merck, Germany) and purified water Milli Q system were used for dilutions and digestions.

All dilutions were performed gravimetrically to avoid uncertainties introduced by the expansion of glassware with increasing temperature.

4. RESULTS AND DISCUSSION

Metals do not degrade naturally. Its accumulation in the environment can be toxic to human being living in the impacted areas. One pathway most known for their spread in the atmosphere is the PM.

The main results obtained in the study are presented in table 1. As it can be observed the older leaf (A) presented the high metal contents mainly for Ce, Pb, Pt, V and Zn. Cooper and Cr were presented in the same order of magnitude in all analyzed sample. It is known that the source of Cu on plants from roadside is due dust and abrasion of metallic gearing [14], brakes release Cu [16]. The automobiles cause about half of Zn contribution to the environment from urbanization [14]. It is known that the Cr pollution is caused by abrasion of Cr plated vehicle parts. Lead is released from the exhaust of the motorized vehicles to the atmosphere in a much higher quantity than other sources [14]. The Pt concentration found in the environment, next to major avenues, indicated catalytic converter origin [15].

ISBN: 978-85-99141-05-2

Table 1. Elemental concentrations in dry deposition in leave *T. granulosa* (Desr.) Cong. (Melastomatacea), in µg/g/m² (unless specified).

Element	A	B	C	D	E
Ce	18.2±0.2*	2.8±0.3*	3.9±0.3*	3.6±0.3*	1.8±0.2*
Cr	3.4±0.3	6.6±0.6	7.3±0.6	6.3±0.6	3.7±0.3
Cu	0.91±0.08	1.5±0.1	3.1±0.1	1.4±0.3	0.82±0.07
Pb	71±6	57±5	48±4	37±3	24±2
Pt	315.5±28.4**	21.8±1.9**	23.0±2.4**	12.2±1.1**	15.9±1.4**
V	4349±391	2495±224	1765±159	1614±145	1695±153
Zn	138±12	122±10	135±12	75±7	49±4

Legend: A-first branch second node; B-first branch third node; C-first branch third node; D-first branch fourth node; E-first branch five node; *mg/g/m²; ** ng/g/m².

Careful analysis of the SEM images revealed that PM was distributed abundantly on the adaxial and abaxial surfaces of the leaf blades of samples from the different node from branch second (Fig. 1). Figures 1A and 1D are the basal portion of the leave surface of sixth node (A); figures 1B and 1E are the apical portion of the leave surface of fourth node (B) and figures 1C and 1F are apical portion of the leave surface second internode (C).

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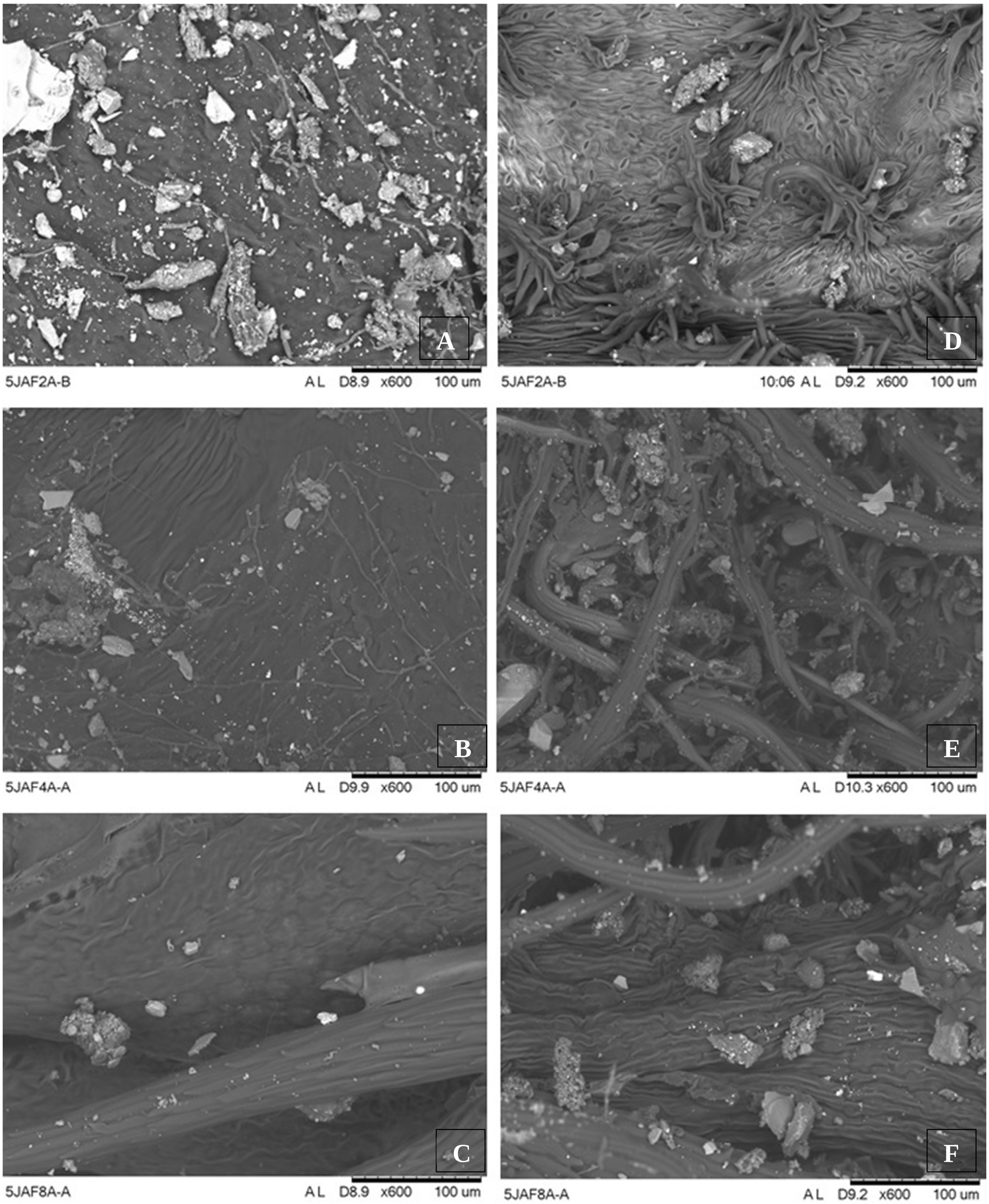

Figure 1. Scanning electron micrographs of leaves of *T. granulosa* (Ders.) Cong. (Melastomataceae) collected from São Paulo city showing particulate matter on the adaxial surface (A, B and C) and on the abaxial surface (D, E and F).

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Categorization of the identified particles is presented in the figures 2 to 4. As it can be observed the particles sites are ranging from less than 2.5 µm to higher than 100 µm. More than 90% the measured particles were below 10 µm, showing that the biomonitor can mostly retain the inhalable fraction of the PM. It is important to notice the high density PM 2.5, representing 80% of the total particles found in all analyze sample.

The morphological diversity of the PM found in leaves' surface suggests multiple and complex sources for the atmospheric particles. In addition, the presence of particles formed by agglomerates also indicates that small particles with relatively larger surface which can interact and form secondary particles [17].

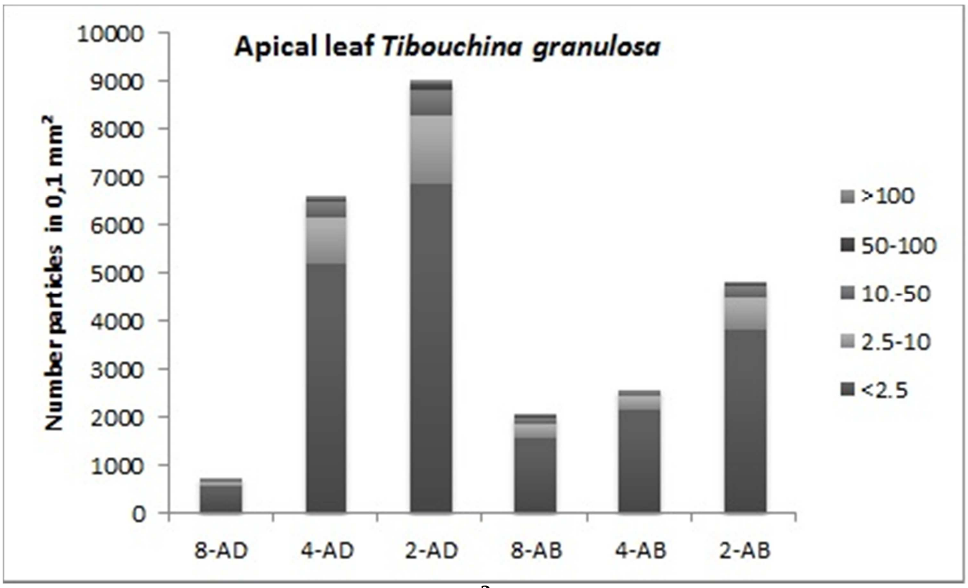

Figure 2. Total numbers of particles in 0.1 mm^2 on the adaxial and abxial surfaces of *T. granulosa* (Ders.) Cong. (Melastomataceae).

Legend: 2-leaves of the second branch first node; 4-leaves of the second branch second node; 8 leaf of the fourth branch; AD-adaxial surface; AB-abaxial surface.

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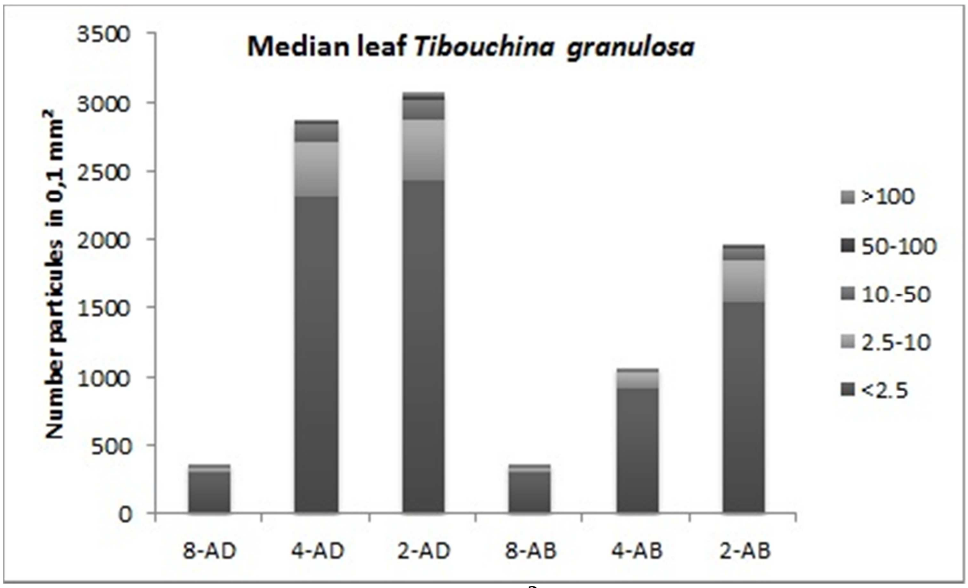

Figure 3. Total numbers of particles in 0.1 mm^2 on the adaxial and abxial surfaces of *T. granulosa* (Ders.) Cong. (Melastomataceae).

Legend: 2-leaves of the second branch first node; 4-leaves of the second branch second node; 8 leaf of the fourth branch; AD-adaxial surface; AB-abaxial surface.

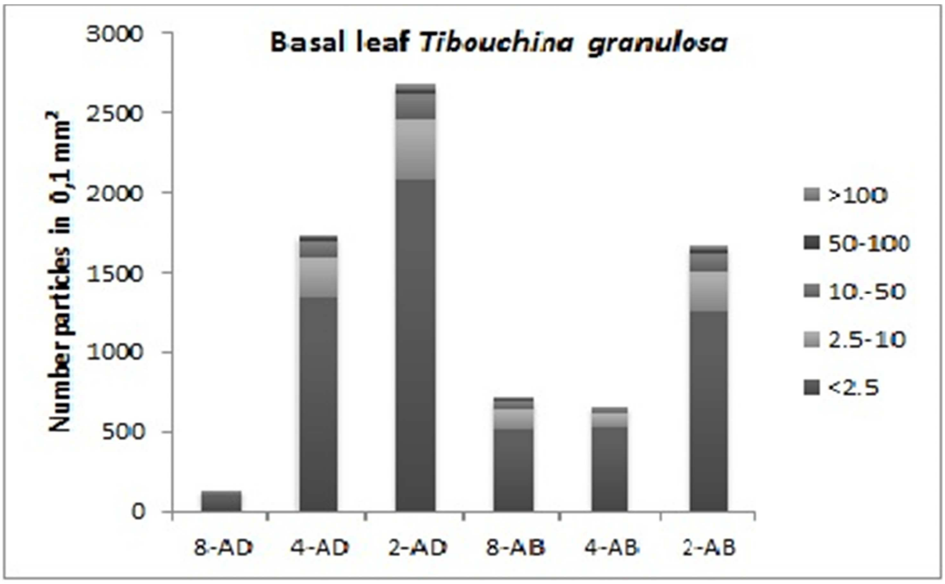

Figure 4. Total numbers of particles in 0.1 mm^2 on the adaxial and abxial surfaces of *T. granulosa* (Ders.) Cong. (Melastomataceae).

Legend: 2-leaves of the second branch first node; 4-leaves of the second branch second node; 8 leaf of the fourth branch; AD-adaxial surface; AB-abaxial surface.

ISBN: **978-85-99141-05-2**

5. CONCLUSIONS

The results obtained in this preliminary work indicated that the capacity of the *T. granulosa* to be used as biomonitor. This specie demonstrated to be able to retain metal particles and to present a pattern y distribution based on the selected nodes. More than 90% of the measured particles were in the range below 10 µm, showing that the leaves *T. granulosa* can mostly retain the inhalable fraction of PM. This study is one the first in the literature using ornamental tree (*T. granulosa* (Ders.) Cong. (Melastomataceae)) to qualify and quantify the elements present in dry deposition.

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