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SPATIAL DISTRIBUTION OF TRACE ELEMENTS IN TOPSOILS ADJACENT TO MAIN AVENUES OF SÃO PAULO CITY, BRAZIL

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ABSTRACT

In the present study, the concentration and distribution of Ba, Cu, Mo, Pb, S, Zn and Zr in soils collected along two main avenues (Pinheiros River Highway and Tietê River Highway) with high traffic density in the metropolitan region of São Paulo, Brazil, are presented, and their possible sources are discussed. These elements are strongly considered as contaminants originated from vehicular emissions. The analytical technique employed was XRF. The data set was evaluated by a *t* test for independent samples (group: avenues) at a 0.05 significance level. According to *t* test, the average contents obtained from Pinheiros River Highways are significantly different than the Tietê River, except for Mo. Multivariate statistic approaches (Pearson Correlation, Cluster and Factorial Analysis - FA) were adopted for data treatment. FA identified two main factors which accounted for about 86% of the total variance. The behavior of Ba, Cu, Pb, S and Zn were explained by the Factor 1. This indicates that the elements may have similar sources, probably related to gas emissions escaping from the vehicle fuel system. Factor 2 included Mo and Zr, suggesting their origin in the sample soils may be associated with the deterioration process of some device in the vehicular engine system or may be associated with the chemical composition of the urban soil analyzed.

1. INTRODUCTION

The compartment soil is considered a fundamental part of the global ecosystem, having the crucial function of supplier of nutrients and mechanical support to plants. Furthermore, soils act as a sink for various chemical compounds, including pollutants from anthropogenic activities. Within city environments the soil plays important roles that include serious effects on human health (by ingestion of soil and inhalation of suspended particles), biodiversity (as a central component of urban natural niches), and landscaping (green areas). As a result, the assessment of urban soil quality is necessary since the whole urban environment is affected by this kind of geological matrix. Notwithstanding, much less is known about the negative effects to the soil properties due to human activities.

São Paulo is the biggest city in South America with a population of around 19 million inhabitants in an 8,000 km^2 area with intense industrial activity and 8,4 million motor vehicles which are the main sources of pollution in the city. Previous work showed that the vehicular pollutant emissions are more important than the industrial emissions in São Paulo city[1].

The vehicular emissions are derived hydrocarbons (HC), nitrogen oxides (NOx) and carbon monoxide (CO) that are released into the environment. Moreover, the automobiles are also responsible to release into the atmosphere particulate matters which present high concentrations of some metals (traffic related elements, such as Ba, Cu, Pb and Zn) derived of fuel oil and other vehicular system devices [2].

The present study was carried out as a part of the research on pollution in urban soils collected from important avenues of São Paulo City, Brazil. This work presents the preliminary concentration results obtained for some traffic related elements (Ba, Cu, Mo, Pb, S, Zn and Zr) in soil samples collected along the Pinheiros River and Tietê River Highways. The analytical technique employed was X-ray fluorescence spectroscopy (XRF). In order to identify the possible vehicular sources of the elements, multivariate statistical approaches (Pearson Correlation, Cluster and Factorial Analysis – FA, with Extraction Principal Components) were applied to the data set[3, 4].

2. EXPERIMENTAL

2.1. Sampling

Urban soil sampling locations were carefully selected to represent a cross-section of high traffic density, in São Paulo City. Soils (n = 60 samples) were collected along transects perpendicular to the traffic-lane, in a depth range of 0-5 cm. To obtain representative soil samples, an area of $1m^2$ was sampled for each sampling point (10-15 cm parallel and 1 m perpendicular to the motorway).

2.2 XRF

Pellets (40 mm diameter) consisting of a mixture of 9 g of the sample and 1.5 g of powdered wax (Hoechst) were prepared and measured in a sequential XRF spectrometer (PW2404, Philips), equipped with a rhodium tube. The accuracy and precision of the results were verified by the analysis of the reference materials GSS-2 and GSS-4, presenting relative errors and precision better than 10%.

2.3 STATISCAL ANALYSIS

Multivariate statistical approaches are mathematical methods which facilitate the reduction, transformation and organization of original data set. These statistical tools create a new set of uncorrelated variables, which are the linear combination of the original ones with the same amount of information [3, 4]. The statistical analysis was done by using the STATISTIC® 6.0 program for Windows.

3. RESULTS AND DISCUSSION

The concentrations of the trace elements determined in urban soils collected from Pinheiros and Tietê River Highway are shown in Table 1. The data set was evaluated by Students *t* test to detect statistical differences between the average elemental concentrations in the soils from each sampling highway. According to *t* test ($p \leq 0.05$) the average concentrations are significantly different, except for Mo. Although the statistical test indicated difference in the soil chemical composition of the two highways, only for Ba and Zn the results were above the residential and industrial intervention guidelines values of Environmental Protection Agency of São Paulo State (CETESB), suggesting that these metals may cause some negative effect for human health (Table 1).

Table 1: Mean and range concentrations (µg g^{-1}) in the urban soils samples; comparison with guidelines values of CETESB[5].

	São Paulo Highway Concentrations (µg g^{-1})						CETESB guidelines values (µg g^{-1})		
	Pinheiros River			Tietê River				Intervention	
Element	***Mean***	***Min***	***Max***	***Mean***	***Min***	***Max***	***Prevention***	***Residential***	***Industrial***
Ba	230	37	504	446	187	761	150	500	750
Cu	53	10	137	93	21	166	60	400	600
Mo	4	1	7	3	1	5	30	100	120
Pb	44	7	120	104	26	205	72	300	900
Zn	140	35	361	519	75	1670	300	1000	2000
Zr	494	292	706	357	197	469	...	...	...
S	121	16	299	363	47	925	...	...	...

...no data reported

To investigate the similarity of trace elements in surface soils, hierarchical cluster analysis (HCA) was performed on log-transformed, standardized and centered data using Wards method on Squared Euclidean distances.

The dendrogram constructed from the data set is shown in Figure 1. Two main clusters form at level of dissimilarity ≈ 160. The first contained Zr and Mo and the second was composed of Zn, Pb, Cu, S and Ba. According to automotive parts manufacturers, some vehicle devices are made up of metals. For example, the three way type automotive catalytic converters which minimize the most important pollutants in vehicle exhaust (CO, NOx and HC) are usually based on a variety the chemical compounds that include Zr and Mo oxides and/or only Mo[1, 6]. Nevertheless, Mo contents (Table 1) were much lower than the prevention guidelines values of CETESB[5], which indicates that this metal should not be considered a problem to the environment and human health, in São Paulo. Accordingly, the first cluster could be considered a lithophile group.

The trace elements (Zn, Pb, Cu, S and Ba) grouped in the second cluster are frequently used to evaluated the pollutant contributions of the vehicular emissions. These elements are present, especially in fuel oil (gasoline and diesel), in alcohol fuel, lubricants and in some parts of the vehicle engine[7].

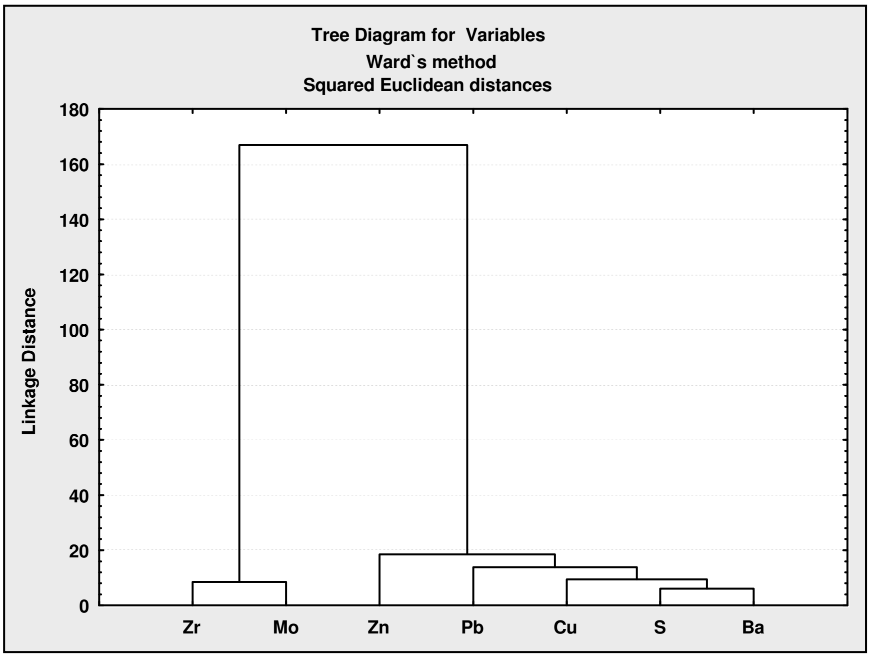

Figure 1. Hierarchical clustering results of trace elements concentrations in urban soils of Pinheiros River and Tietê River Highways

Although HCA represents a useful tool for investigating relationships between variables where the researcher has no *a priori* knowledge of the number of groups, the statistical approach can force the objects to form cluster that can not be separated, thus misleading clusters formed early may be propagated throughout the process[3,4]. An alternative and increasingly popular approach to the analysis of multivariate geochemical data is Factorial Analysis – FA, with Extraction Principal Components.

The FA method describes the behavior of the variables in complex environmental compartments by finding summarizing factors, which are often causally explained. The first component is the combination of variables that explain the greatest amount of variance. The second component defines the next largest amount variance and is independent to the first component. Kaiser criterion is commonly used to determine the number of components for the data set[4]. The structure of these components (or variables contained in them) may be used to identify common characteristics or processes, for example: common sources for the considered variables. Summarizing, the extracted factors (according to mathematical fundamentals) reflect the main part of information of the data set[4].

In the FA (with Extraction Principal Components) for data sets, applying the varimax-raw rotation, two principal components were considered, which accounted for about 86% of the total variance, according to Kaiser criterion used to assess the results of initial eigenvalues (Table 2). The matrix of the components for the data set indicated that Ba, Cu, Pb, Zn and S presented good correlation and were associated into the first component (F1), with a factor loading of ≥ 0.86, while Mo and Zr were associated into the second factor (F2).

Table 2: Factor Loadings (Varimax normalized)
Extraction: Principal components
(Marked loadings are > 0.70)

Variable	Factor 1	Factor 2
Ba	**0,90**	-0,41
Cu	**0,88**	-0,18
Mo	-0,01	**0,97**
Pb	**0,88**	-0,06
Zn	**0,86**	0,00
S	**0,89**	-0,23
Zr	-0,32	**0,91**
Eigenvalue	4,46	1,55
%Total Variance	63,77	22,19
% Cumulative	85,95	

F1 contains the elements the possible contaminants linked with anthropogenic activities. S and Ba are derived (especially) from diesel cycle engines, while Zn, Cu, Pb are derived from emissions of lubricants and gasoline fuel. Earlier study based on the composition of light-duty motor vehicle exhaust particulate matter suggested that Cu/Zn ratios of 0.21 ± 0.15 and 0.01 ± 0.003 are characteristics gasoline and diesel powered vehicle, respectively[8]. The Cu/Zn mean ratios (in this wok) were 0.37 for Pinheiros River Highway and 0.19 for Tietê River Highway. Therefore, the comparison of the Cu/Zn ratios with the literature results[8] suggests the gasoline vehicular emissions are the main sources of Cu and Zn in the urban soils analyzed. Accordingly, F1 indicated that the variables are strongly associated with the traffic of São Paulo City.

F2 includes the metals Mo and Zr, whose origins may be associated to engine components[1,6] Nonetheless, comparison Mo results with CETESB guidelines values[5] indicated that there is no risk for environment and human health. Thus, the behavior of Mo and Zr was not well established in the FA.

Similar information was observed for Pearson correlation (Table 3). The coefficients showed a strong relationship between Mo and Zr, while Ba, Cu, Pb, Zn and S are strongly correlated, presenting coefficient values ≥ 0.65 (Table 3).

Therefore, the same behavior was observed for the trace elements analyzed in the urban soil samples, according to the statistical tests used to evaluate the data obtained for the present study.

Table 3: Pearson´s Correlation
Marked correlations are significant at $p < 0.050$

Variable	*Ba*	*Cu*	*Mo*	*Pb*	*Zn*	*S*	*Zr*
Ba	1,00	**0,87**	-0,42	**0,81**	**0,77**	**0,88**	-0,43
Cu		1,00	-0,15	**0,78**	**0,68**	**0,78**	-0,43
Mo			1,00	-0,08	-0,04	-0,20	**0,83**
Pb				1,00	**0,65**	**0,70**	-0,34
Zn					1,00	**0,77**	-0,26
S						1,00	-0,50
Zr							1,00

4. CONCLUSIONS

The comparison of some metal concentrations in the urban soils from important highways of São Paulo City with CETESB guidelines values indicated that only Ba and Zn may be considered environmental pollutants in the sampling locations.

The multivariate statistical tests pointed two main groups to explain the behavior of the trace elements:

- Mo and Zr presented strong relationship, with an origin that could not be determined.
- Ba, Cu, Pb, Zn and S were strongly correlated and their principal source in the soil samples from Pinheiros River and Tietê River Highways may be associated with vehicular emissions in São Paulo City.

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REFERENCES

1. C. P. R. Morcelli, A. M. G. Figueiredo, J. E. S. Sarkis, M. Kakazu, J. Enzweiller and J. B. Sigolo, “PGEs and other traffic related elements in roadside soils from São Paulo, Brazil”, *Sci.Total Environ.*, **345**, pp. 81-91 (2005).
2. M. Moldovan, M. A. Palacios, M. M. Gomez, G. Morrison, S. Rauch, C. Mcleod, R. MA, S. Caroli, A. Alimonti, F. Petrucci, F. Bocca, P Schramel, M. Zischka, C. Pettersson, U. Wass, M. Luna, J. C. Saenz and J. Santamaria, “Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters”, *Sci. Total Environ.*, **296**, pp. 199-208 (2002).

3. A. Facchinelli, E. Sacchi, L. Mallen "Multivariate statistical and GIS-based approach to identify heavy metal sources in soils", *Environmental Pollution*, **114**, pp. 313-324 (2000).
4. P.M.B. Landim, *"Análise estatística de dados geológicos multivariados"*. Texto Didático - DGA, IGCE, UNESP/Rio Claro, Lab. Geomatemática, 2000.
5. CETESB - Companhia de Tecnologia de Saneamento Ambiental *"*Qualidade do ar no Estado de São Paulo - Série Relatórios*",* São Paulo, 2007. http://www.cetesb.sp.gov.br/Ar/publicacoes.asp.
6. J. D. Whiteley, *Autocatalyst derived platinum group elements in the roadside environment occurrence mobility and Fate*, PhD Thesis. Murdoch University, Austrália, 358p (2004).
7. M. F. Silva, *Emissão de metais por veículos automotores e seus efeitos à saúde pública. Dissertação*, Dissertação (Mestrado) – Universidade de São Paulo, Brasil, (2007).
8. S. H. Cadle, P. A. Mulawa and E. C. Hunsanger, "Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area", *Environ. Sci. Tech.*, **33**, pp. 2328-2339 (1999).