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Evaluation of the spatial variability of the elements in tree barks used as biomonitors of atmospheric pollution

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ABSTRACT

Tree barks have proven to be a valuable source of information on air quality. Nowadays, studies with this biomonitor are constantly being developed. However, data of several factors that affect the accumulation of the pollutants in the barks, such as bark porosity, duration of the deposition on the bark and dispersion or variability of pollutants in a defined area, are scarce in the literature. The aim of this study was to evaluate the spatial variability of chemical elements concentrations accumulated on Sibipiruna (*Cenostigna pluviosarum*) barks in order to examine their aerial dispersion in two small urban areas of the Metropolitan Area of São Paulo. The neutron activation analysis (NAA) applied in the analyses consisted of irradiation the aliquots of the sample together the synthetic element standards at the IEA-R1 nuclear reactor. Concentrations of the As, Br, Ca, Co, Cr, Cs, Fe, K, La, Mn, Rb, Sb, Sc, V and Zn were determined in tree barks using short and long irradiations. Results obtained in the analyses of the tree bark samples indicated that the variability of element concentrations depends on the element, study area and numbers of trees. The variability of element concentrations in general was higher for elements presenting low concentrations. Quality control of the analytical results was evaluated by the analysis of INCT-MPH-2 Mixed Polish Herbs Certified Reference Material and these results presented good accuracy with values of standardized difference or $|\zeta \text{ score}| \leq 2$, indicating that the procedure of NAA applied is suitable for the analyses.

Keywords: **Air pollution, Biomonitoring, Tree barks, Neutron Activation Analysis.**

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1. INTRODUCTION

Air pollution is a serious problem that affects the health and well-being of people [1]. The pollution in the environment has intensified mainly by the increase emissions of the industries, vehicular traffic and other anthropogenic activities. Consequently, a continuous monitoring of the atmospheric emissions is necessary and important to ensure that air quality levels are within acceptable standards and to identify their possible sources of pollutants [2].

The conventional and physical-chemical instrumental methods commonly used for monitoring air quality in large urban centers are generally time consuming and expensive. An alternative method for air quality assessment would be the use of living organisms and this technique is known as "biomonitoring". The biomonitors utilized in this technique are organisms (or parts of an organism or a community of organisms) that contain information on the quantitative aspects of the environment [3].

Several biological species have been used for air pollution biomonitoring. These species are epiphytic lichens [4, 5], vascular plants such as *Tradescantia pallida* [6, 7], bromeliad *Tillandsia usneoides* [8, 9] and tree barks [10, 11]. Among these biomonitors in this study, tree barks were chosen due to their easy sampling, wide geographical availability, resistance of tree species to environment variations and aerosol retention on bark surfaces [12]. According to Chrabąszcz and Mróz, tree barks have proven to be a valuable source of information on air quality and nowadays studies with this biomonitor are continuously being developed [13].

The retention of pollutants in tree barks depends on the several factors such as bark porosity, duration of the deposition, dispersion of aerosols that contain element pollutants and climate conditions. The tree barks have been analyzed for using in biomonitoring, however studies on the influence of these parameters are scarce.

Within this context, in the present research the spatial variability of the elements in tree barks was evaluated for Sibipiruna (*Cenostigna pluviosarum*) tree species collected from two small urban areas of the Metropolitan Area of São Paulo (MASP). In most of studies, the mean spatial variation has assessed across a broad metropolitan area, instead of focusing on fine-scale variation within a very small area [14].

Concerning the analytical methodology for element determinations in biomonitors, several techniques have been applied such as X-ray fluorescence spectrometry [15, 16], neutron activation analysis [17, 18] and inductively coupled plasma atomic emission spectrometry [19]. In this study, neutron activation analysis (NAA) was applied in the tree bark analyses. This method is known as highly sensitive, precise and accurate analytical technique and very suitable for element determinations in tree barks due to its multielement character and without sample dissolution.

The aim of this study was to evaluate the spatial variability of chemical elements concentrations accumulated on tree barks to examine their aerial dispersion. The tree barks were collected in the urban areas of Congonhas (SP) and Santo André, where are the air pollution monitoring stations of Companhia Ambiental do Estado de São Paulo (CETESB).

2. MATERIALS AND METHODS

2.1. Tree bark sample collection and treatment for the analyses

The chosen arboreal species to collect bark samples was Sibipiruna (*Cenostigna pluviosarum*), since this tree species is quite abundant in the MASP. The samples were collected in two small areas of the MASP: Congonhas (SP) and Santo André. The area of Congonhas (with an area of about 0.45 km²) is a commercial area near a Congonhas airport and with a route of intense vehicular traffic and samples of 8 trees were collected in this area. The collection in Santo André was in the Paço Municipal (with about 0.66 km²), a commercial region with high vehicular traffic and in this area barks from 11 trees were collected.

Sample collection and treatment for analyses were carried out according to Santos (2017) and Moreira (2015) [12, 20]. The barks were collected at a height of about 1.5 m from the topsoil and they were removed manually from the four faces of the trunks presenting diameters of approximately 50 cm. The bark samples were stored in paper envelopes to prevent mold formation.

The preparation of the barks for the analyses consisted of a cleaning using with a nylon dental brush to remove the surface dust. A Ti grater was used to remove about 2 mm of the bark. These samples were ground using an agate-type ball mill (Fritsch, Pulverisette 0) for homogenization. The pulverized samples were transferred to polyethylene bottles and stored in a desiccator.

2.2. Certified reference material

The Certified Reference Material (CRM) INCT-MPH-2 Mixed Polish Herbs provided from the Institute of Nuclear Chemistry and Technology of Warsana, Poland was analyzed to evaluate precision and accuracy of the results and to ensure the metrological traceability of the results in this study. To calculate element concentrations on dry weight basis, the humidity of CRM was determined. This determination consisted on drying an aliquot of the CRM at temperature of 85ºC for 48 hours. The percentage of humidity obtained was 10.56 %.

2.3. Preparation of the synthetic element standards

The standard solutions provided by Spex Certiprep Chemical, USA were diluted in single or multi-element solutions. Fifty microliters of these solutions were pipetted using an Eppendorf pipettor onto sheets of Whatman No. 40 filter paper. The calibration of all pipettes and volumetric flasks were verified before their use. These filter sheets were placed in a desiccators to dry the aliquots at room temperature. After drying, these sheets were folded using tweezers and inserted in to clean polyethylene bags, which were heat sealed. The elements in the standards and the quantities of each element in µg (in parentheses) were the following: As (1.5), Br (5.0), Ca (500.6), Co (0.2), Cr (2.0), Cs (0.6), Fe (361.6) K (500.7), La (0.6), Mn (4.0), Rb (10.0), Sb (0.6), Sc (0.1), V (20.0) and Zn (36.1).

2.4. Neutron activation analysis procedure

About 150 to 180 mg of the reference material or of the tree bark sample were weighed in polyethylene bags using a Shimadzu analytical balance with a precision of 0.00001 g for element determinations by the NAA method.

The samples were irradiated at the IEA-R1 nuclear research reactor together the synthetic element standards. Short irradiations of 20 s under a thermal flux of about 1.9×10^{12} n cm^{-2} s^{-1} were carried out for the determination of Mn and V. Long irradiations of 16 h under a thermal neutron flux of about 4.5×10^{12} n cm^{-2} s^{-1} were carried out for As, Br, Ca, Co, Cr, Cs, Fe, K, La, Rb, Sb, Sc and Zn determinations.

The gamma-ray activities of the radioisotopes formed in the irradiations were measured using a hyperpure Ge detector coupled to a Digital Spectrum Analyzer DAS 1,000, both from Canberra. The resolution (FWHM) of the system was 0.90 keV for 122 keV gamma-ray peak of ^{57}Co and 1.87 keV for 1,332 keV gamma-ray peak of ^{60}Co. For the acquisition of the spectral data and its processing, the software Genie 2,000 version 3.1 from Canberra was used.

For NAA using short-term irradiation, the counting times of 300 s and 600 s were used and the sample and the standards were measured at least twice for different decay times. For long-term irradiation, the counting times varied from 5,400 s to 50,000 s depending on the gamma activities of the radioisotopes and their half-lives. Samples and standards were measured in three different decay times. The first counting was carried out after about 3 days of decay time and the elements As, Ca, K and La were determined. In the second counting carried out after about 10 days of decay time, the elements Br and Rb were determined and in the third counting carried out after about 17 days of decay time, the elements Co, Cr, Cs, Fe, Sb, Sc and Zn.

The radioisotopes of gamma-ray spectra were identified according to their half-lives and gamma-ray energies. The radionuclides used in tree barks analysis with its gamma-ray energy and half-life (in parentheses) were: ^{76}As (559.10 keV, 26.32 h), ^{82}Br (776.52 keV, 35.3 h), ^{47}Ca (1,297.09 keV, 4.54 d), ^{60}Co (1,173.24 keV, 5.27 y), ^{51}Cr (320.08 keV, 27.7 d), ^{134}Cs (795.85 keV, 2.06 y), ^{59}Fe (1,099.25 keV, 44.5 d), ^{42}K (1,524.58 keV, 12.36 h), ^{56}Mn (1,810.72 keV, 2.58 h), ^{86}Rb (1,076.60 keV, 18.66 d), ^{124}Sb (1,690.98 keV, 60.2 d), ^{46}Sc (889.28 keV, 83.81 d), ^{52}V (1,434.08 keV, 3.75 min) and ^{65}Zn (1,115.55 keV, 243.9 d). The element concentrations were calculated by comparative method [21].

2.5. Treatment of the results obtained in the analyses

The statistical parameters of arithmetic mean, standard deviation, relative standard deviation and relative error were calculated for the results obtained. In the results of CRM the standardized difference or ζ-score [22] values were also calculated in order to evaluate the accuracy of the results. The ζ-score values were calculated using equation (1).

$$\zeta\text{-score} = \frac{X_i - X_{ref}}{\sqrt{u_x^2 + u_{ref}^2}} \qquad (1)$$

where X_i is the obtained value, X_{ref} is the "assigned value", u_{ref} is the standard uncertainty of the assigned value and u_x is the standard deviation of the results was used for the uncertainty value.

The accuracy of the results is classified according to criteria: if $|\zeta\text{-score}| \leq 2$ the result is considered satisfactory; if $2 < |\zeta\text{-score}| < 3$ the result is considered uncertain; and if $|\zeta\text{-score}| \geq 3$ the result is considered unsatisfactory [22].

3. RESULTS AND DISCUSSION

3.1 Quality control of the results

In Table 1, results obtained in the analyses of CRM INCT-MPH2 Mixed Polish Herbs are presented with its certificate values [23]. The results indicate a good accuracy with relative errors varying from 0.04 to 13.6 % for most of elements. They also show good precision with relative standard deviations lower than 15 %. Less precise results were obtained for La and V due to statistical counting errors obtained in the measurements of ^{140}La and ^{52}V.

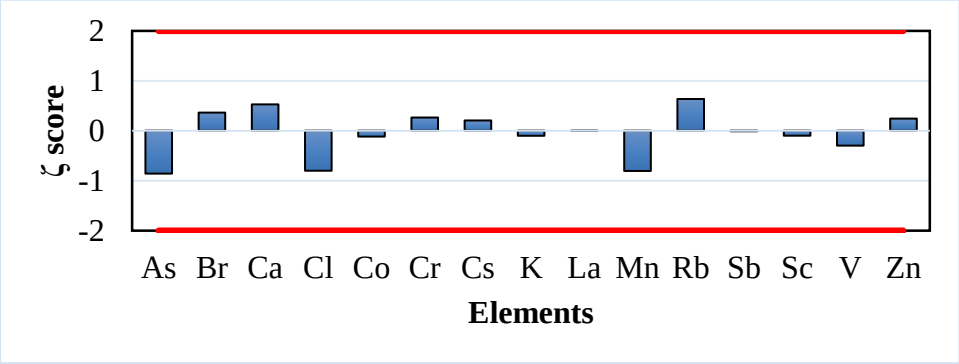
Table 1: Element concentrations obtained in the CRM INCT-MPH-2 Mixed Polish Herbs

Elements	Values of the Certificate	$\bar{x} \pm s$[a]	RSD[b], %	RE[c], %
As, ng g^{-1}	191 ± 12	175 ± 15	14.7	8.4
Br, µg g^{-1}	7.71 ± 0.31	7.90 ± 0.41	5.2	2.4
Ca, mg g^{-1}	10.8 ± 0.4	11.21 ± 0.69	6.2	3.8
Co, ng g^{-1}	210 ± 13	208 ± 13	13.5	1.0
Cr, µg g^{-1}	1.69 ± 0.07	1.92 ± 0.21	10.8	13.6
Cs, ng g^{-1}	76.0 ± 3.5	78.0 ± 6.6	8.5	2.6
Fe, µg g^{-1}	460[d]	530 ± 30	5.7	-
K, mg g^{-1}	19.1 ± 0.6	18.8 ± 2.7	14.1	1.5
La, ng g^{-1}	571 ± 23	571 ± 101	17.6	0.04
Mn, µg g^{-1}	191 ± 6	183.2 ± 7.5	4.1	4.1
Rb, µg g^{-1}	10.7 ± 0.4	11.06 ± 0.45	4.1	3.4
Sb, ng g^{-1}	65.0 ± 4.6	64.9 ± 6.1	9.4	0.2
Sc, ng g^{-1}	123 ± 5	122.2 ± 6.1	5.0	0.6
V, ng g^{-1}	952 ± 82	901 ± 150	16.6	5.4
Zn, µg g^{-1}	33.5± 1.1	33.82 ± 0.84	2.5	1.0

a. Arithmetic mean and standard deviation based from 4 determinations. b. Relative standard deviation. c. Relative error. d. Informative value.

In Figure 1, the values of ζ score obtained in the results of CRM INCT-MPH-2 Mixed Polish Herbs are between -2 and 2, indicating that the results are satisfactory and agree with the certified values.

Figure 1: *ζ score values obtained for CRM INCT-MPH-2 Mixed Polish Herbs*



3.2 Results obtained in the tree bark analyses

In Table 2 element concentrations determined in tree barks collected in Congonhas and Santo André are presented together with the results obtained by Santos [12] for comparison. As can be seen in this Table, elements Ca and K were found at the highest levels of mg g^{-1}, Br, Cr, Fe, Mn, Rb, V and Zn at the µg g^{-1} level and the elements As, Co, Cs, La, Sb and Sc at the lowest concentrations of ng g^{-1}.

Concerning Fe, Cr and Rb found in the tree barks, their origin might be associated with the suspension of soil dust deposited by the wind. The origin of Br, Ca, La, Mn, Sb and Zn may be associated with vehicular emissions and brake and tire wear. The presence of elements such as Br, Co and Zn may be related to industrial zones and may be associated to the presence of anthropogenic emission sources [4, 24, 25].

In Table 2 the ranges of element concentrations show the variability of the elements from the tree barks collected in Congonhas and Santo André areas. For most of elements, the concentrations ranged from 1.3 to 4.7 times. The variation of the element concentrations obtained for Congonhas trees indicates that the elements that presented the higher variability were Cs that varied 7.8 times

and Co that varied 4.2 times. For Santo André samples, the elements that presented higher concentration variations were Br that varied 12.6 times and V that varied 4.7 times.

In this study, bark sample of each tree was analyzed separately while Santos [12] analyzed a composite sample prepared from barks of various trees. A comparison between the mean concentrations obtained in this study with those presented by Santos [12] indicates that for most of elements the mean concentrations obtained are similar to the results obtained for composite sample.

Table 2: Element concentrations in tree bark samples

	Congonhas			**Santo André**		
	This Study		**Santos [12]**	**This Study**		**Santos [12]**
Elements	$\bar{x} \pm s$ [a]	**Range**	$c \pm s$ [b]	$\bar{x} \pm s$ [a]	**Range**	$c \pm u$ [b]
As, ng g^{-1}	82 ± 38	54 - 165	92 ± 26	110 ± 40	71 - 199	96 ± 39
Br, µg g^{-1}	2.34 ± 0.55	1.29 - 2.93	1.71 ± 0.70	1.88 ± 0.70	0.22 - 2.78	2.81 ± 0.30
Ca, mg g^{-1}	42.9 ± 4.3	35.5 - 47.4	35.2 ± 4.8	46.4 ± 8.8	31.0 - 58.6	41.0 ± 5.9
Co, ng g^{-1}	302 ± 148	149 - 619	255 ± 68	297 ± 47	218 - 377	262 ± 33
Cr, µg g^{-1}	1.81 ± 0.80	0.83 - 2.89	1.84 ± 0.53	2.50 ± 0.83	1.73 – 4.65	2.39 ± 0.31
Cs, ng g^{-1}	66 ± 21	38 - 94	66 ± 13	67 ± 22	39 - 102	58 ± 13
Fe, µg g^{-1}	537 ± 248	239 - 857	527 ± 144	672 ± 201	472 - 1,154	647 ± 156
K, mg g^{-1}	1.51 ± 0.42	0.85 – 2.14	1.42 ± 0.29	1.37 ± 0.43	0.92 – 2.23	1.16 ± 0.15
La, ng g^{-1}	958 ± 398	487 – 1,451	890 ± 160	1,140 ± 349	708 – 2,005	990 ± 210
Mn, µg g^{-1}	35.1 ± 6.2	21.1 - 41.8	29.2 ± 4.4	31.8 ± 3.5	25.3 - 37.8	28.5 ± 2.9
Rb, µg g^{-1}	3.57 ± 0.50	2.98 - 4.22	3.53 ± 0.52	3.23 ± 1.31	1.70 - 5.50	2.92 ± 0.76
Sb, ng g^{-1}	587 ± 297	276 - 1,029	523 ± 137	581 ± 207	350 - 948	558 ± 210
Sc, ng g^{-1}	108 ± 48	47 - 164	101 ± 20	127 ± 52	80 - 235	113 ± 39
V, µg g^{-1}	1.09 ± 0.56	0.53 – 1.93	1.06 ± 0.16	1.16 ± 0.53	1.16– 0.53	1.16 ± 0.53
Zn, µg g^{-1}	54 ± 23	29 - 96	45 ± 15	69 ± 27	36 - 108	66 ± 26

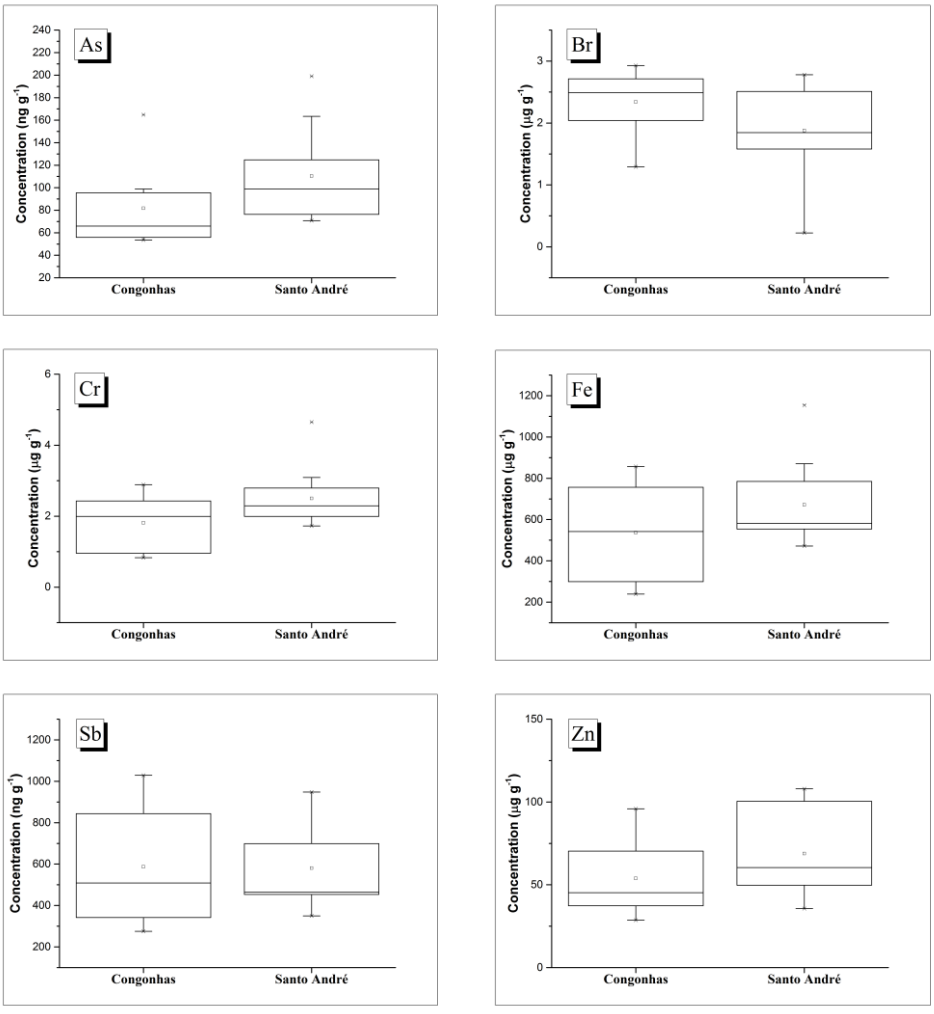
a. Arithmetic mean and standard deviation of results obtained individually in barks from 8 trees of Congonhas and 11 of Santo André, b. Concentration and uncertainty results obtained in the analysis of a composite sample of barks.

In order to compare between concentration variations of elements determined in samples from Congonhas and those from Santo André, boxplot graphics were obtained and presented in Figure 2 for As, Br, Cr, Fe, Sb and Zn concentrations. In these graphics, the median of concentrations is represented by the line cutting the block and the mean is represented by the small central square [26]. The graphics of boxplots show that the element concentrations found for this two area are of the same order of magnitude. However, the variations of the concentrations are different. For

example, for As, Br and Zn, the concentration variations in samples from Santo André are higher than those of Congonhas while for the Cr, Fe and Sb concentration variations are lowest in samples from Santo André.

These variations in the element concentrations found in these barks may be attributed to the factors such as the number of trees whose sample were collected, the distance among the trees, the distance between the sampling points and emission sources and the wind directions.

Figure 2: *Boxplot graphics showing the variability of the As, Br, Cr, Fe, Sb and Zn concentrations in tree barks samples collected in Congonhas (SP) and Santo André.*



4. CONCLUSION

In this study, the variability of the element concentrations in tree barks was studied for samples collected in two small urban areas of Congonhas and Santo André in the Metropolitan Area of São Paulo. The findings indicated that several factors might affect the retention of pollutants in tree barks even in small urban area. The results showed that the degree of variability of element concentrations or its dispersion depends on the element and the study area.

From these results, it can be concluded the importance to collect barks from a sufficient number of trees to obtain lower variability in their concentrations. In addition, the result of bark analyses collected at a specific sampling point can not be extrapolated to the extended geographic region.

About the method applied in this study, NAA proved to be very suitable for the element determinations in tree barks. The results obtained in certified reference material presented good precision and accuracy.

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REFERENCES

[1] LU, J. G. Air pollution: A systematic review of its psychological, economic, and social effects. **Curr Opin Psychol**, v. 32, p. 52–65, 2020.

[2] WHO – World Health Organization. **Ambient air pollution: a global assessment of exposure and burden of disease**, Geneva: WHO, 2016. 121 p.

[3] MARKERT, B. Definitions and principles for bioindication and biomonitoring of trace metals in the environment. **J Trace Elem Med Biol**, v. 21, p. 77-820, 2007.

[4] FUGA, A.; SAIKI, M.; MARCELLI, M.; SALDIVA, P. P. H. N. Atmospheric pollutants monitoring by analysis of epiphytic lichens. **Environ Pollut**, v. 151, p. 334-340, 2007.

[5] KOCH, N. M.; BRANQUINHO, C.; MATOS, P.; PINHO, P.; LUCHETA, F.; MARTINS, S. M. A.; VARGAS, V. M. F. The application of lichens as ecological surrogates of air pollution in the subtropics: a case study in South Brazil. **Environ Sci Pollut Res**, v. 23, p. 20819–20834, 2016.

[6] CAMPOS, C. F.; CAMPOS JÚNIOR, E. O. C.; SOUTO, H. N.; SOUSA, E. F.; PEREIRA, B. B. Biomonitoring of the environmental genotoxic potential of emissions from a complex of ceramic industries in Monte Carmelo, Minas Gerais, Brazil, using *Tradescantia pallida.* **J Toxicol Environ Health A,** v. 79, p. 123–128, 2016.

[7] SPOSITO, J. C. V.; CRISPIM, B. A.; ROMÃN, A. I.; MUSSURY, R. M.; PEREIRA, J. G.; SENO, L. O.; GRISOLIA, A. B. Evaluation the urban atmospheric conditions in different cities using comet and micronuclei assay in *Tradescantia pallida.* **Chemosphere,** v. 175, p. 108–113, 2017.

[8] LOURENÇO, L. F. A.; MOREIRA, T. C. L.; SOUZA, V. C. O.; BARBOSA JÚNIOR, F.; SAIKI, M.; SALDIVA, P. H. N.; MAUAD, T. The influence of atmospheric particles on the elemental content of vegetables in urban gardens of São Paulo. **Environ Pollut,** v. 216, p. 125–134, 2016.

[9] GUSTAVSON, P. C.; FERNANDES, F. F.; ALVES, E. S.; VICTORIO, M. P.; MOURA, B.; DOMINGOS, M.; RODRIGUES, C. A.; RIBEIRO, A. P.; NIEVOLA, C. C.; FIGUEIREDO, A. M. G. *Tillandsia usneoides*: a successful alternative for biomonitoring changes in air quality due to a new highway in São Paulo. **Environ Sci Pollut Res,** v. 23, p. 1779–1788, 2016.

[10] FERREIRA, A. B.; SANTOS, J. O.; SOUZA, S. O.; JÚNIOR, W. N. S.; ALVES, J. P. H. Use of passive biomonitoring to evaluate the environmental impact of emissions from cement industries in Sergipe State, northeast Brazil. **Microchem J,** v. 103, p. 15–20, 2012.

[11] GURGATZ, B. M.; OLIVEIRA, R. C.; OLIVEIRA, D. C.; JOUCOSKI, E.; ANTONIACONI, G.; SALDIVA, P. H. N.; Reis, R. A. Atmospheric metal pollutants and environmental injustice: A methodological approach to environmental risk analysis using fuzzy logic and tree bark. **Ecol Indic,** v. 71, p. 428-437, 2016.

[12] SANTOS, E. C. **Estudo da poluição aérea de elementos químicos pelas análises de cascas de árvore.** Dissertação (Mestrado em Tecnologia Nuclear). Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, São Paulo, 2017. 132 p.

[13] CHRABĄSZCZ, M.; MRÓZ, L. Tree bark, a valuable source of information on air quality. **Pol J Environ Stud,** v. 26, p. 453-466, 2017.

[14] LONGLEY, I.; TUNNO, B.; SOMERVELL, E.; EDWARDS, S.; OLIVARES, G.; GRAY, S.; COULSON, G.; CAMBAL, L.; ROPER, C.; CHUBB, L.; CLOUGHETERY, J. E. Assessment of spatial variability across multiple pollutants in Auckland, New Zealand. **Int J Environ Res Public Health,** v. 16, p. 1567, 2019.

[15] GURGARTZ, B. M.; OLIVEIRA, R. C.; ANTONIACONI, G.; SALDIVA, P. H. N.; HUERGO, L. F.; REIS, R. A. Spatial distribution of atmospheric pollutants through biomonitoring in tree bark using X-Ray fluorescence. **Ecletica Quim J,** v. 43, p. 59-64, 2018.

[16] MOREIRA, T. C. L.; OLIVEIRA, R. C.; AMATO, L. F. L.; KANG, C. M.; SALDIVA, P. H. N.; SAIKI, M. Intra-urban biomonitoring: Source apportionment using tree barks to identify air pollution sources. **Environ Int,** v. 91, p. 271–275, 2016.

[17] MADADZADA, A. I.; BADAWY, W. M.; HAJIYEVA, S. R.; VELIYEVA, Z. T.; HAJIYEV, O. B.; SHVETSOVA, M. S.; FRONTASYEVA, M. V. Assessment of atmospheric deposition of major and trace elements using neutron activation analysis and GIS technology: Baku – Azerbaijan. **Microchem J,** v. 147, p. 605–614, 2019.

[18] KLOS, A.; ALEKSIAYENAK, Y. A.; ZIEMBIK, Z.; RAJFUR, M.; JERZ, D.; WACLAWEK, M.; FRONTASYEVA, M. V. The use of neutron activation analysis in the biomonitoring of trace element deposition in the Opole province. **Ecol Chem Eng,** v. 20, p. 677-687, 2013.

[19] COCOZZA, C.; RAVERA, S.; CHRUBINI, P.; LOMBARDI, F.; MARCHETTI, M.; TOGNETTI, R. Integrated biomonitoring of airborne pollutants over space and time using tree rings, bark, leaves and epiphytic lichens. **Urban For Urban Green,** v. 17, p. 177–191, 2016.

[20] MOREIRA, T. C. L. **Biomonitoramento intra-urbano da poluição de origem veicular: utilização da casca de árvore na identificação de fontes de poluição atmosférica.** Tese (Doutorado), Faculdade de Medicina, Universidade de São Paulo, 2015. 109 p.

[21] DE SOETE, D.; GILBELS, R.; HOSTE, J. **Neutron activation analysis**. London: Wiley-Interscience, 1972.

[22] ISO - International Organization for Standardization. **ISO 13,528: Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons,** Geneva: ISO, 2015. 89 p.

[23] INCT - Institute of Nuclear Chemistry and Technology. **Polish certified reference material for multielement trace analysis: mixed polish herbs (INCT-MPH-2),** Warszawa: INCT, 2002. 4p.

[24] FIGUEIREDO, A. M. G.; NOGUEIRA, C. A.; SAIKI, M.; MILIAN, F. M.; DOMINGOS, M. Assessment of atmospheric metallic pollution in the metropolitan region of São Paulo, Brazil, employing *Tillandsia usneoides* L. as biomonitor. **Environ Pollut,** v. 145, p. 279-292, 2007.

[25] THORPE, A.; HARRISON, R. M. Sources and properties of non-exhaust particulate matter from road traffic: A review. **Sci Total Environ,** v. 400, p. 207-282, 2008.

[26] FERREIRA, J. E. V.; PINHEIRO, M. T. S.; DOS SANTOS, W. R. S.; MAIA, R. S. Graphical representation of chemical periodicity of main elements through boxplot. **Educ. Quim,** v. 27, n. 3, p. 209-216, 2016.