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Tracking atmospheric dispersion of metals in Rio de Janeiro Metropolitan region (Brazil) with epiphytes as bioindicators

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ABSTRACT

The atmospheric dispersion atmospheric plume of the metropolitan region and neighborhoods of the city of Rio de Janeiro was investigated through elemental analyzes (Na, K, Al, Mn, Pb, Ni, Cr) and stable lead isotopes in two epiphytes; the lichen *Parmotrema crinitum* (Ach.) and the bromeliad *Tillandsia usneoides* (L.). All the elements had lower concentrations in epiphytes than in rocks of the local geological basement, with the exception of K, which was similar to rocks. This behavior was attributed to the nutritional essentiality and abundance of this element in the environment. The concentrations of Na, Pb and the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios indicated the presence of spatial gradients in the path (a) sea shore → continent, and (b) urban center → farmlands. These patterns were associated with the mesoscale atmospheric circulation regime, in which, during the arrival of cold fronts, air masses from the metropolitan region of Rio de Janeiro are transported towards the mountainous region of Teresópolis, which acts as a barrier to the dispersion of pollutants. The bromeliad *Tillandsia usneoides* and the lichen *Parmotrema crinitum* were linked to Na and Pb atmospheric levels, respectively.

Key words: Stable lead isotopes, atmospheric pollution, *Parmotrema crinitum* (Ach.), *Tillandsia usneoides* (L.)

INTRODUCTION

The air quality of urban centers is affected by a range of substances, mostly associated with the burning of fossil fuels and industrial activities. These sources emit a great variety of pollutants into the atmosphere, among which stand out particulate matter, nitrogen and sulfur gases, ozone and metallic compounds (Marquita 2010). The particulate matter

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accumulates most of the metallic elements emitted into the atmosphere, such that there is a direct relationship between the concentrations of these two components (Kandlikar and Ramachandran 2000). The fine fraction of the particulate matter (PM2.5-10) is the most striking, because it has a longer residence time in the atmosphere (~10 days) and can be transported over considerable distances (Minami et al. 1990, Van Valin et al. 1981).

Lead (Pb) is the trace metal with the highest emission rates for the atmospheric environment of urban areas (Marquita 2010). High lead concentrations are frequently reported in aerosols sampled at these areas. Its impact in the environment, as well as for the human health, has been the target of several studies in the last decades (Alloway and Ayres 1997, Harrison and Laxen 1981, Manahan 2000). However, based only on measurements of Pb concentration, it is not frequently possible to determine the cause of its high content or to distinguish between natural and anthropogenic sources and among multiple origins from specific Pb end-members. The results of these studies have shown that stable lead isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) can be successfully used for elucidating sources of air pollution and for tracing the influence of urban and industrial pollution plumes in surrounding areas.

Lead has four main isotopes present in the environment: ^{208}Pb (52%), ^{206}Pb (24%), ^{207}Pb (23%) and ^{204}Pb (1%). The radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb are products of radioactive decay from the natural series of ^{238}U, ^{235}U and ^{232}Th, respectively. Otherwise, ^{204}Pb is the only primordial lead stable isotope with a fixed abundance on Earth, while the abundance of radiogenic isotopes in a sample depends strictly on the concentrations of U and Th as well as their paths of decay, given by the half-lives (t1/2) of the parent isotopes, besides the primordial lead content. The abundance of ^{207}Pb has strongly changed with time compared to ^{206}Pb because most ^{235}U has already decayed while ^{238}U still has a relatively high abundance on Earth. The isotopic composition of Pb is not significantly affected by physico-chemical fractionation processes; therefore, Pb isotopes provide an efficient tool for determining the sources and pathways of Pb pollution (Komárek et al. 2008).

Several studies on atmospheric pollution, as well as air quality monitoring programs, have used bioindicators. The vast majority of these studies used epiphytic organisms, such as lichens (Conti et al. 2016, Giordani 2007, Szczepaniak and Biziuk 2003, Van Dobben and Ter Braak 1999) and certain bromeliads (Alves et al. 2008, Brighigna et al. 2002, Figueiredo et al. 2007, Pyatt et al. 1999) as indicators. Such organisms uptake nutrients from the atmosphere and have the ability to accumulate well beyond their physiological needs (Godinho et al. 2009). This approach is an advantageous alternative to monitoring using pumps and filters, due to its low cost, its efficiency to monitor wide geographical areas for long periods of time, and the possibility to evaluate metallic elements that accumulate in the environment (Fuga 2006, Fuga et al. 2008).

The present study aims to evaluate lichen *Parmotrema crinitum* (Ach.) and bromeliad *Tillandsia usneoides* (L.) (also named "elder beard") as indicators of atmospheric pollution by metallic elements in the metropolitan region of Rio de Janeiro and its surroundings, a metropolis with 12 million inhabitants. For this purpose, the concentrations of Na, K, Al, Mn, Pb, Ni and Cr and the lead stable isotopic composition (^{206}Pb/^{207}Pb and^{208}Pb/^{206}Pb) were determined in epiphytes sampled in different areas at various distances from the city of Rio de Janeiro. The results were also compared to metallic contents of rocks from each area.

MATERIALS AND METHODS

SITE DESCRIPTION

The study was undertaken near the shore region of Rio de Janeiro City (Brazil) and in inner areas surrounding the metropolitan region at the municipalities of Guapimirim, Teresópolis and Nova Friburgo. These last are located in the “Serra do Mar” mountain, northward from the city (Figure 1). The Rio de Janeiro metropolitan area (RJMA) is the second country’s largest urban agglomeration, with 12 million inhabitants (IBGE 2011). The area has the second largest industrial park of the country, which includes metallurgic, shipping yards, petrochemical, gas-chemical, textile, printing, pharmaceutical industries, and oil refineries (FEEMA 1979, 2004). The hydrocarbon atmospheric levels of the RJMA decreased in the last years (Massone et al. 2015) and air quality parameters range from normal to above the limits according to Brazilian legislation (CONAMA 1990). The Municipality of Guapimirim, with 57,000 inhabitants, located 50 km from the center of the city of Rio de Janeiro, has large preserved forest areas. Likewise, Teresópolis and Nova Friburgo are in not overpopulated region (respectively 174,000 and 185,000 inhabitants), located at ~1000 m above sea level, about 170 km from Rio de Janeiro downtown (IBGE 2011).

The climate of the region varies from tropical semi-humid, with dry winters and abundant rainfall in the summer. Annual average temperatures are 22-24 °C in the lowland till meso-thermic mild super-humid according Köppen classification (Alvares et al. 2013) with mild summers and annual

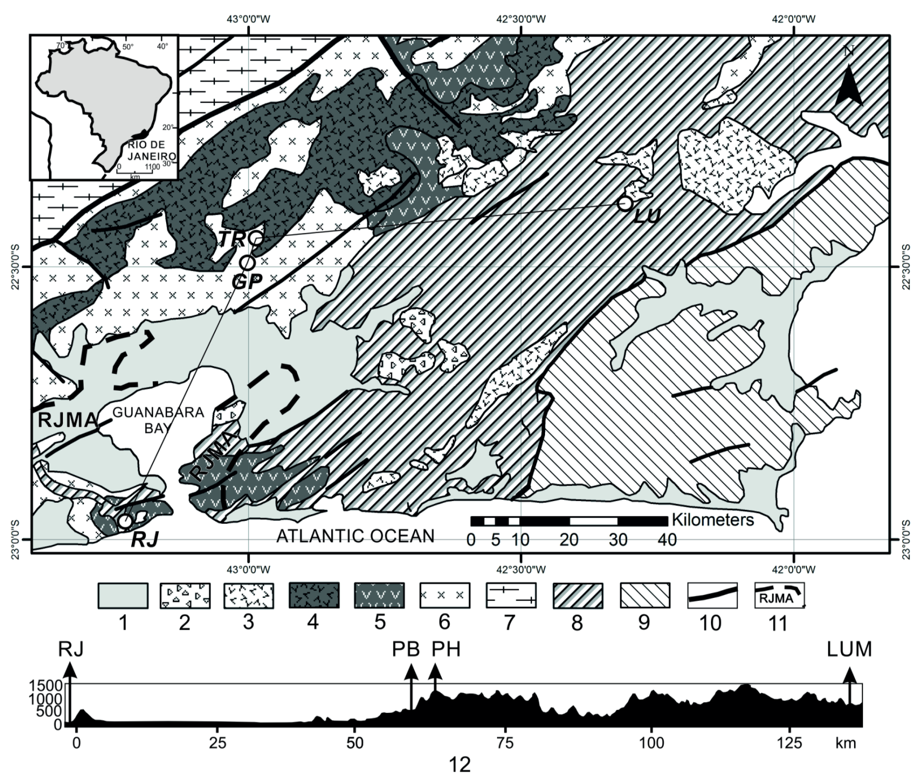

Figure 1 - Map of the Central and North Region of Rio de Janeiro State, showing the geological and topographical setting of the study area and the sampling sites of epiphytes (circle). Geological information: 1. Cenozoic deposits, 2. KT igneous alkaline rocks, 3. biotite granites (510–480 Ma), 4. Granites (560 Ma), 5. leucogranites and charnockites (590–560 Ma), 6. Rio Negro magmatic arc and related suites (790–620 Ma), 7. Paraíba do Sul complex, 8. paragneisses, 9. orthogneisses, amphibolites and paragneisses, 10. Faults, 11. Rio de Janeiro Metropolitan Area (RJMA), 12.Topographic profile throughoutthesampling sites. Modified from Monna et al. (2017).

averages of 13-23 °C in the hill region. Rainfall varies between 1,500 and 2,000 mm, but levels of up to 3,600 mm are observed with some frequency in some mountainous areas (Castro 2008, FIDERJ 1978).

The topography of the region presents great contrasts and is composed to the south by coastal plains, and to the north by mountains with 2000 m of altitude, which extend up to 60 km distance from the coast ("Serra do Mar"). This mountainous region is parallel to the coastline and forms part of the Ribeira Belt, a Neoproterozoic to Cambrian orogenic belt of West Gondwana. This crystalline complex is composed by granitic and metamorphic rocks and lies 1400 km along the Atlantic coast of Brazil in a NE-trend (Almeida et al. 1981, Hasui et al. 1975, Heilbron et al. 2004, Trouw et al. 2000). The study area outcrop rocks are mainly Neoproterozoic paragnaisses (mainly silimanate-biotite-gnaisse) and ortognaisses, and by Neoproterozoic, Ordovician and Cambrian granites. We present below the mainly features of the sampling locations.

Rio de Janeiro Botanical Garden (*RJ*) - This site is a park and research center founded by The King of Portugal, Brazil and Algarve during the 19th century. Today, ***RJ*** is an urban area of Rio de Janeiro municipality, located 5 km away from the sea.

Guapimirim (*GP*) and Teresópolis (*TR*) - The ***GP*** and ***TR*** sampling sites are located at 50 and 60 km far from downtown, in areas belonging to The "Serra dos Órgãos" National Park (PARNASO). This park covers approximately 20 thousand hectares. It presents a strongly mountainous relief without flat surfaces, and its vegetation is predominantly composed by extensive areas of dense ombrophyllous forest. The ***GP*** and the ***TR*** sites are close to each other, but exhibit important difference in elevation: 600 m and 1200 m above sea level, respectively. The climate of this region is super-humid subtropical. The bromeliad *T. usneoides* was not found in these sites.

Lumiar (*LU*) - This site is mainly occupied by small farms and located 100 km far from Rio de Janeiro downtown, in the region of Lumiar, municipality of Nova Friburgo. Besides the rural area, there are preserved forest patches ("Área de Proteção Ambiental de Macaé de Cima"). The protected area is composed of ombrophyllous hill dense forest in humid subtropical climate, with approximately 7 thousand hectares of, and is located at 1,100 m above sea level (a.s.l.).

SAMPLING AND ANALYTICAL METHODS

Sampling of epiphyte *Parmotrema crinitum* (***PAR***) lichens and *Tillandsia usneoides* (***TIL***) bromeliads was performed at trees in four sites comprising urban, rural and national park forest areas during April 2011. At all sites, about 12-15 individual talli of *P. crinitum* (Ach.) were sampled. Moreover, 14-15 samples of the bromeliad *T. usneoides* ("elder beard") were also collected at the rural and urban sites. The samples were collected with plastic gloves and inert material from trunks and/or branches of living trees at a height ranging from one to three meters of the ground in a circle with 10 m of radius. The samples were stored in plastic bags and impurities such as bark of trees and any residues were removed manually in laboratory. The samples were then washed with Milli-Q water in an ultrasonic bath for 1 minute to remove dust and any remaining debris from the leaf (Getty et al. 1999). After this step, the samples were oven dried (45 °C until constant weight) and hand grinded in agate mortar to obtain a fine and homogeneous powder.

METALLIC ELEMENT ANALYSIS

The metallic elements Na, K, Al, Mn, Pb, Ni and Cr were determined after total digestion of 60-100 mg of samples with a 2 ml mixture each of concentrated supra pure acids (Merck): HNO_3, HCl and HF (1:1:1) on hot plate. The solutions were evaporated and retaken with HNO_3, and appropriately diluted with Milli-Q water.

The analytical determinations of the elements were performed with an ARCOS ICP-AES. Blanks (n=8) and certified reference material (processed intermittently with epiphyte samples): Leaves of peach (NIST-1547); Estuarine sediment (BCSS-1), Basalt (BCR-2); Freshwater (SLRS-4 and SLRS-5). Blank concentrations appeared always to be in the baseline and the values obtained for reference material never exceeded 10-15% range of their nominal concentrations. All results were based in five runs.

The metallic element data from rocks of each region were obtained from reports of Geological Survey of Rio de Janeiro State (CPRM 2012), and also from personal communication with local geologists.

LEAD STABLE ISOTOPE ANALYSIS

The following isotopic ratios were determined in epiphyte stems: $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$. About 100 mg samples, previously dried and grinded, were digested in Teflon beakers with 6 ml mixture (1:1:1) of concentrated supra pure HNO_3:HCl:HF (Merck) on hot plate. Lead isotopic compositions ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios) were measured with a high resolution-inductively coupled plasma mass spectrometer (HR-ICP-MS) Element 2. Instrumental mass bias was corrected by sample-standard bracketing techniques, using a NBS 981 solution as the bracketing standard (Monna et al. 1998, 2000). The analytical precision up to the third decimal place are typically of 2–3 for $^{206}Pb/^{207}Pb$ and 4–7 for $^{208}Pb/^{206}Pb$ ratios (at a 95% confidence level). Lead blanks were determined for each eight epiphyte samples. They were low so that sample results did not require any correction.

More details about standard procedures, settings, blanks, analytical precision and detection limits can be found in (Monna et al. 1998, 2006).

STATISTICAL ANALYSIS

Descriptive statistics (mean and range) were determined for metallic elements and stable lead isotope ratios. Nonparametric tests were applied when the assumptions of parametric tests could not be met with either the non-transformed or transformed data.

A Kruskal-Wallis (KW) test was performed to determine the significant differences among the likens sampled in four sites (***RJ*** – Botanical Garden of Rio de Janeiro City; ***GP*** – Serra dos Órgãos National Park – Guapimirim; ***TR*** – Serra dos Órgãos National Park – Teresópolis and ***LU*** - Lumiar). Dunn's nonparametric comparison was used as *post hoc* KW testing. T-test was used for bromeliads sampled in two sites (***RJ*** and ***LU***). Correlations among the parameters (metal concentrations and isotope ratios of stable isotopes of Pb) were examined through Spearman Correlation Analysis and Principal Component Analysis (PCA). The data were transformed using log (x+1) or cubic root in order to get normal distribution (Zar 1984). All statistical tests were performed with the program PAST, version 2.17b (Hammer et al. 2001).

RESULTS

METALLIC ELEMENTS IN EPIPHYTES AND GEOLOGICAL SETTLEMENTS

Metal concentrations in the lichen *Parmotrema crinitum* (***PAR***) and the bromeliad *Tillandsia usneoides* (***TIL***), as well as in the rocks (outcrop) from the different sampling areas are presented in Table I and box plots of Figure 2. Sodium, aluminum, manganese, chrome and nickel concentrations were lower in both ***PAR*** and ***TIL*** than rocks. Significant variations were observed for Na, Al and Cr in *Parmotrema crinitum* between Botanical Garden (***RJ***) and mountain sites (***GP*** and ***TR***) (Kruskal-Wallis; $p < 0.05$). Otherwise, potassium concentrations in the epiphytes and

TABLE I
Metallic element concentrations and lead isotopic ratios in *Parmotrema crinitum* (Ach.) and *Tillandsia usneoides* (L.).

		Na (µg g-1)	K (µg g-1)	Al (µg g-1)	Mn (µg g-1)	Pb (µg g-1)	Ni (µg g-1)	Na (µg g-1)	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
PAR - RJ	Mean	331.43	3772.1	2105.9	20.90	25.1	1.7	2.6	1.173	2.078
	Min - Max	197.13 - 581.70	2360.8 - 6254.2	961.30 - 4177.1	10.78- 34.15	11.3- 90.1	0.8 - 4.2	1.7 - 4.7	1.157 - 1.180	2.063 - 2.097
PAR - GP	Mean	61.524	2286.0	749.70	179.75	4.21	1.1	1.3	1.165	2.088
	Min - Max	31.870 - 96.377	1544.6 - 3927.5	163.95 - 1182.6	6.1221- 1318.9	2.17 - 8.11	0.4 - 1.8	0.9 - 1.9	1.161 - 1.168	2.082 - 2.094
PAR - TR	Mean	83.957	3017.4	896.87	143.19	3.55	1.9	1.5	1.168	2.083
	Min - Max	53.819 - 110.32	1115.0 - 4722.1	405.43 - 2427.0	17.198 - 1294.7	2.11 - 5.76	0.6 - 4.0	0.9 - 2.8	1.164 - 1.174	2.076 - 2.091
PAR - LU	Mean	232.67	3462.5	4566.01	113.99	6.20	2.5	3.3	1.179	2.111
	Min - Max	84.136 - 479.32	1591.7 - 4550.7	1241.96 - 7595.15	43.672 - 237.09	3.26 - 8.86	1.2 - 4.0	1.2 - 5.8	1.168 - 1.193	2.083 - 2.162
TIL - RJ	Mean	2326.4	6768.67	1128.4	59.683	9.58	1.9	2.2	1.156	2.102
	Min - Max	608.12 - 5568.8	3572.65 - 13840.5	430.26 - 2049.7	20.896 - 110.76	3.49 - 51.3	1.1 - 3.6	1.0 - 9.1	1.153 - 1.162	2.093 - 2.107
TIL - LU	Mean	225.94	9513.05	2050.7	101.46	3.82	1.8	1.6	1.171	2.098
	Min - Max	144.31 - 533.36	6971.36 - 13951.6	857.93 - 3468.3	65.284 - 170.19	2.70 - 5.19	1.1 - 2.6	1.0 - 2.3	1.153 - 1.174	2.084 - 2.107

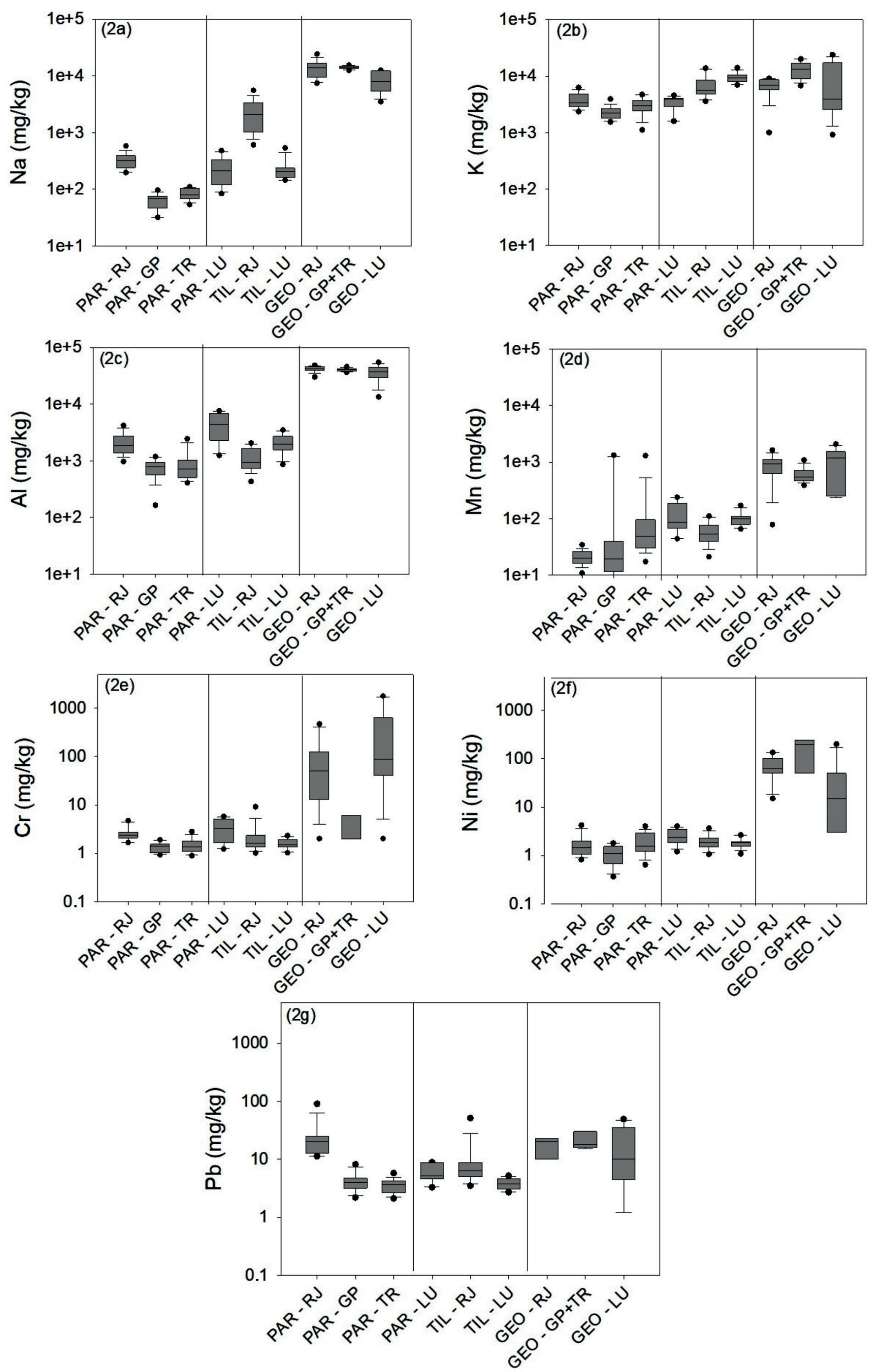

Figure 2 - “Boxplot” of metallic element concentrations (Na, K, Al, Mn, Cr, Ni and Pb) in *Parmotrema crinitum* (Ach.), *Tillandsia usneoides* (L.) and rocks from sampling area in Rio de Janeiro State.

rocks were in the same order of magnitude for all study sites. Finally, lead concentrations were highest in likens from the urban site (***RJ***).

The most remarkable feature of Na in epiphytes was the reduction of concentrations with the shore distance (***RJ***>***LU***>***GP*** ~ ***TR***). The sodium concentrations were respectively 5 and 10 times higher in the epiphytes of the Rio de Janeiro sampling site (***RJ***) than in those of the PARNASO forest and Nova Friburgo sites (***GP***, ***TR*** and ***LU***, respectively). The sodium concentrations in rock outcrops of the city of Rio de Janeiro and PARNASO were similar and their averages were approximately twice as high as in the Lumiar region (Figure 2). The epiphytes did not show spatial patterns in concentration for Al, Cr and Ni. However, chrome and nickel concentrations in rocks were: ***GP*** ~ ***TR***>***RJ***>***LU***.

The average concentrations of metallic elements in the two species and in the rocks of each site (***RJ***; ***GP***; ***TR***; ***LU***) were normalized by each Al average. These ratios ([Met] / [Al]) are presented in the Figure 3 for both species of each sampling site. Sodium and nickel concentrations in epiphytes were similar of those of the respective rocks of geological basement (Figure 2a, f). The exception to this pattern was *T. usneoides* from the urban area (***RJ***), which presented the average [Na] / [Al] ratio higher than that of the local geology (Figure 3a). The [Mn] / [Al] ratios in the epiphytes and rocks of Rio de Janeiro (***RJ***) and Nova Friburgo (***LU***) were similar (Figure 3c). This pattern was also observed for the [Cr] / [Al] ratios at the urban area sampling site (***RJ***). Otherwise, these ratios for *P. Crinitum* in PARNASO sites (GP, TR) were approximately twice than the average values for local geology (Figure 3e).

The concentration ratios [Pb] / [Al] were always higher in the epiphytes than in the rocks in the three areas (***RJ***, ***TR***, ***LU***) (Figure 3f). A second pattern observed for the Pb was the decrease of the ratios in both species gradually from the metropolitan region toward the countryside of Rio de Janeiro State. The [Pb] / [Al] ratios for plants indicate a spatial gradient of concentrations as follows: ***RJ***>***GP***-***TR***>***LU***.

STABLE LEAD ISOTOPE RATIOS IN EPIPHYTES

The lead isotope ratios (^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb) of epiphytes are presented in Table I and compared with sediments of Guanabara Bay (***BG***), one of the main polluted coastal environments, which is located in the study area (Figures 1 and 4). As mentioned earlier, *P. critinum* collected in the four sites (***RJ***, ***GP***, ***TR***, ***LU***) and *T. usneoides* in two (***RJ***, ***LU***).

The ^{208}Pb/^{206}Pb ratios had smaller range in *Tillandsia usneoides* than in *Parmotrema crinitum*, varying from 2.084 to 2.107 in the bromeliad and between 2.063 and 2.162 in the lichen (Table I, Figure 4a, b). On the other hand, the distribution of the isotopic ratios of the epiphytes allows distinguishing two groups based on the location of the sampling area. The first group consists of samples that define an axis of atmospheric dispersion in the direction of Rio de Janeiro-Guapimirim-Teresópolis (***RJ***, ***GP***, ***TR***). The second one by the samples from Nova Friburgo (***LU***), where there are the major extension of the farmlands of Rio de Janeiro State. The plot ^{208}Pb/^{206}Pb vs ^{206}Pb/^{207}Pb for the epiphytes (Figure 4) showed that the 1st group (atmospheric dispersion) is linearly related, especially in the case of *Parmotrema crinitum*, while the 2nd group (farmlands) is quite scattered.

DISCUSSION

Metal concentrations in epiphytes of the different studied areas showed distinguished patterns, which are related with the distance from the urban area, distance from the shore, elevation above sea level (a.s.l.) and geochemical composition of rocks in each region (***RJ*** – densely populated area at sea level; ***GP*** – Ombrophyllous Forest at 600 m a.s.l;

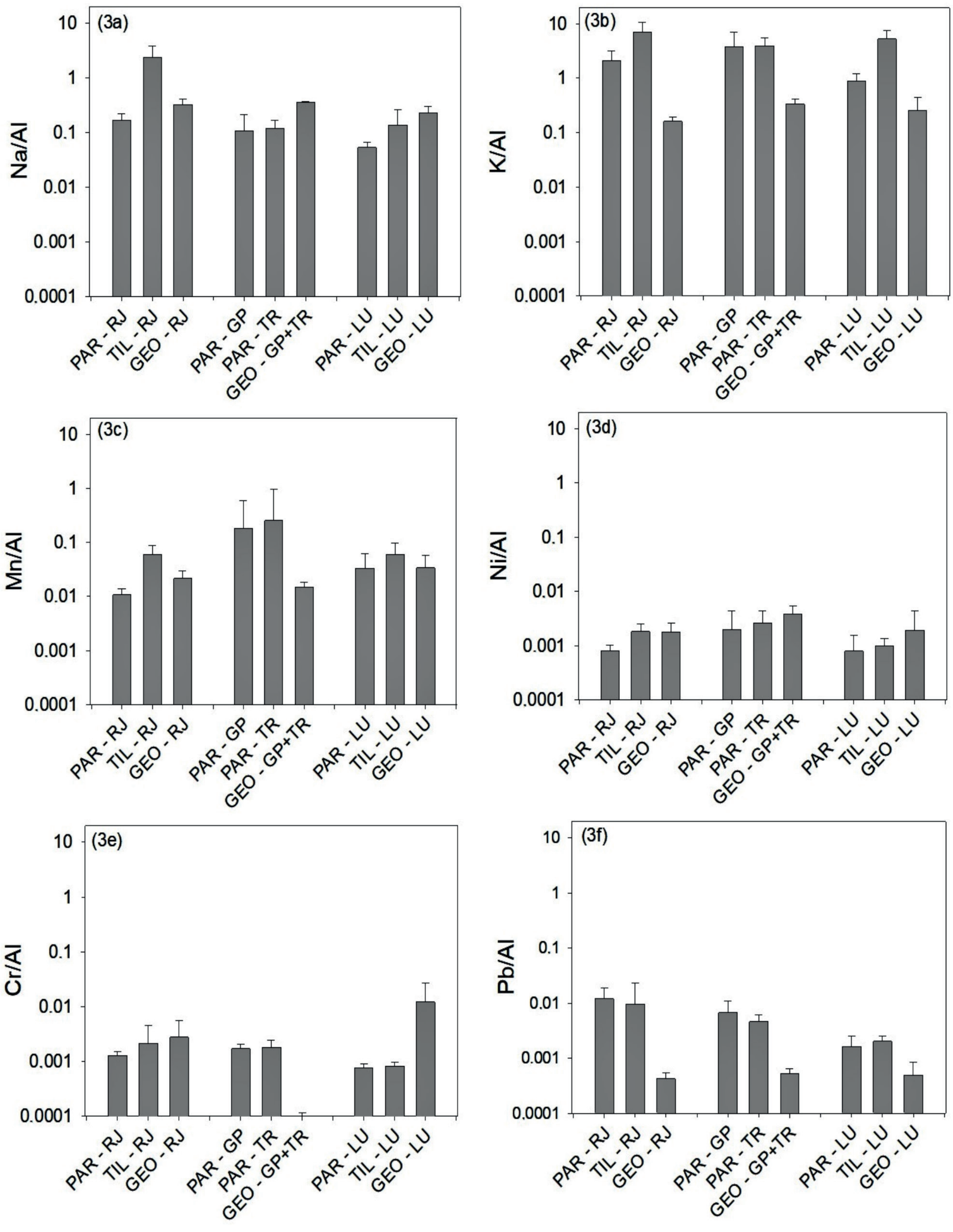

Figure 3 - Histogram of metallic elements (Na, K, Mn, Cr, Ni and Pb) normalized by Al for *Parmotrema crinitum* (Ach.), *Tillandsia usneoides* (L.) and rocks from sampling area in Rio de Janeiro State.

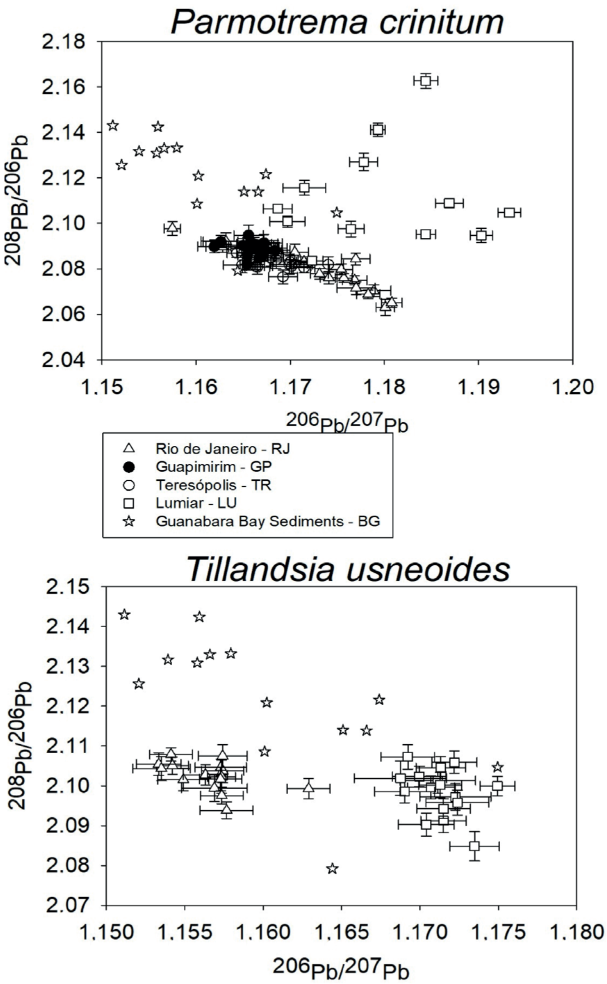

Figure 4 - Plot of lead isotope ratios ($^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{206}Pb$) for *Parmotrema crinitum* (Ach.) and *Tillandsia usneoides* (L.). Guanabara Bay sediments (BG).

TR – Pristine Ombrophyllous Forest at 1200 m a.s.l; ***LU*** – Farmlands with low demography at 900 m a.s.l.).

Studies comparing metal concentrations in epiphytes organisms with background levels, as local rocks, are lacking, and no work of such kind was known in Brazil. The average concentrations of Na, Al, Mn, Cr, Ni and Pb measured in the epiphytes in this study tended to be lower than those of the local rocks, while they were in the same order of magnitude as those reported for other bioindicators in Brazil (Figueiredo et al. 2004), South America (Abril et al. 2014) and European countries (Agnan et al. 2015, Basile et al. 2008, Jeran et al. 2002, Loppi and Pirintsosb 2003).

The potassium appears as an exception, since it was more enriched in epiphytes than the geological settings (Figure 1b). Nevertheless, potassium concentrations were in the same order of magnitude as those reported in other studies for epiphytes in Brazilian urban centers and in other countries (Figueiredo et al. 2004, 2007, Jeran et al. 2002). The potassium excess is highlighted by the [K] / [Al] ratios, which are always greater than 1 in the epiphytes ($K_{epi}/Al_{epi} > 1$) (Figure 2b). Potassium is a macronutrient essential for plant development, included epiphytes, and its uptake may not be exclusively by the atmospheric source, but indeed assimilated through the leaching of the foliage of the trees (Läuchli and Pflüger 1978). Thus, the observed behavior of K can be related with epiphyte metabolic activity produced by the K-Na pump, which is the mechanism leading the cells to sucking essential K, while discarding reactive Na. Besides, potassium is highly soluble and tends to be replaced in minerals being leached from weathered rocks.

Sodium and lead also distinguished by particular behaviors in epiphytes. The first by its high concentrations in epiphytes of the urban site (***RJ***), particularly in *T. usneoides*. This species showed Na concentrations higher than *P. crinitum*in Botanical Garden, as well as around five times higher than the epiphytes of the other sampling sites. The affinity of *T. usneoides* for Na can be attributed to anatomical particularities (Koz et al. 2010), but relatively high concentrations of Na have also been reported for epiphytes in the metropolitan region of São Paulo, the largest Brazilian city (Figueiredo et al. 2007). In this study, the presence of a spatial gradient in Na concentrations was described as follows: Rio de Janeiro (***RJ***) >Guapimirim (***GP***) >Teresópolis (***TR***) > Nova Friburgo (***LU***).This pattern is explained by the fact that the Botanical Garden (***RJ***) is located in the coastal area of the city of Rio de Janeiro, therefore under strong influence of the marine salt spray. In the other hand, the high Na concentration in bromeliad *T. usneoides* suggests that it would be a better indicator to trace de marine spray than *P. crinitum*.

Similar to the Na behavior, Pb also presented its highest concentrations in the epiphytes collected in the urban region (***RJ***). However, unlike the Na case, the concentrations of atmospheric Pb appear to be best mimicked by the lichen *Parmotrema crinitum*. Thus, in the urban area, this species presented the highest concentrations of Pb of the whole study, which were even similar to those of the rocks (Figures 2 and 3). A recent study about air quality in the same region using perturbation vectors, observed singular behavior for Pb in the two epiphytes (Monna et al. 2017) as occurred in the present study. High lead levels may be related with anthropogenic sources, as fuel burning, industrial processes and solid waste incineration, as recognized for some other urban areas in the world (Komárek et al. 2008, Monna et al. 2006). This is reinforced by the fact that the relatively high concentrations in epiphytes of the urban site, the Botanical Garden (***RJ***) are similar to those of other urban areas in Brazil and the world as well (Abril et al. 2014, Agnan et al. 2015, Basille et al. 2008, Figueiredo et al. 2007, Jeran et al. 2002, Käffer et al. 2012, Loppi and Pirintsosb 2003). In addition, Na and Pb stood out together with the isotopic ratio $^{206}Pb/^{207}Pb$, forming a group on the second axis of the principal component analysis (PCA) performed for *P. crinitum* (Figure 5). In Brazil, the use of Pb as an additive for gasoline was interrupted in 1986. However, residual Pb levels still remaining in the environment may have as main source the vehicle emissions (Fernández 2004). The $^{206}Pb/^{207}Pb$ ratio values obtained for both epiphytes in the urban site (***RJ***) were similar to those reported for gasoline in Brazilian cities such as São Paulo (Migliavacca et al. 2012). The observed pattern for the aerosol of this city is that the highest concentrations of Pb in the atmosphere coincide with large fireworks

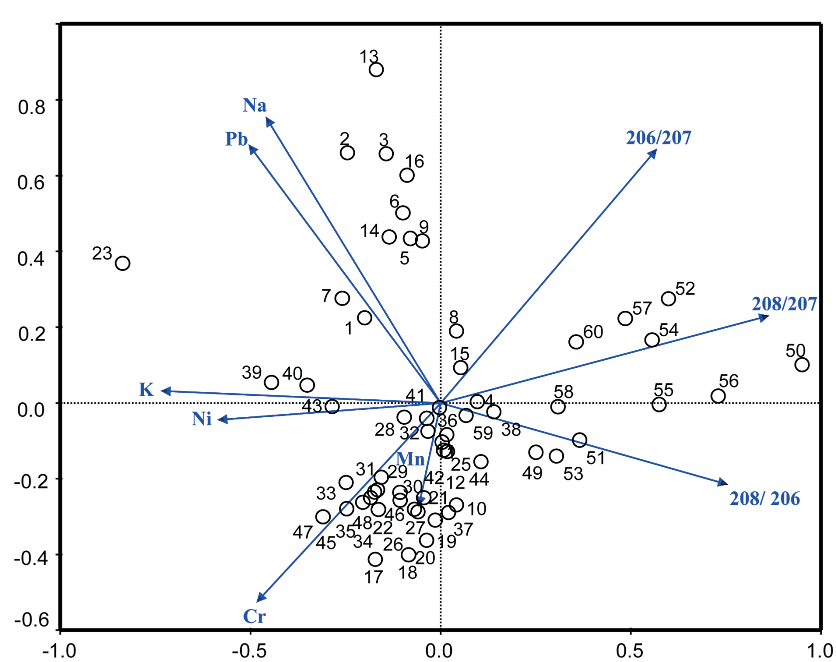

Figure 5 - PCA plot for metallic elements and isotope ratios of *Parmotrema crinitum* (Ach.) from four sampling sites in Rio de Janeiro State.

during celebration events and associated with high traffic occurrence (Gioia et al. 2010).

The distribution patterns of Na, Pb and $^{206}Pb/^{207}Pb$ ratios in Rio de Janeiro are likely driven by the wind regime. This suggests that the drivers of Pb dispersion should be related with circulation of major air masses by convection from polluted areas into the atmospheric boundary layer. In other words, frequent cold fronts in the region would transport air masses from the metropolitan region of the city of Rio de Janeiro towards the mountainous region of Teresópolis. These mountains, located approximately 60 km to the north, could act as a barrier to the moisture in these air masses, causing frequent orographic rainfall. Since the region of Nova Friburgo is located at the east side of the National Park (PARNASO) and far from the Rio de Janeiro downtown, it would be less affected by this system of atmospheric dispersion.

In contrast, the observed correlations between K, Ni and the $^{208}Pb/^{206}Pb$ ratio, responsible for the greater part of explanation of the PCA first axis seemed to be related to other factors. The potassium is assumed to be related to nutritional aspects, while the others (Ni and $^{208}Pb/^{206}Pb$ ratio) are supposed as fingerprints of local geology. High ^{208}Pb levels of epiphytes in Lumiar (Figure 4) suggest influence of monazite fluvial deposits that occurs in several places of the “Serra do Mar”(Overstreet 1967) as can be seen from samples 50 to 62 and $^{208}Pb/^{206}Pb$ vector (Figure 5). This could indicate a contribution of metals from rocks to epiphytes through aerosol deposition.

Positive correlations between chemical elements may indicate that they come from the same source (Hoff Brait and Filho 2010). For instance, one source related to atmospheric pollution could be represented by the correlation between Pb concentrations and the $^{206}Pb/^{207}Pb$ ratio in the epiphytes from the urban area ($R = 0.592$; $p<0.05$). Thus, it is evident that the first axis of the PCA plot is described by a natural (geological and/or nutritional) factor, while the second axis is associated with the anthropogenic factors. A study carried out in the Belém City metropolitan area (north Brazil) also clearly distinguished between natural Pb from lithosphere, and that derived from anthropogenic contribution, using the $^{206}Pb/^{207}Pb$ ratios. In the first case, the value of the $^{206}Pb/^{207}Pb$ ratio was around 1.20, whereas the anthropogenic Pb would have a $^{206}Pb/^{207}Pb$ ratio of equal or less than 1.15 (Moura et al. 2004). These values are comparable with those obtained in the epiphytes of this study.

CONCLUSIONS

Among all the metallic elements analyzed, the K was the only whose the concentrations in epiphytes were similar to those of the rocks of the local geological basement. All other elements presented higher concentrations in the rocks. Such an excess of K is attributed to its essentiality, as a macronutrient, for epiphytes development. The sodium, aluminum, manganese, chrome, nickel and lead concentrations in epiphytes were of the same order of magnitude of those reported in other studies conducted in Brazil, South America and European countries. Sodium and lead constituted a particular and differentiated group, distinct to the other elements. The first showed high affinity for the bromeliad *Tillandsia usneoides*, the second one for the *Parmotrema crinitum* and both of them presented their highest concentrations in the downtown Rio de Janeiro Botanical Garden. The concentrations of Na in the plants of the Botanical Garden were 5 times higher than those of the epiphytes from the other sites. That is attributed to the influence of the salt marine spray. The second aspect related to Na and Pb was the existence of a spatial concentration gradient (Rio de Janeiro >> Nova Friburgo > Guapimirim ~ Teresópolis). This pattern is attributed to the incidence of air masses from the metropolitan area of Rio de Janeiro to the Teresópolis mountainous region through cold fronts in the south - north direction and subsequent orographic precipitation, which is corroborated by the $^{206}Pb/^{207}Pb$ ratios. The results allowed elucidating a close connection between the pollution dispersion from the urban region of Rio de Janeiro and the slopes of "Serra do Mar". Both lichen *Parmotrema crinitum* and bromeliad *Tillandsia usneoides* are suitable to be used as bioindicators to evaluate the dispersion of atmospheric pollution by metallic elements in the State of Rio de Janeiro.

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