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DETERMINATION OF TRACE ELEMENT LEVELS IN LEAVES OF *NERIUM OLEANDER* USING X-RAY FLUORESCENCE

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ABSTRACT

The environmental pollution by human activity has been one of the most concerns in the last years, principally due to rapid urban growth in the cities and the industrialization process. The air pollution can be increased due to several different kinds of emissions: urban traffic, industrial activities, burning fuel, civil industry of construction/demolition, fires and natural phenomena. Many of these emissions move from long distances due to convections currents and finally tend to deposit mainly in the plants leaves and in the soil. Thus, the plants leaves works as a natural sampler by the emissions deposit in these ones. In this study *Nerium oleander* leaves were used to measure the environmental pollutions levels in different sampling urban regions in the city of Rio de Janeiro/RJ: Andaraí, Benfica, Bonsucesso, Caju, Engenho de Dentro, Engenho Novo, Estácio, Grajaú, Inhaúma, Lins, Maracanã, Maria da Graça, Méier, Praça da Bandeira, Riachuelo, Rio Comprido, São Cristóvão, Tijuca, Vila Isabel and city Center. The control samples were collected in Campo Grande near of Parque Nacional da Pedra Branca/RJ (National Park of Pedra Branca/RJ). The leaves were collected from adult plants and after the collection the samples were cleaned and placed in the greenhouse for drying, then were mashed and pressed into tablets forms. The analyses were performed using the energy dispersion X-ray fluorescence (EDXRF), developed on the own laboratory and based in a SiPIN detector and a mini X ray tube. It was possible to detect 16 elements in the analyzed samples: K, Ca, Cr, Mn, Fe, Cu, Zn, Br, Rb, Sr, Ba and Pb. The results shows that, in the studied areas, the analysis of the *Nerium oleander* plant shows a low-cost option and with a substantial efficiency as an environmental pollution biomonitor.

1. INTRODUCTION

The environmental pollution by the human activity has been one of the most concern in the last years, mainly due to the fast urban growth and the industrialization process. The trace elements can be released into the atmosphere by the human activity due to several kinds of emissions: urban traffic, industry activity, fuel burning, construction/demolition civil industry, fires; and natural phenomena. Many of these movements of emission of long distance, due to convection currents finally tend to deposit mainly in plants leaves and soil. Trace elements in plants, animals and soil can influence the structure and function of the ecosystem, including its ability of self regularization, thus affecting the live quality. Nowadays many researchers have studied organisms that act as bioindicators / biomonitors of environmental pollution. Among these biomonitors highlight the utilization of plants, lichens, mosses, growth rings, leaves and bark trees.

Some plants species absorb the air pollutant by the atmosphere and, then fixed them in its matrix, thus becoming a pollution biomonitor in that area. Thus, the foliar analysis of these vegetal species can be used to environmental monitoring [1-3]. One of the plants that have the ability to retain certain chemical elements in the environmental and used as a biomonitor is the *Nerium oleander*, that is an ornamental plant from the Mediterranean, well adapted to the tropical weather and in Brazil is popularly known as “espirradeira” [4]. In Brazil this plant is usually used as an ornamental plant in streets, parks and gardens.

The X Rays Fluorescence is a multielement analytical technique very popular and applied in many scientific and technology areas, and has been used in the last years, mostly, in analysis of environmental samples (air, sediment, water, soil and plants). Its mainly advantages over the other analytical techniques are: non destructible, fast qualitative analysis, few interference between lines, simplicity in preparation of the samples, large zone of elements that can be analyzed (Al – U) and the detection limits (from percentage until μgg^{-1} may reach until ngg^{-1}) [5-7].

In this study were used *Nerium oleander* leaves to measure the environmental pollution levels in four different urban areas in the Rio de Janeiro city. X-rays fluorescence technique was used to analyze trace elements in these plants.

2. MATERIALS AND METHOD

2.1. Study area

The *Nerium oleander* leaves were collected from four different urban areas in the city of Rio de Janeiro/RJ. The areas selected were constituted by the following districts:

a) Region 1 – Andaraí, Estácio, Grajaú, Maracanã, Rio Comprido, Tijuca and Vila Isabel;
b) Region 2 – Engenho de Dentro, Engenho Novo, Lins, Maria da Graça, Méier and Riachuelo;
c) Region 3 – Benfica, Caju, Praça da Bandeira, São Cristóvão and city Center;
d) Region 4 – Bonsucesso, Inhaúma.

The logistics of search and identification of the plants were realized by the “Street View” tool available on “Google Earth”. From this tool was possible to identify the plants and its coordinates. The figure 1 shows the distribution of the collected sites in the four regions. The colors in the markers indicate the sites of the collected regions.

2.2. Sampling

The samples of *Nerium oleander* were collected from adult plants drawn randomly so as not favoring one side of the plant. Usually the adult plants have an average high from 4.0 to 6.0 m, the flowering period is from April until October with flowers in the colors pink, red and white depending of the specimens. The average diameter of the crown is about 3.0 m (Figure 2).

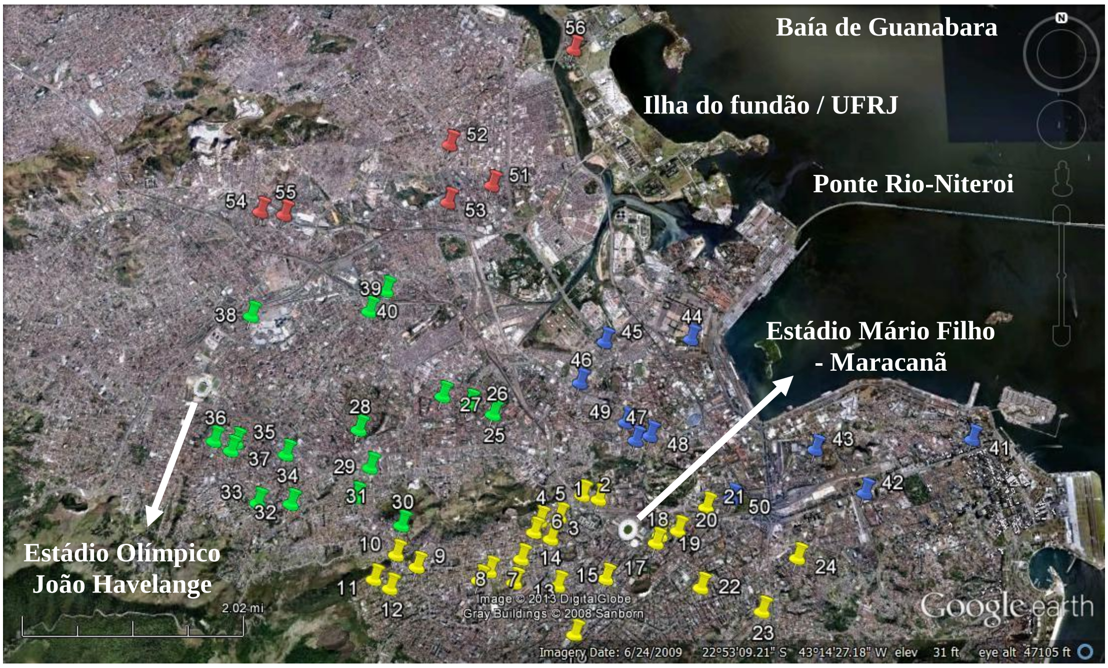

Figure 1: Map indicating the regions studied (Google earth 2013). The marker indicate the regions: Region 1 - Yellow; Region 2 - Green; Region 3 - Blue and Region 4 - Red.

Figure 2: Adult *Nerium oleander* plant

During collection were notice the color of the flower, wind direction, traffic intensity, precipitation, humidity, temperature and the position of the plant relative of the traffic and the buildings. The samples were collected in February, 2012 (summer). All the leaves were collected at a distance superior of a 1.5 m relative to the soil. The samples were packed in plastic bags and after the arrival in the Laboratory were placed under refrigeration at 5º C.

2.3. Sample preparation

In the laboratory the samples were cleaned with a brush with soft bristles to remove dust. In addition, we obtained the mass and dimensions of each leaf (length and width). After that, the samples were placed in the stove at 60º C until constant mass (to complete dryness). Next, the leaves were powdered (325 mesh). The grade control process is made by a strainer with a nylon mesh. After this process, aliquots of 500 mg mass were pressed at a pressure of 2.32×10^8 Pa for about 15 minutes, order to obtain thin pellets with a diameter of 2.54 cm and superficial density of 100 mg/cm^2. The Figure 3 shows some steps of the tablets production. Three replications were made for each sample.

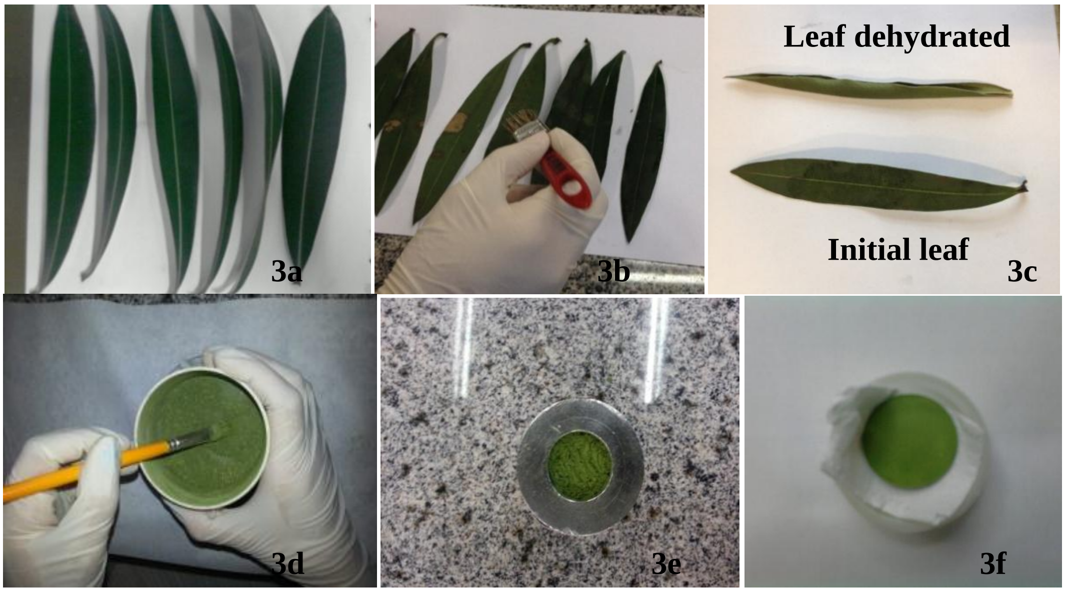

Figure 3: Samples preparation: 3a) *Nerium oleander* leaves after the collection; 3b) The cleaning process of the leaves; 3c) Leaves after drying; 3d) The milling process and the control of the grain size; 3e) Pellet preparation , and 3f) pressed-pellet.

2.4. Analytical method

The *Nerium oleander* samples analysis were performed using the energy dispersive X-ray fluorescence technique (EDXRF). The instrumental apparatus used were developed in the own laboratory (Laboratório de Instrumentação Eletrônica e Técnicas Analíticas – LIETA/UERJ) and consist of a portable XRF system formed by a mini X-ray tube of low power with a silver anode (maximum corrent 200 µA, maximum tension 40 kV) and a SiPIN detector, model XR-100CR. The experimental system is shown in the Figure 4.

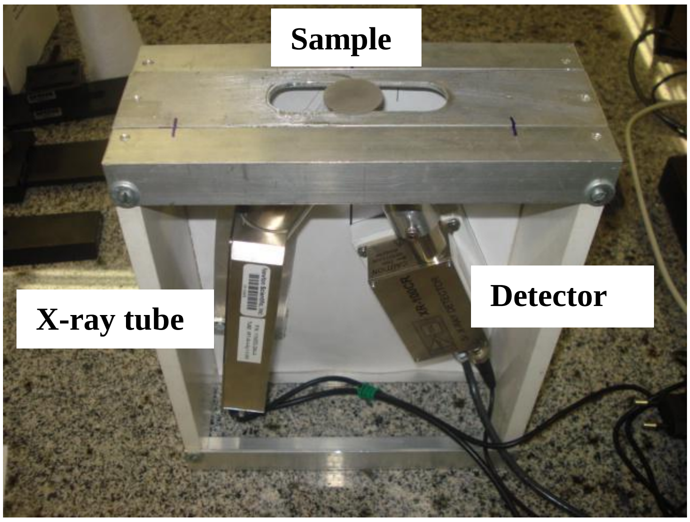

Figure 4: Portable EDXRF system developed in the Laboratory for the XRF analysis

3. RESULTS AND DISCUSSION

The table 1 shows a comparison between the obtained results using the EDXRF and the certificated results for the V-10 samples. It can be seen that the relative errors vary from 1% to Potassium until 16% to Iron. All measured values were within the confidence interval of the certified values.

Table 1 – Comparison table between experimental results and the certificated reference sample V-10. Concentration values in μgg^{-1}

Elements	Certified		Experimental[2] (n=3)	Relative Error (%)
	Average	Confid. Interval[1]		
K	21000	19600 - 22500	21166 ± 1483	1
Ca	21600	21000 - 22200	22590 ± 734	5
Mn	47	44 - 51	53 ± 8	13
Fe	186	177 - 190	215 ± 50	16
Zn	24	23 - 25	26 ± 3	8
Br	8	7 - 11	9 ± 2	13
Sr	40	37 - 44	38 ± 3	5

1. Confidence interval (95 %)
2. Average ± standard deviation

The Figure 5 shows a X-ray fluorescence spectrum of one of the samples. It was possible to detect eleven elements in all analyzed samples: K, Ca, Mn, Fe, Cu, Zn, Br, Rb, Sr, Ba and Pb. The table 2 shows the elements concentration obtained in the four regions and the control. It can be seen that the elements K, Ca, Fe, Cu, Zn, Br, Rb, Sr, Ba and Pb presented superior values compared to the control in every regions. However, the elements Ca, Fe, Br and Pb show superior concentration them 50% in relation to control concentration found.

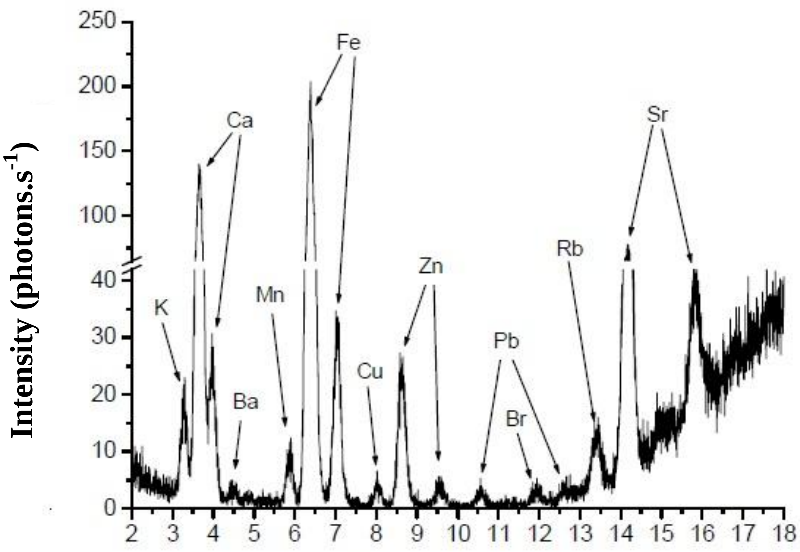

Figure 5: XRF spectrum obtainded from a *Nerium oleander* sample

Table 2: Elements concentration ± standard deviation in the regions studied and the control sample

Elements	**Control**	**Regions**			
		1	**2**	**3**	**4**
K	12700 ± 1000	16900 ± 1500	18300 ± 1700	19000 ± 1700	13400 ± 1600
Ca	19990 ± 470	46600 ± 3900	40100 ± 2700	32800 ± 2400	53700 ± 2300
Mn	51 ± 7	46 ± 11	74 ± 18	44 ± 18	55 ± 17
Fe	124 ± 13	504 ± 72	431 ± 66	486 ± 34	366 ± 42
Cu	9 ± 1	16 ± 4	16 ± 4	15 ± 5	11 ± 3
Zn	45 ± 1	59 ± 10	57 ± 8	85 ± 12	50 ± 14
Br	3.6 ± 0.3	11 ± 2	12 ± 3	12 ± 3	11 ± 3
Rb	21 ± 2	23 ± 5	37 ± 9	31 ± 8	25 ± 5
Sr	79 ± 2	159 ± 26	130 ± 17	103 ± 14	170 ± 18
Ba	73 ± 4	107 ± 18	94 ± 15	106 ± 17	80 ± 13
Pb	1.0 ± 0.1	3.0 ± 1.0	2.0 ± 0.9	3.0 ± 1.0	1.9 ± 0.8

These results are corroborated by the results obtained from the relative intensity (region studied/control) shown in figure 6. Probably these results suggest that these factors are derived from anthropogenic sources present in concentrations above the control.

The table 3 shows Pearson`s correlation coefficient performed for the found elements in the *Nerium oleander* samples, obtained through the SPSS 15.0 software for Windows.

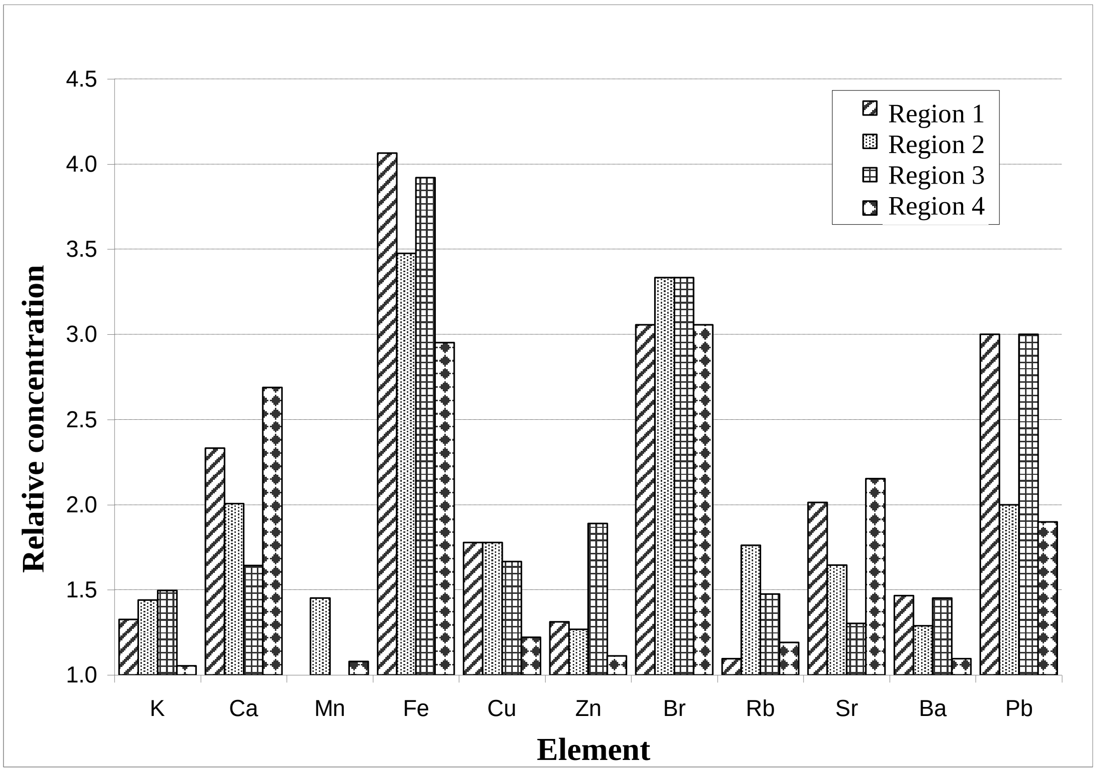

Figure 6: Relative concentrations of detected elements in the *Nerium oleander* leaves samples

Table 3: Pearson`s correlation coefficient between each pair of elements of samples from *Nerium oleander*

	K	Ca	Mn	Fe	Cu	Zn	Br	Rb	Sr	Ba	Pb
K	1										
Ca	-0.78**	1									
Mn	-0.13	-0.03	1								
Fe	-0.03	-0.04	0.27*	1							
Cu	0.59**	-0.53**	0.12	0.35**	1						
Zn	0.20	-0.22	0.34**	0.73**	0.42**	1					
Br	0.41**	-0.37**	-0.04	-0.05	0.04	-0.08	1				
Rb	0.76**	-0.56**	-0.21	-0.20	0.38**	-0.03	0.21	1			
Sr	-0.67**	0.85	-0.13	-0.05	-0.52**	-0.27*	-0.32*	-0.50**	1		
Ba	0.10	-0.09	0.20	0.85**	0.31*	0.66**	0.03	-0.13	-0.06	1	
Pb	-0.09	0.14	0.13	0.78**	0.27*	0.68**	-0.12	-0.29*	0.12	0.67**	1

* = $p < 0.05$
** = $p < 0.01$

The Bromine showed concentrations greater than three times the concentrations in control. This result can be explained by influence of the proximity of the points studied in relation to the sea. Figure 1 shows that the points studied are closed to the sea (an average distance of approximately 5.0 km). The control point is at the entrance of the National Park of Pedra Branca western slope and is located at a distance of approximately 20 km from the sea.

The table 3 shows a strong positive correlation between the elements Fe, Zn, Ba and Pb. The iron concentration also was very high in all the four regions. The high concentration of iron can be associated to the intense car traffic in these regions. The image 6 shows that these elements (Fe, Zn, Ba, Pb) present the highest concentrations in the regions 1 and 3. These regions have a large concentration of houses and therefore a high vehicle traffic. In the literature these elements (Fe, Zn, Ba and Pb) are associated to the intense movement of vehicles that contribute with exhaust emissions, internal parts wear and friction tires with asphalt [8].

The elements Ca and Sr shows a strong positive correlation ($r = 0.85$). The element calcium is associated, mainly by resuspension of the soil dust. The Sr follows the same behavior of the Ca due to your chemical affinity. The elements K and Rb are also associated to the same source. Furthermore, the region 1 is around of Maracanã Stadium which is currently undergoing for many makeovers, due to the events that it will host. With this, many construction materials are been released in the air and been accumulated in the plants. Thus, the elements Ca, Fe, Cu, Sr, Ba and Pb may also be related to dust from construction material.

The Cu shows higher concentrations in all the regions relative to the control. One of the most important sources of this element can be the particles from the braking of vehicles [9].

4. CONCLUSION

The X rays Fluorescence portable system developed in our laboratory shows efficient, fast and with a low cost in the multielement analysis of the leaves of *Nerium oleander*. It was possible to detect and quantify the concentration of the following elements: K, Ca, Mn, Fe, Cu, Zn, Br, Rb, Sr, Ba and Pb. All elements show higher concentrations than that found in the control samples. This finding could indicate that the biggest source of pollution in these areas has anthropogenic origins as fossil fuel burning in internal combustion engines of motor vehicles, industry and activities associated to the civil construction.

The plant used as a biomonitor shows efficient in the environmental evaluation of several elements and can be indicated as a low cost option to the ornamentation of inside and outside areas in the industry with a polluter potential with the intension of preservation and alert in case of an incident with the release of polluter material. The study is been completed with analysis of the same points in other seasons of the year, to study the seasonal effects in the elements concentrations and the study of the soil in the sites where the plants were collected.

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