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SPATIAL DISTRIBUTION OF METALS IN SOIL SAMPLES FROM ZONA DA MATA, PERNAMBUCO, BRAZIL USING XRF TECHNIQUE

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ABSTRACT

Soil contamination is today one of the most important environmental issues for society. In the past, soil pollution was not considered as important as air and water contamination, because this was more difficult to be controlled, becoming an important topic in studies of environmental protection worldwide. Based on this, this paper provides information on the determination of metals in soil samples collected in Zona da Mata, Pernambuco, Brazil, where normally the application of pesticides, insecticides and other agricultural additives are used in a disorderly manner and without control. A total of 24 sampling points were monitored. The analysis of Mn, Fe, Ni, Zn, Br, Rb, Sr, Pb, Ti, La, Al, Si and P were performed using Energy Dispersive X-Ray Fluorescence. In order to assess the development of analytical method, inorganic Certified Reference Materials (IAEA-SOIL-7 and SRM 2709) were analyzed. In each sampling site, the geoaccumulation index were calculated to estimate the level of metal contamination in the soil, this was made taking into account the resolution 460 of the National Environmental Council (CONAMA in Portuguese). The elemental distribution patterns obtained for each metal were associated with different pollution sources. This assessment provides an initial description of pollution levels presented by metals in soils from several areas of Zona da Mata, providing quantitative evidence and demonstrating the need to improve the regulation of agricultural and industrial activities.

1. INTRODUCTION

Heavy metals are natural components of the earth's crust, and together with other elements, are part of the crystal structure of rocks. These metals in certain concentrations, are essential for human survival, as well as play a key role in the development of civilizations and the performance of modern society, with the transformation of raw materials into manufactured products. The problem arises when it occurs disorderly industrial use and without social responsibility, which ultimately affects health, as a consequence of population growth in urban areas and rapid industrialization, particularly in developing countries.

Small amounts of metals are incorporated into living organisms, mainly through food, drinking water and air. Although some of them are essential (V, Mn, Fe, Co, Cu, Zn, Sr and Mo), to the development of vital functions of organisms, in excessive amounts are harmful or even lethal for living beings, with a very small margin between toxicity and essentiality [1], [2]. The risk of heavy metals is higher because they are not chemically or biologically degradable, and once in the soil, are absorbed and can remain in the environment for hundreds of years [3].

Studies indicate that these elements enter the environment as a result of natural processes and human activities [4], [5]. Natural sources include volcanic activity, erosion, among others. The anthropogenic sources include human activities, such as the discharge of effluents of many industries (plastics, production of hygiene and cleaning materials, production of furniture, mattresses and ceramics), vehicle emissions, the mining work, the application of fertilizers and pesticides in mechanized farming areas, thus increasing the concentrations of metals in the environment with risks often unknown.

To determine the impact of human activities, it is necessary highly sensitive and reliable analytical techniques, among them are Atomic Absorption Spectrometry with flame, Optical Emission Spectrometry with Inductively Coupled Plasma, Mass Spectrometry with Inductively Coupled Plasma, Neutron Activation Analysis, X-Ray Fluorescence (XRF), among others [6]–[11].

The soil along with water, air and sunlight are the basis of life in terrestrial ecosystems, and has a wide variety of organisms, being considered a natural resource of great importance, which performs functions on earth's surface as natural reactor and "habitat" of living organisms, as well as infrastructure support and source of non-renewable materials. In recent years, the contamination of soil in developed countries becomes the main focus of research to avoid compromising other sources such as water and food. On this basis, this study aimed to determine some trace metals, including Mn, Fe, Ni, Zn, Br, Rb, Sr, Pb, Ti, La, Al, Si and P in soil samples collected in the state of Pernambuco. Analysis of these elements was carried out by XRF technique. The analytical results were evaluated through the use of Certified Reference Materials (CRM). They were presented spatial distribution maps of the content of metals, which can be used to find different sources of contamination in Zona da Mata, Pernambuco.

2. MATERIALS AND METHODS

2.1. Study Area

The study area is located in Zona da Mata, state of Pernambuco. This subdivision is located along the northeastern coast of Brazil, parallel to the Atlantic Ocean (Fig. 1), corresponding to the strip of land that extends from Atlantic coast to the foothills of the Plateau of Borborema, with an area a little higher than 11.000 km^2.

Figure 1: Location of Zona da Mata, Pernambuco.

The choice of this area was given for present the most urbanized, industrialized and economically developed of Pernambuco, concentrating the majority of the population and the largest number of Northeast industries [12].

2.2. Sample Collection and Preparation

In the region of Zona da Mata samples were taken with three repetitions each. In total, 110 samples were collected, with a depth of 10 to 40 cm, at 24 points (see Fig. 2). For the collection of the samples were opened trenches of 0.7 x 0.7 m, as recommended by EMBRAPA [13].

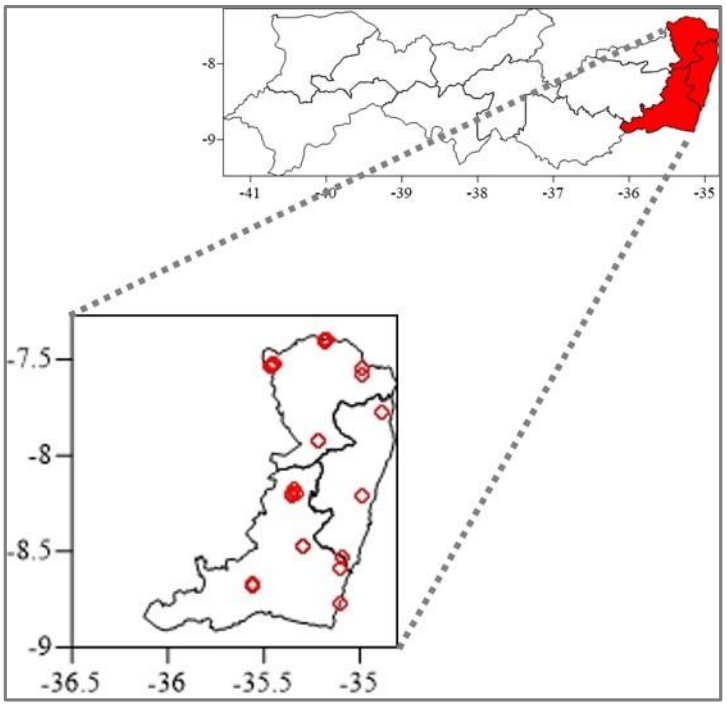


Figure 2: Sampling sites.

The samples were dried in the shade to air and passed through sieve to a size of 2 mm. They were then macerated in agate mortar and sieved through a sieve with opening 75 µm (ABNT/ASTM 200).

2.3. Measurement System

The Energy Dispersive X-ray Fluorescence Spectrometer - EDXRF, EDX model 720, Shimadzu, is composed of a rhodium tube for generating X-rays, sealed chamber for sample analysis in vacuo and the Si(Li) detector for quantification of the incident radiation.

For the construction of calibration curves, reference materials were used with mass fractions variables, to allow adequate range for determining geological matrices. The reference materials used were SEM 1646a (estuarine sediment), SEM 1944 (New York / New Jersey waterway sediment) and SEM 2710 (montana soil), produced by the National Institute of Standards & Technology (NIST), as well as IAEA-SL-1 (lake sediment) and IAEA–SOIL-7, produced by the International Atomic Energy Agency (IAEA). The analytical portions of reference materials were transferred to containers covered with polypropylene, ensuring smooth surface for the analyzes. Independent test portion of the SRM 2709 and IAEA-SOIL-7 materials was prepared to assess the quality of the analytical procedure. After the energy calibration of the equipment, all samples were subjected to vacuum to perform the analyzes. The analysis time was 300 seconds, with a dead time of at most 35% for each of the chemical elements. For the elements Co, Fe, La, Mn, Ni, Pb, Rb, Sr, Ti, Zn and Br, the voltage was set to 50 kV, and Mo filter was used, whereas for Al and Si, the voltage was 15 kV with Al filter. The results were expressed as dry weight (water content of 1%). The estimation of the uncertainty was based on the variability between replicates and accuracy of the calibration curve [14], [15].

For quality evaluation of the analytical procedure, we used the number En (equation 1). The adequate range for the results of reference materials was considered between -1 and 1 as recommended by ISO 13528 (2005) [16].

$$E_n = (x_{obs} - x_{ref})/\sqrt{(U_{obs})^2 - (U_{ref})^2} \quad (1)$$

where: X_{obs} is the value obtained in the analysis of the sample; X_{ref} is the certificate or reference value; U_{obs} expanded analytical uncertainty at the 95% confidence level of the obtained value and U_{ref} the expanded analytical uncertainty of the sample in 95% confidence level of the certified or reference value.

2.4 Geoaccumulation Index

The level of heavy metal contamination in the soil is analyzed and determined by geoaccumulation index (Igeo), which was established by Muller (1969) [17]. Igeo is obtained by comparing the contamination levels before contamination and present contamination (equation 2).

$$I_{geo} = log_2[(C_n/1.5B_n)] \quad (2)$$

where: Cn is the measured mass fraction of the metal (mg kg^{-1}); B_n is the background mass fraction of the metal (mg kg^{-1}) (in the present study was considered as B_n to those values established by CONAMA [18]) and 1.5 was introduced to minimize the effect of possible variations in the background values.

3. RESULTS AND DISCUSSION

3.1 Analysis of CRMs

The quality of the analytical procedure was based mainly on Certificates Reference Materials analysis. The results obtained for Mn, Fe, Ni, Zn, Br, Rb, Sr, Pb, Ti, La, Al, Si and P in the analysis of the CRM are summarized in Table 1. The concentration values were expressed as the mean for six replicates (n = 6) in the case of SRM 2709 and for n = 8 in the measurements of SOIL-7 and the corresponding expanded analytical uncertainties in the 95% level of confidence derived from the combination of individual uncertainties related with the precision and accuracy of the CRM results.

Table 1: Analysis of SOIL-7 and SRM 2709 CRM (values expressed in mg kg^{-1})

Element	Cert. value	XRF	E_n
Mn	631 ± 46[b]	564 ± 49	-0.99
	538 ± 17[c]	538 ± 51	-0.01
Fe	25700 ± 1100[a,b]	23948 ± 1396	-0.99
	35000 ± 1100[c]	33276 ± 1398	-0.97
Ni	26 ± 8.0[a,b]	23 ± 4.8	-0.28
	88 ± 5[c]	80 ± 6.8	-0.96

Zn	104 ± 12[b]	98 ± 17	-0.31
	106 ± 3.0[c]	112 ± 17	0.36
Br	7.0 ± 3.5[a,b]	8.6 ± 2.8	0.36
	NC[c]	-	-
Rb	51 ± 9.0[b]	51 ± 5.2	0.01
	96 ± 2.0[a,c]	104 ± 5.6	0.99
Sr	108 ± 11[b]	102 ± 10	-0.38
	231 ± 2.0[c]	257 ± 11	0.98
Pb	60 ± 16[b]	54 ± 12	-0.28
	19 ± 0.50[c]	22 ± 12	0.25
Ti	3000 ± 1100[a,b]	2998 ± 285	0.00
	3420 ± 240[c]	3559 ± 290	0.37
La	28 ± 2.0[b]	28 ± 4.4	0.09
	23 ± 4.6[a,c]	29 ± 5.1	0.95
Al	47000 ± 7000[a,b]	47252 ± 4806	0.03
	75000 ± 600[c]	70106 ± 4908	-0.99
Si	180000 ± 32000[a,b]	183681 ± 29423	0.08
	296600 ± 2300[c]	268264 ± 29433	-0.96
P	460 ± 2.0[a,b]	516 ± 196	0.29
	620 ± 50[c]	446 ± 170	-0.98

[a] informative value
NC. not certified
[b] SOIL-7
[c] SRM 2709

In the table, it can be seen that for all quantified chemical elements, no significant differences were detected between the calculated concentration and the certified values for all elements corresponding. The E_n values were obtained between -1 and 1, range considered adequate according to ISO 13528 (2005) recommendation [16]. It is noteworthy that for Pb in SRM 2709, was quantified with low metrological level, since the expanded analytical uncertainty reached 55%. According to the data obtained, it can be affirmed that the EDXRF method can be reliably applied to the analysis of the interest metals in soil samples.

3.2 Contamination Level for Ni, Zn and Pb

The geoaccumulation index was calculated only for the metals Ni, Zn and Pb, due to only were found in the resolution 460 of CONAMA [18], the background values of the elements mentioned. In Table 2 are found the values of this index.

Table 2: Heavy metal contamination in soils (Igeo)

Sample point	Ni	Zn	Pb
1	0.93	0.45	1.38
2	0.83	0.48	1.66
3	1.07	0.33	1.65
4	0.81	0.35	1.60
5	0.97	0.67	0.98
6	0.93	0.43	0.81

7	1.28	0.29	1.50
8	1.13	0.29	2.08
9	0.83	0.18	1.24
10	1.21	0.35	1.43
11	0.75	0.44	0.15
12	0.34	0.13	0.66
13	0.82	1.04	1.68
14	0.53	0.16	1.14
15	0.62	0.48	1.85
16	1.03	0.05	0.97
17	0.66	0.50	1.69
18	0.33	0.25	1.40
19	-0.20	0.09	1.18
20	-0.02	0.10	1.22
21	0.57	0.41	1.98
22	1.60	0.77	1.00
23	1.00	0.26	0.89
24	0.48	0.38	1.26

The background values for Ni, Zn and Pb for soil samples is 9.0, 35 and 13 mg kg^{-1}, respectively. In general, Ni and Zn show the lowest Igeo values for most the sampling points, representing soils unpolluted to moderately polluted ($0 < Igeo \leq 1$). Highest values was obtained for Pb, with mean value of 1.31, showing moderately polluted soils ($1 < Igeo \leq 2$) [17]. Ranges in Igeo values for the metals are very wide, varying from 0 to 1.98, confirming the variability of urban soils.

Concentrations of the heavy metals in urban soils of Zona da Mata were compared with those of other cities in the world, Table 3.

Table 3: Mean concentration (mg kg^{-1}) in urban soils from different cities in the world

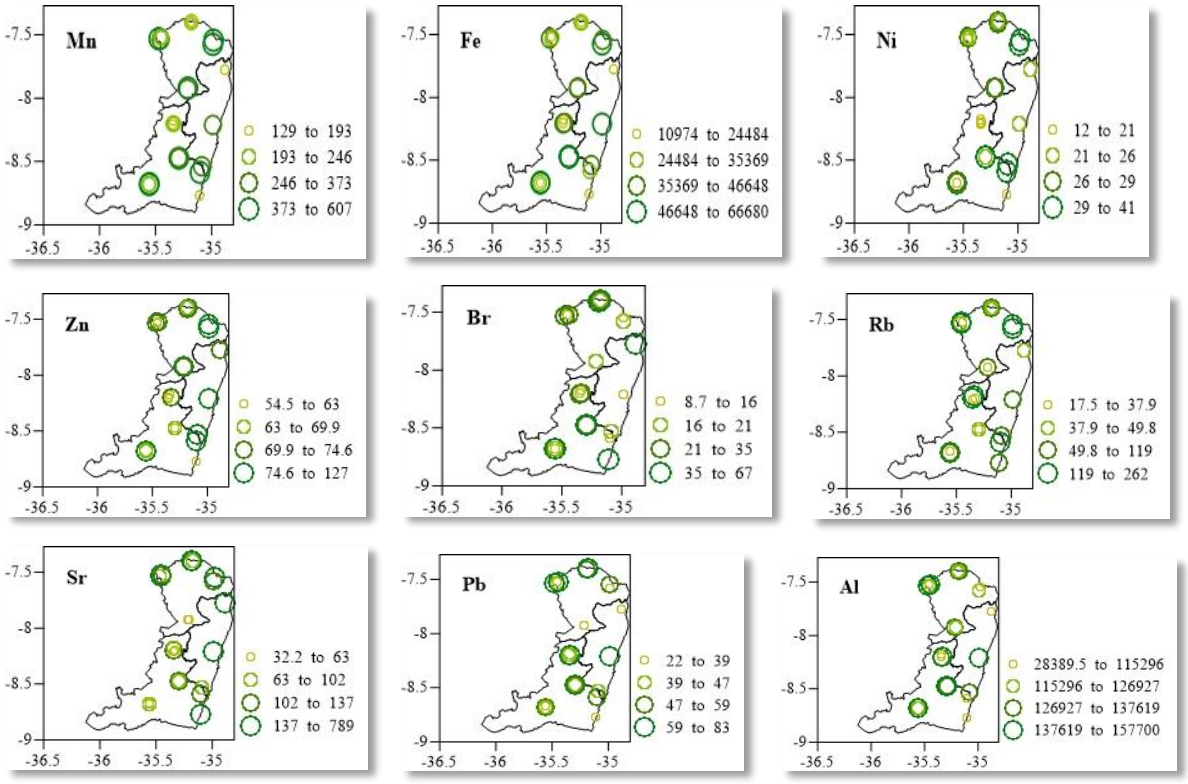
City/Country	Mn	Fe	Ni	Zn	Pb	Reference
Tuscany, Italy	-	-	59	128	219	[19]
Missouri, USA	298	9951	16	96	49	[20]
Talcahuano, Chile	-	-	23	333	35	[21]
Havana, Cuba	-	-	66	240	101	[22]
Fallujah, Iraq	24	236	8.9	5.5	3.8	[23]
Guangdong, China	371	5.09	26	-	51	[24]

Ghaziabad, India	21	433	147	187	147	[25]
Chittagong, Bangladesh	161	-	860	139	7.3	[26]
Zona da Mata, Brazil	285	36693	25	74	49	This study

The Fe mean concentration in Zona da Mata was significantly higher than their corresponding concentrations in other cities of the world. The mean concentrations of Ni, Zn and Pb were higher than their background values for this study, while Ni and Zn display lower concentrations than other cities shown in Table 3. For Pb, a similar concentration between Missouri, Talcahuano, Guangdong and the present study was obtained.

3.3 Obtaining of the Distribution Maps

Fig. 3 shows the classed post maps for each element analyzed. The sampling sites are represented by circles and the size of them corresponds to the elemental concentration levels on these points. As can be seen the metals analyzed are widely distributed in Zona da Mata of Pernambuco, with the highest concentrations to Mn, Fe, Al, Ti and Si.



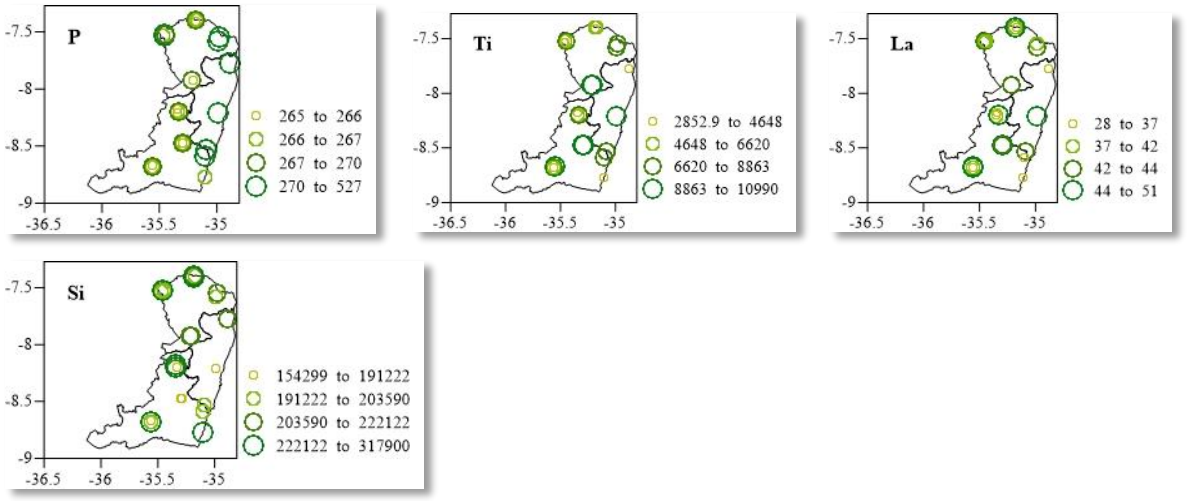


Figure 3: Elemental distribution profiles (values expressed in mg kg^{-1}).

Correlations between the values obtained for the analyzed elements were calculated. Commercial software for data processing SPSS version 15.0 was used, verifying that there are no significant differences to a significance level less than 0.05, justified by the correlation coefficients obtained between Fe, Ti, La, Al, Si, Ni, Mn, Rb and Zn, and between P, Br, Pb and Sr (see Table 4).

Table 4: Correlation matrix for study elements

	Mn	Fe	Ni	Zn	Br	Rb	Sr	Pb	Ti	La	Al	Si	P
Mn	1												
Fe	0.67	1											
Ni	0.44	0.68	1										
Zn	0.39	0.45	0.47	1									
Br	-0.23	0.05	0.22	-0.07	1								
Rb	-0.22	-0.48	-0.4	-0.2	-0.44	1							
Sr	-0.2	-0.3	0.03	-0.11	-0.01	0.23	1						
Pb	0.08	0.19	0.04	0.09	-0.14	-0.23	-0.26	1					
Ti	0.59	0.86	0.55	0.39	0.02	-0.45	-0.3	0.14	1				
La	0.56	0.88	0.73	0.39	-0.04	-0.39	-0.04	0.12	0.77	1			
Al	0.48	0.63	0.43	0.34	-0.12	-0.23	-0.46	0.62	0.59	0.57	1		
Si	-0.35	-0.69	-0.46	-0.28	-0.21	0.56	0.25	-0.5	-0.57	-0.48	-0.59	1	
P	-0.15	-0.19	0.07	0.2	0.55	-0.02	0.39	-0.48	-0.21	-0.23	-0.5	0.09	1

Note: the correlations are significant at the 0.01 level.

After obtaining the concentration profiles and element correlations, proceed to the multivariate statistical analysis (principal components or factors) which aims to reduce variables and identify potential sources of contamination. Statistical analysis was performed using SPSS (the rotation method was the Varimax with Kaiser normalization). These factors or components help for better identification and understanding of potential sources of pollution. In Table 5 loads of components obtained with the SPSS program are observed.

The composition of the factors is related to natural and anthropogenic sources of pollution. Factor 1 shows a correlation, mainly from natural sources which relates elements that come from soil (Fe, Ti, La, Al, Si, Ni, Mn, Rb and Zn) or as result of anthropogenic activities (Fe, Ti, La, Al, Ni and Zn). The elements of Factor 2 (P, Br, Pb and Sr) are correlated each other, where their presence are, in most cases originated from marine aerosols.

Tabla 5: Loads of the main components extracted by applying rotation Varimax and Kaiser normalization

Element	Factor 1	Factor 2
Fe	0.94	0.12
Ti	0.86	0.08
La	0.84	0.14
Al	0.79	-0.41
Si	-0.75	-0.06
Ni	0.71	0.42
Mn	0.68	-0.03
Rb	-0.56	-0.33
Zn	0.52	0.24
P	-0.29	0.85
Br	0.02	0.69
Pb	0.39	-0.55
Sr	-0.37	0.41

4. CONCLUSIONS

The Mn, Fe, Ni, Zn, Br, Rb, Sr, Pb, Ti, La, Al, Si and P concentrations were analyzed, in soil samples of Zona da Mata, Pernambuco, using EDXRF technique. According to the results obtained, it was concluded that the soils are not high levels of these metals. Maps of elemental distribution were created. Principal Components Analyses was performed to study the correlations between the different chemical elements. It is recommended for future work to determine the concentration of other metals for a better correlation to the contamination sources.

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