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Poincianella pluviosa as biomonitor of heavy metals in the municipality of Volta Redonda, RJ, Brazil

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ABSTRACT: The present study aimed to determine heavy metal concentrations in the tree bark of the species *Poincianella pluviosa* in Volta Redonda municipality, Rio de Janeiro. Four sets of barks of eight trees with three replicates each from sectors 1 (W), 2 (S), 3 (E), and 4 (N) of the Volta Redonda center corresponding to the cardinal points were collected. The samples were digested in a nitroperchloric mixture and the lead (Pb), cadmium (Cd), nickel (Ni), copper (Cu), zinc (Zn), iron (Fe), and manganese (Mn) contents were determined by atomic absorption spectrophotometry. The cluster analysis (CA) formed 12 groups; among them, group 3 (G3) showed the presence of all seven elements in sector 1 and group 8 (G8) showed the presence of Pb, Zn, Fe, Ni, and Mn in sector 2. Kruskal-Wallis and Bonferroni tests showed that all elements presented statistically different values among the four sectors when compared with each other ($p > 0.05$). Sectors 1, 2, and 3 had the highest concentrations of heavy metals, which are directly associated with vehicle and railroad flow and iron and steel activities that are concentrated in these sectors. Bark can be used as an effective method for the monitoring of air pollution in urban areas.

Key words: atmospheric pollution, urban ecology, sibipiruna

Poincianella pluviosa como biomonitora de metais pesados no município de Volta Redonda, RJ, Brasil

RESUMO: Objetivou-se com o presente estudo determinar a concentração de metais pesados em cascas de árvores da espécie *Poincianella pluviosa* no município Volta Redonda, Rio de Janeiro. Foram coletadas cascas de oito árvores, com três repetições de cada, nos setores 1 (W), 2 (S), 3 (E) e 4 (N) do centro de Volta Redonda correspondente aos pontos cardeais. A digestão das amostras foi realizada em mistura nitro-perclórica e a determinação dos teores de Pb, Cd, Ni, Cu, Zn, Fe e Mn por espectrofotometria de absorção atômica. A análise de agrupamento (AA) formou 12 grupos, entre eles o grupo 3 (G3) demonstrou a concentração dos sete elementos analisados no setor 1 e o grupo 8 (G8) agrupou os elementos Pb, Zn, Fe, Ni e Mn no setor 2. Os testes de Kruskal-Wallis e Bonferroni demonstraram que todos os elementos apresentaram valores estatisticamente diferentes entre os quatro setores comparados ($p > 0,05$). Os setores 1, 2 e 3 apresentaram as maiores concentrações de metais pesados, que estar diretamente associados ao fluxo de veículos, linha férrea e as atividades da siderurgia que se concentram nesses setores. O uso da casca de árvore pode ser utilizado com um método eficaz para o monitoramento da poluição atmosférica em áreas urbanas.

Palavras-chave: poluição atmosférica, ecologia urbana, sibipiruna

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Introduction

In Latin America alone, more than 35,000 people die every year due to air pollution-related problems (Gurgatz et al., 2016). Therefore, most countries that have advanced environmental legislation (for example, Brazil) are concerned with the regulation of atmospheric emissions (Zeri et al., 2011). Air monitoring networks are expensive to implement and operate, and in many cases do not represent a high priority for public investment, especially in developing countries (Yi et al., 2015). Gurgatz et al. (2016) still emphasize the need for ample sampling in time and space that can representatively increase its efficiency but also decrease its cost.

The use of environmental biomonitoring has the advantage of permanent field presence (even in remote areas), ease of sampling, and does not need costly technical equipment for data collection (Wolterbeek, 2002; Marć et al., 2015).

In addition to other services, trees can also act as passive biomonitors since they can be influenced by trace element components of heavy metals (Serbula et al., 2013; Santos et al., 2014; Dadea et al., 2017). In this study, the use of biomonitoring as a tool to identify the distribution of metals in the air has already been widely used (Lötschert & Köhm, 1978; Catinon et al., 2009; Guéguen et al., 2011; Moreira et al., 2016). According to Ukpebor et al. (2010), peels with higher roughness have a higher absorption surface in relation to fine peels, and the outer layer contains higher concentrations of heavy metals because they are more exposed to pollution. In addition to presenting rough bark, the species *Poincianella pluviosa* (DC.) L. P. Queiroz (sibipiruna), belonging to the Fabaceae family, is widely distributed in Brazil and is widely used in the afforestation of cities (Henrique et al., 2010). These favorable characteristics support their choice for biomonitoring studies.

Thus, the objective of this study was to determine heavy metal concentrations that accumulated in barks of the species *Poincianella pluviosa* (DC.) LP Queiroz (sibipiruna) followed by the identification of sites affected by vehicular and industrial pollution in the municipality of Volta Redonda, Rio de Janeiro.

Material and Methods

The municipality of Volta Redonda (22° 29' 00'' S; 44° 05' 00'' W) belongs to the Paraíba do Sul river basin, located south (S) of the state of Rio de Janeiro between the Serras do Mar and Mantiqueira.

The mean temperature of Volta Redonda is 21 °C with a minimum annual mean of 16.5 °C and maximum annual mean of 27.8 °C. The annual rainfall is 1,337 mm with an mean annual humidity of 77%. The predominant climate is mesothermal tropical with cold and dry winters and hot and rainy summers (Rocha & Souza, 2017).

Volta Redonda is the most populous municipality in the Middle Paraíba region, with more than 262,000 inhabitants (29% of the region's total) and a high population density (1,441 inhab km^{-2}). The municipality presents the fourth highest Human Development Index (HDI) of the state and the largest gross domestic product (GDP) in the region (R$ 10.4 billion). The service sector represents 45% of the gross value added (GVA) of the municipality followed by industry (39%), public administration (16%), and agriculture and livestock (2%) (SEBRAE, 2016; IBGE, 2017).

Volta Redonda has more than 140,000 vehicles consisting of different categories registered in the National Traffic Department (DENATRAN). This number represents 2% of the state's fleet. About 40% of the vehicles are fueled by gasoline, 15% gasoline + natural gas, 26% ethanol + gasoline, 8% ethanol + gasoline + natural gas, 5% ethanol, and 4% diesel (DENATRAN, 2017).

For biomonitoring studies, the authors adopted four distinct positions in the municipality that corresponded to the cardinal points: (1) Sector 1: west - W (Vila Santa Cecília, street 14); (2) Sector 2: south - S (Vila Santa Cecília, street 33); (3) Sector 3: east - E (Laranjal); and (4) Sector 4: north - N (Vila Mury).

Three replications of barks from eight individuals of *Poincianella pluviosa* (sibipiruna) species with a circumference of 0.40 to 0.55 m at 1.30 m of soil in each zone were collected. The outer shell layers (about 10 mm thick) were collected, stored in paper bags, and taken to the Soil and Water Laboratory of the Fluminense Federal University (UFF), Volta Redonda. All samples were dried in an oven with air circulation at 70 °C and ground up in a knife mill. Lead (Pb), cádmium (Cd), nickel (Ni), copper (Cu), zinc (Zn), iron (Fe), and manganese (Mn) were determined by flame atomic absorption spectrophotometry with air/acetylene (Tedesco et al., 1995).

The metals Pb, Cd, Ni, Cu, Zn, Fe and Mn were subjected to descriptive and exploratory analysis (mean, median, mode, variance, maximum and minimum values) followed by the construction of beanplot graphs, R version 3.4.2 (R Development Core Team, 2017). To test the hypothesis of residue normality and homogeneity of variance of the data, the parametric Shapiro-Wilk (SW) and non-parametric test of Fligner Killeen (FK) ($p > 0.05$) (Brower & Zar 1984) using the R software version 3.4.2 (R Development Core Team, 2017) was done.

For cluster analysis (CA), the concentration of each of the seven analysed heavy metals was considered as objects. Subsequently, the conversion of the primary data matrix into a square matrix was carried out in which the similarities between the metal concentrations in each study sector considered were measured using the co-behavioural correlation coefficient and the hierarchical grouping method unweighted pair-group method using arithmetic averages (UPGMA) (Moreira et al., 2016) via the Past program (Hammer et al., 2001).

Results and Discussion

The descriptive analysis of the heavy metals in the municipality of Volta Redonda showed that the lowest mean concentrations and standard deviations were recorded for Cd (0.12 ± 0.06 mg kg^{-1}), Ni (1.73 ± 1.67 mg kg^{-1}), Pb (2.05 ± 2.76 mg kg^{-1}), and Cu (7.08 ± 2.70 mg kg^{-1}). Fe (1373.65 ± 102.25 mg kg^{-1}), Mn (67.58 ± 83.96 mg kg^{-1}), and Zn (35.03 ± 28.19 mg kg^{-1}) presented the highest mean concentrations and standard deviations. All concentrations, however, were within ranges considered normal for plant material (Ross, 1994).

Similar studies of heavy metal biomonitoring using bark as a starting source are found in Brazil (Ferreira, 2009; Martins, 2009; Santos et al., 2014). However, the quality of scientific discussion on this subject is hampered by the scarcity of studies and the need to incorporate standardized methods into plant biomonitoring programs throughout the country. The use of one or more tree species for sampling is the main factor that differentiates the studies, and it is difficult to interpret whether the differences or similarities among heavy metals concentrations in the bark are related to the bioaccumulative capacity of the species or to atmospheric pollution levels.

The dendrogram (Figure 1) shows clustering of heavy metal concentrations in the different sectors of the municipality. The Fenon line, indicated in Figure 1, was drawn after considering 50% of the similarities in order to highlight the concentrations of metals in homogeneous groups. Based on the CA technique, there were 12 groups: (1) group 1 (G1); (2) group 2 (G2); (3) group 4 (G4); group 6 (G6); group 7 (G7); group 10 (G10); group 11 (G11); and group 12 (G12) with only one element each.

Group 3 (G3) contained all of the analysed metals from sector 1 in the center of Volta Redonda (W). Group 5 (G5) had two metals dispersed in the S and N sectors. Pb, Zn, Fe, Ni, and Mn concentrations were observed in the sector S of the center of Volta Redonda, and finally group 9 (G9) in the E sector of the municipality had concentrations of Pb, Ni Mn , Zn and Fe concentrations. The co-behavioral correlation coefficient was 0.89. The coefficient of correlation coefficient > 0.7 shows that the CA technique was adequate to summarize the information to the data set used in the study.

The data obtained did not present a normal distribution according to the SW and FK tests. Therefore, the Kruskal-Wallis (KW) and Bonferroni tests were used for multiple mean comparison and demonstrated that other than nickel (Ni), the other metals evaluated presented statistically different values among the four sectors compared in the study, considering the value $p > 0.05$ (Table 1 and Figure 2).

The analysis of the Figure 2 (beanplot) for all of the heavy metals in the municipality demonstrated a high variability of heavy metals in all sectors. With the exception of Ni, the concentrations of heavy metals showed a reduction in heavy metal concentrations in sectors 1 and 2 in relation to sectors 3 and 4, which presented either a symmetrical or asymmetric distribution of the metals.

The KW test showed that all heavy metals presented significant differences between 0.00078 and 0.0232, for a $p < 0.05$ value of probability. The results obtained from the Bonferroni test and the beanplot graphs (Table 1 and Figure 2)

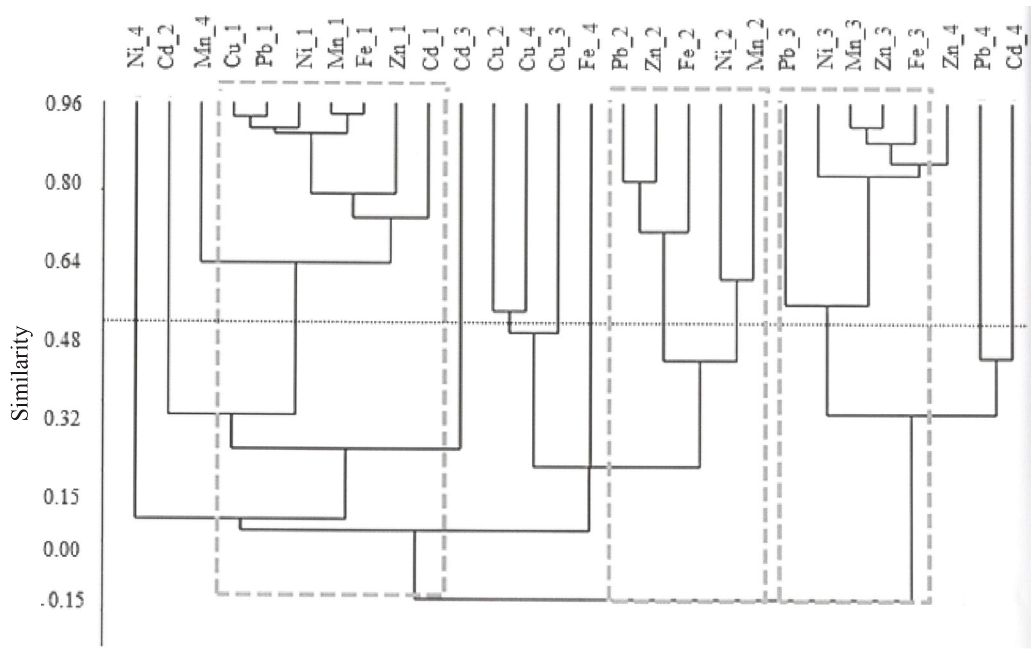

Figure 1. Dendrogram (Cluster Analysis) applied to the concentrations of the heavy metals (copper [Cu], lead [Pb], nickel [Ni], manganese [Mn], iron [Fe], zinc [Zn], and cadmium [Cd]) in mg kg^{-1} among the west (1), south (2), east (3) and north (4), based on the method of the unweighted pair-group method using arithmetic averages (UPGMA) connection

Table 1. Kruskal test and multiple comparisons of means of heavy metals (Pb, Cd, Cu, Ni, Mn, Fe and Zn) in the sectors (1, 2, 3 and 4) by the Bonferroni Test

Heavy metals	Heavy metals means (mg kg^{-1})				p value
	Sector 1	Sector 2	Sector 3	Sector 4	Kruskal Wallis
Pb					0.00660 *
Cd	0.106 b	0.098 b	0.116 ab	0.155 a	0.02320 *
Cu	8.274 a	7.280 ab	6.731 ab	6.030 a	0.01790 *
Ni	1.805 a	2.091 a	1.446 a	1.558 a	0.00078 *
Mn	89.802 a	81.743 a	59.681 ab	39.100 b	0.00040 *
Fe	2071.042 a	1740.878 ab	1053.854 bc	628.823 c	0.00010 *
Zn	54.983 a	32.953 ab	29.983 b	26.286 b	0.01920 *

Equal averages - a, b, c; Different averages - ab

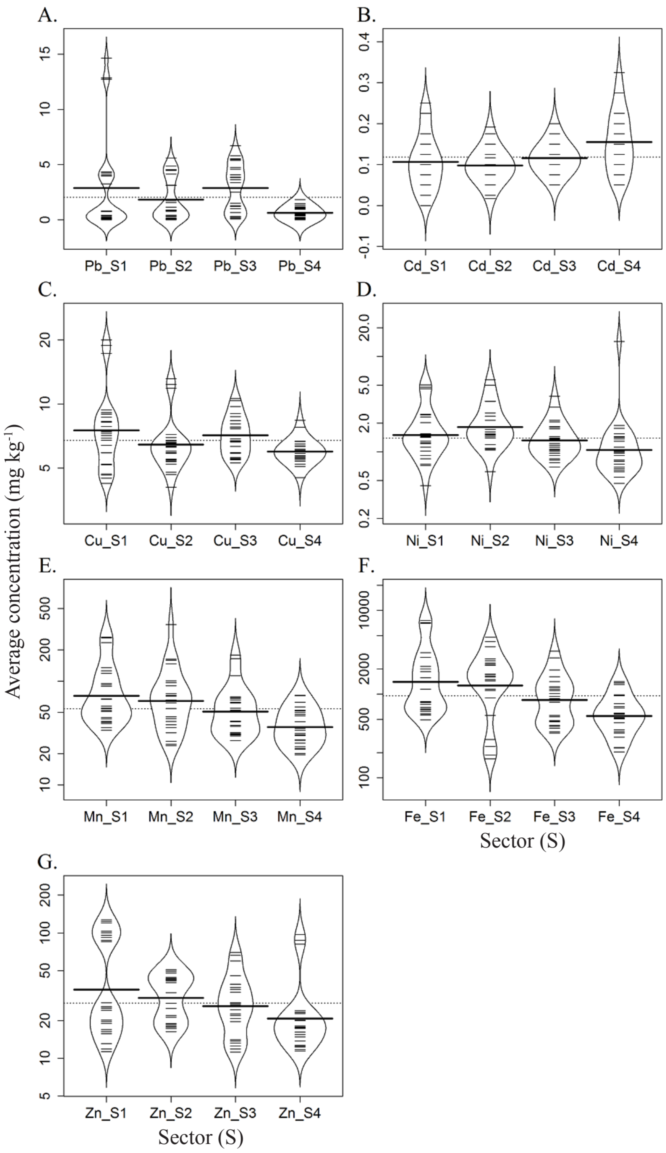

Figure 2. Beanplot of heavy metals (A) Pb, (B) Cd, (C) Cu, (D) Ni, (E) Mn, (F) Fe and (G) Zn in the municipality of Volta Redonda in the four sectors (1, 2, 3, and 4)

for the averages of the adopted sectors point to a significant difference between the mean in sector 3 in relation to the other sectors for the heavy metals Pb, Cd, and Mn followed by sector 2 for Zn. Cd stands out for having the lowest concentration means of heavy metals (Figure 2) followed by high variability of the data with symmetrical distributability in sectors 2 and 3. However, Pb, Mn, and Zn showed an asymmetric distribution followed by high temporal variability of the data and a mean that is farthest from the center of the normal distribution curve followed by a decrease in the mean values of heavy metals with values above and below of the midline (Figure 2).

Besides the large fleet of vehicles, the municipality has companies with other potentially pollution-related activities. According to Sor et al. (2008), Volta Redonda is the second municipality with the largest emission of particulate matter (PM10) in the state of Rio de Janeiro (4031 tons in 2003), with metallurgy being one of the industrial activities that contributes most to the emission of atmospheric pollutants.

According to Cardoso et al. (2017), the metals Cu, Mn, Fe, and Zn differ from other heavy metals in nature since their emissions are related to the traffic and particles of soot emitted from the vehicles. However, Almeida et al. (2016) and Antunes et al. (2017) showed that there is a difference in the content of metals present in the composition of the fuels; for example, Al, Ca, Fe, Mg, and Si are present in diesel followed by Mn, Zn, Cu, Fe, Mg, and Pb in ethanol and Zn, Cu, Pb, and Cd in gasoline.

In a study by Santos et al. (2015) carried out in the municipality of Ribeirão Preto, São Paulo, high concentrations of Fe, Pb, and Zn in urban areas with high vehicular traffic were observed using the plant *Tradescantia pallida* as biomonitor. However, it should be noted that the heavy metal averages were higher than the median and the pattern found in the municipality. The exception was the identified pattern of Cd and Fe that presented values above the median and the median of 0.13 and 1142.92 mg kg^{-1}. Pb, Cu, Ni, Mn, Fe, and Zn presented a trend below or equal to the median.

According to Carneiro et al. (2011) and Moreira et al. (2016), the use of the biomonitoring network may be used in the future as a vehicle-based street classification instrument since it is possible to differentiate particulates and emission sources from one point to another although a small area. Baltrėnaitė et al. (2014) warned of the fact that small concentrations of heavy metals in the environment are already a serious risk, especially for species chain moles (such as man) since heavy metals have the capability to bio-accumulate and biomagnify in the ecological pyramid.

Based on the results, the use of *P. pluviosa* bark as a suitable passive biomonitor to estimate the spatial distribution of heavy metals in urban areas can be recommended.

Conclusions

1. The use of *Poincianella pluviosa* tree bark proved to be an effective method for biomonitoring of atmospheric pollution in urban areas, showing significant differences in Pb, Cd, Cu, Mn, Fe, and Zn metal concentrations among the sectors compared in the study.

2. The concentrations of Mn, Fe, and Zn stand out compared to the other heavy metals adopted in the study for Volta Redonda.

3. Sectors 1, 2, and 3 of Volta Redonda presented the highest heavy metal concentrations. The results allow a direct association with the flow of automotive vehicles, railway lines, and the activities of the steel industry activities that are concentrated in these sectors to be formed.

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