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Detection and Evaluation of metals in soil under influence of mining by Dispersive Energy X-ray Fluorescence Spectrometry (EDXRF), Lavras do Sul/RS

Cristiane Heredia Gomes*, Diogo Gabriel Sperandio, Rafael Lima Dessart e Dionatan Daniel Giusti

Universidade Federal do Pampa, Campus Caçapava do Sul, RS, Brasil

Abstract

Rocks are the primary source of chemical elements found in the earth. Among them metallic elements, which are distributed in most natural environments and their distribution in soils is widespread. Knowledge of the soil chemical composition will provide subsidies for a prediction of phytotoxicity and possible groundwater contamination. Concentrations of metals, in the right quantities, are essential for maintaining life. Although, if in high quantities (toxicity), can cause damage to plants, animals, and humans. This work consists of a chemical analysis of soil samples in the region of Lavras do Sul / RS, where mineral deposits occur. Until the year 1981 mining activities occupied the area without municipality, resulting in ore and waste deposits at inappropriate places, generating environmental liabilities, contributing to soil chemistry, and consequently affecting public health. Through the energy dispersive X-ray fluorescence spectrometry (EDXRF) method, 20 soil samples were analyzed in two profiles surrounding the municipality. Among them, high concentrations of Zn, Cu, Ce and Cd were detected, possibly contributing to anthropic activities and seasonal fluctuations.

Keywords: *Geology; Soil; Mining*

* cristianegomes@unipampa.edu.br

1 Introduction

Metals are distributed in most of the natural environment, their distribution in soils widespread. The availability of these elements depends on the physical, chemical and mineralogical attributes of the soil. However, the metals present may have lithogenic and anthropogenic sources depending on the origin. The natural origin depends on the soil source material and weathering rates, as well as the surrounding human activity which can increase their concentration (IMPERATO et al, 2003).

Rocks are the primary source of chemical elements found in soil. Many of these elements, in the right amounts, are essential for maintaining life. However, if in low amounts (deficiency) or in high amounts (toxicity) it can damage plants, animals and human beings (CENTENO et al, 2016).

Therefore, the knowledge of the chemical composition of the soil provides subsidies for the prediction of the phytotoxicity and possible contamination of the water table, since if a certain capacity is exceeded, the metal has the potential to be leached (BOSCOV et al, 1999). Thus, the concentration of these metals may be higher than allowed since it has a cumulative effect on organisms (BRASIL, 2009). The direct effects are caused by the ingestion of contaminated vegetables, once they are absorbed (LAKE, 1987). The indirect effect is through the ingestion of previously contaminated animals or by-products prepared with the vegetables coming from this soil.

The investigation of soils in Lavras do Sul/RS city is a unique opportunity since it is known for its occurrences of mineral deposits, among them, hydrothermal products consisting of Au-quartz veins with some Fe sulfide Cu and/or Pb embedded in granite and andesitic rocks (PESTANA; FORMOSO, 2003). Mining activities in the region date from the late nineteenth century, where until 1981 sterile and tailings were deposited in improper places. Additionally, gold was recovered by amalgamation with mercury, generating many environmental liabilities, contributing to chemical alteration of the soil and consequently affecting the health of the population.

In order to detect and evaluate metals in the city's soils in a simple, fast and low-cost way, the X-ray spectrometry by dispersive energy- EDXRF was used in the evaluation of the modifications in the contents of chemical elements present in the soil (WASTOWSKI et al, 2010). In addition, the EDXRF is a device that allows its use *in situ*, having a high potential of application in areas where there is a need for correlation between metals and non-metals, toxic or non-toxic. This method utilizes X-ray signals to excite an unknown sample, causing the individual elements present in the soil to emit their characteristic (fluorescent) X-ray, thereby determining the chemical composition of the sample. The use of EDXRF can be extended to any type of material and dimension allowing the analysis of various elements simultaneously. Among the advantages of the EDXRF method, we can highlight the simplicity, rapidity, and reliable data collection, as well as the possibility of simultaneous analysis of oxides and other elements in samples. The device has an analyzer system with monochromator crystals, where its operating principle is X-ray diffraction, data acquisition, and processing, through the use of an internal library, allowing it to obtain real-time results (BRUKER, 2017).

An atom and its abundance can be identified or measured through the X-ray emission (JENKINS et al, 1981). In this sense, the fluorescence radiation identifies the element and its intensity as its concentration varies throughout the sample.

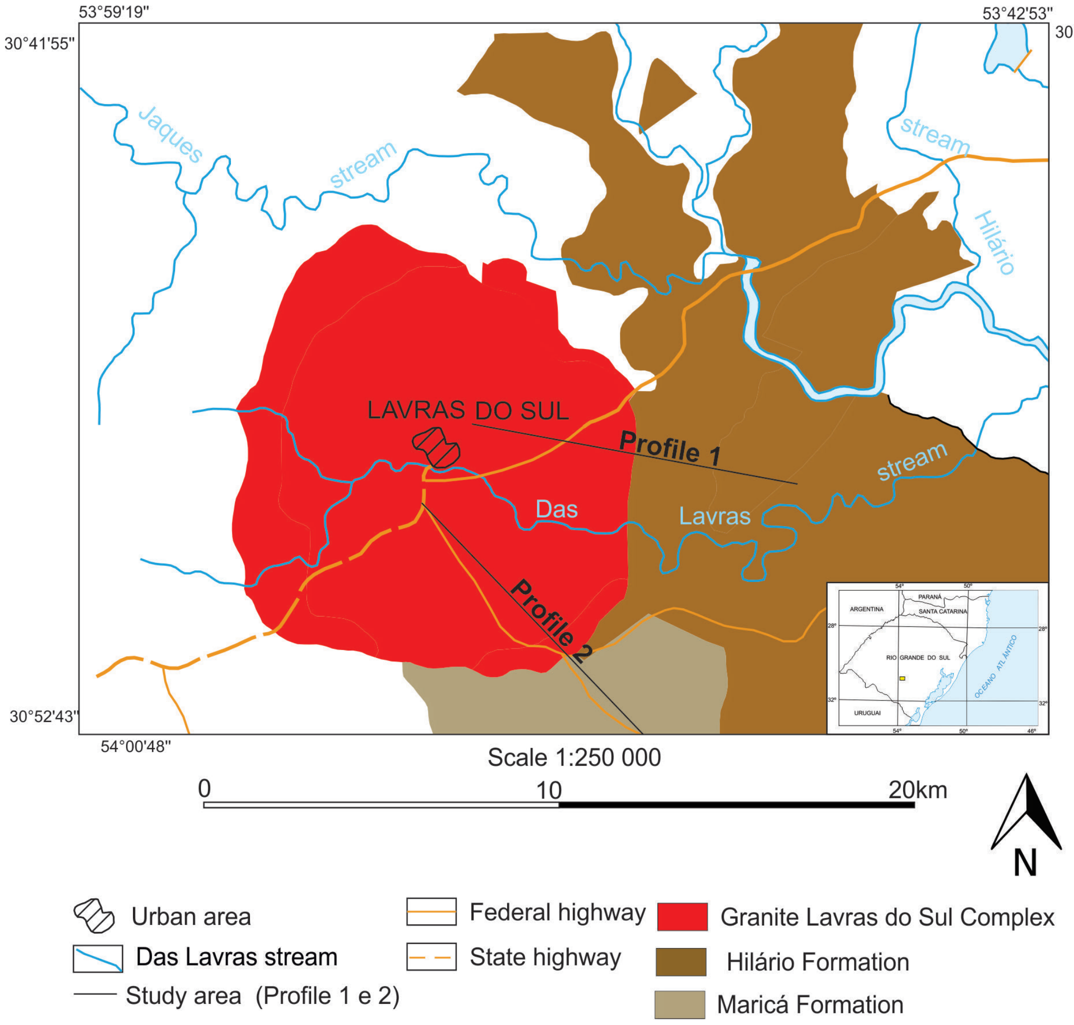
The aim of this paper is to characterize the changes in the chemical parameters of metals and non-metals in different levels of soil, especially the most important ones for human health, aiming to contribute to the integration of knowledge in this area, with the EDXRF technique.

2 Geological characterization of the study area

The study area is located at Lavras do Sul, Rio Grande do Sul, 324 km southwest of Porto Alegre, between Caçapava do Sul and Bagé, with access highways BR-290, BR-392 and RS-357 (Figure 1).

The location is well known for its mining activity, including the occurrence of mineral deposits constituted by auriferous mineralization and primary gold-copper related to the Granite Lavras do Sul Complex and the volcanic rocks from Hilário Formation (Figure 1). The copper is found in forms of sulfide minerals, such as chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S). Carbonated in form of copper hydroxide as azurite ($Cu_3(OH)CO_3$). The mineralization embedded in granitic rocks have predominant mineralogy based on iron disulfide in the mineralogical form of pyrite (FeS_2) and those embedded in andesitic and sedimentary rocks from the Hilario formation have dominant copper mineralogy (HORBACH et al, 1986). There is also secondary mineralization in colluvium, as well as alluvial streams that run through the regions that carry the primary mineralization (KAUL, 1975).

Figure 1-Geological map of the study area in Lavras do Sul, RS-Brazil, highlighting the sampling locations (after PORCHER; LOPES, 2000)



The official knowledge of the existence of gold in Lavras do Sul dates to the late eighteenth century (GRAZIA; PESTANA, 2008). At first, the gold was exploited in alluviums, in the Camaquã river and its tributaries. It was not until 1845 that the company Gold Mining started exploration in auriferous veins. Other companies such as Companies Lape, Tahourne, Bega and Gold Field Mining Company were also active in the area. Due to the fall in contents and technological precariousness of the exploration, the activities did not prosper for long. During the 70's, using proper advanced technology, the Companhia Riograndense de Mineração (CRM) resumed work in Lavras do Sul. Based on this initiative and the revaluation of gold in the international market in the 80's, exploration of ore in this region was once again popular (PORCHER; LOPES, 2000). Until 1981, barren and tailings were deposited in improper sites and gold was recovered by amalgamation with mercury, generating many environmental liabilities.

Along the soil sample profile are alkaline granites from the Granitic Complex Lavras do Sul and andesite and conglomerate from Hilário Formation. The granitoids, in general, are in outcrops such as slabs, leucocratic, medium phaneritic texture, equigranular arrangement, moderately altered, some with feldspathic matrix (Figure 2) and well-developed plagioclase. The andesites occur locally near the conglomerates, are equigranular and have low alteration degree. The conglomerates are characterized by the slab outcrop, they have volcanic debris and subordinate sedimentary.

The soils of the study area are shallow (Figure 2), they present horizon A resting on partially altered or unaltered rock and are classified as Litho-Dystrophic Neolsols on granitoids and Eutrophic Litholic Neosols on andesitic volcanic rocks (STRECK et al, 2002). The area presents recent and little-evolved soils with portions of high (eutrophic) and low (dystrophic) saturation by bases, acidity and high levels of aluminum and sodium (EMBRAPA, 1999).

Figure 2 – Photograph of soil classified as Litholic Neosol in road outcrop of the studied area (author)

3 Experimental part

3.1 Materials and Method

Soil sampling was performed in a systematic way consisting of sampling in two profiles surrounding the Lavras do Sul city, one to NW and another to SE of the urban area (Figure 1). Ten samples were collected in each profile, totaling 20 soil samples of 30 cm depth (each location separated at the top and base), with the collection of material every 500 meters, for a path of 13.4 km total. For the packing were used plastic bags properly labeled and identified according to the collection point number and their respective depth.

For the drying process, the samples were transferred to polypropylene containers and allowed to dry at room temperature for three days (BRASIL, 2009). After drying the samples were disaggregated in porcelain grade to obtain a uniform appearance. About 500 g of sample was quartered manually to promote splits in halves successively until the desired sample size was reached. Thus, about 50 g of each sample was separated for the EDRXF analyzes.

The analyzes of chemical elements and their quantities present in soil were carried out in the Laboratory of Mineralogy and Petrography (LMP -Unipampa), by a dispersive energy X-ray fluorescence spectrometer, model S1 Turbo SD. The following operating conditions of the equipment were selected: tube voltage of 15 keV (Na to Sc) and 50 keV (Ti to U) with current in the tube of 184 and 25 μA respectively; 10 mm collimator; 120 s of real-time integration. The equipment uses an Ag anode which allows the measurement of 25 elements and a detector of 10 mm^2 with thermoelectric cooling and resolution of ~145 eV to MnKα that allows maintaining a speed of 100.000 counts per second. The analytical method used allows obtaining the sensitivity curve of the equipment for each element of interest when a sample of a known chemical composition is submitted to well defined instrumental parameters. The sensitivity curve of the equipment relates the calculated theoretical fluorescence intensity and the measurement of each element (BONA et al, 2007; TEIXEIRA et al, 2017).

4 Results and Discussions

All concentrations obtained (Table 1) with the analysis of major elements and traces are below the maximum permissible values of metals in soils, according to Conama Resolution 420, including Fe (< 3000 $mg.kg^{-1}$) (BRASIL, 2009; MACDONALD et al, 2000).

In terms of major elements, the silicon values obtained are higher in profile 2 than in profile 1. In general, for both profiles, the topsoil samples present lower silicon amount than the base soil samples. TiO_2 varies similarly to SiO_2, except for the samples 1, 2, 5, 8, 9, 10 and 11 that presented higher amounts at the top. Al_2O_3 values in profile 2, suffer a drop-in depth, sample 20 is an exception because it presents a reverse behavior. In profile 1 the values of Al_2O_3 do not present the same homogeneous behavior. While in samples 2, 3, 5, 6, 7, 8 and 10 the highest values were detected at the bottom, samples 1, 4 and 9 were detected at the top. Fe_2O_3 in profile 1 show highest values at the top, with exception of sample 5. In profile 2 Fe_2O_3 is detected with higher values at the bottom, with the exception for the sample 12, 15 and 20.

The concentration of MnO, MgO, CaO, and K_2O varies in proportion with higher values at the surface or subsurface, regardless the profile. In this way, a correlation of element mobility and constitution of analyzed material was not possible. In profile 1 no chlorine concentrations were detected, this suggests that the Cl values were below the concentration analyzed by the equipment. In profile 2 the Cl amount varies in proportion with higher values in the surface or in the subsurface.

In terms of trace elements, copper was only detected in profile 2 especially in the samples 18, 19 and 20. Pb was detected in depth in samples 3, 6 and 14. in samples 19 and 20, Pb was detected at both top and bottom, however at higher concentrations at the top. The behavior of Mo is similar to Pb, being detected at the top of sample points 4, 5, 6, 12 and 13. Zn was detected in almost all samples with approximate values for top and bottom. Only samples from points 1 and 10 do not have zinc. Cd was detected in all soil samples varying in proportion with higher values either on the surface either in the subsurface.

Table 1 – Percentage of major elements and traces from the analyzed soils

Profile	Sample	ID	Si	Ti	Al	Fe	Mn	Mg	Ca	K	Cl	P	Cu	Ni	Zn	Cr	Pb	V	S	Zr	Nb	Mo	Rb	Sr	Cd	Rh	Pd	Y	Ce	As
1	1	T	42,20	0,45	8,19	1,38	0,03	3,06	0,66	3,55	nd	nd	nd	nd	nd	nd	nd	nd	100	130	nd	nd	50	120	1,60	0,5	nd	nd	11	nd
		B	44,50	0,29	8,94	1,35	0,03	2,93	0,70	3,56	nd	nd	nd	nd	nd	nd	nd	nd	nd	160	nd	nd	50	120	1,50	0,3	nd	nd	nd	nd
	2	T	42,50	0,63	10,70	2,14	0,04	0,77	0,61	3,29	nd	nd	nd	nd	500	nd	nd	nd	100	180	nd	nd	60	120	1,50	0,5	nd	nd	nd	nd
		B	43,00	0,60	10,50	2,14	0,04	0,75	0,50	2,50	nd	nd	nd	nd	500	nd	nd	nd	100	180	nd	nd	60	120	1,50	0,5	nd	nd	nd	nd
	3	T	31,10	0,72	11,00	4,67	0,07	4,05	0,71	2,83	nd	nd	nd	nd	100	nd	nd	nd	nd	110	20	nd	60	130	1,50	0,5	nd	10	23	nd
		B	31,10	0,72	9,99	4,14	0,06	5,24	0,64	2,73	nd	nd	nd	nd	100	nd	100	100	nd	100	20	nd	60	120	1,70	nd	nd	nd	nd	nd
	4	T	38,90	0,98	11,80	4,81	0,06	3,55	0,19	2,59	nd	nd	nd	nd	100	nd	nd	nd	nd	400	20	20	50	40	1,80	0,5	nd	10	nd	nd
		B	37,90	1,07	12,00	4,45	0,06	2,06	0,15	2,66	nd	nd	nd	nd	100	nd	nd	100	nd	430	20	nd	50	50	1,80	0,4	nd	10	nd	nd
	5	T	39,60	0,77	15,10	5,05	0,03	2,96	0,19	4,57	nd	nd	nd	nd	100	nd	nd	nd	200	320	20	10	30	10	1,10	0,4	nd	10	10	nd
		B	36,40	0,73	14,80	5,54	0,03	1,52	0,18	4,43	nd	nd	nd	nd	300	nd	nd	nd	nd	400	30	nd	30	30	1,20	nd	0,6	20	10	nd
	6	T	43,20	0,95	11,50	5,42	0,07	4,53	0,41	4,10	nd	nd	nd	nd	200	nd	nd	nd	100	430	30	20	30	20	1,10	0,2	nd	10	12	nd
		B	42,30	1,25	11,20	5,34	0,08	3,16	0,36	3,75	nd	nd	nd	nd	200	nd	100	nd	nd	400	40	nd	30	20	1,40	nd	0,5	20	12	nd
	7	T	38,70	0,83	7,12	5,29	0,13	3,68	1,90	1,43	nd	nd	nd	nd	100	nd	nd	100	300	130	10	nd	20	80	1,60	0,5	nd	nd	nd	nd
		B	38,10	0,83	6,63	4,44	0,14	1,89	1,54	1,27	nd	nd	nd	nd	100	nd	nd	nd	100	140	nd	nd	20	90	1,70	0,4	nd	10	12	nd
	8	T	25,50	0,76	12,90	9,64	0,05	0,00	0,29	1,22	nd	nd	nd	nd	100	nd	nd	nd	200	800	nd	nd	30	20	2,10	0,4	nd	10	19	nd
		B	26,40	0,45	11,90	9,40	0,05	0,00	0,29	1,22	nd	nd	nd	nd	100	nd	nd	nd	100	400	nd	nd	30	20	1,90	0,4	nd	10	17	nd
	9	T	29,40	0,80	8,25	5,88	0,10	3,79	1,02	1,63	nd	nd	nd	nd	200	nd	nd	nd	nd	100	nd	nd	30	90	2,10	0,5	nd	10	17	nd
		B	35,00	0,73	9,83	5,75	0,12	3,94	0,45	1,91	nd	nd	nd	nd	100	nd	nd	100	nd	70	nd	nd	20	40	1,50	nd	nd	nd	nd	nd
	10	T	39,00	0,80	8,06	4,21	0,07	3,82	0,61	2,15	nd	nd	nd	nd	nd	nd	nd	nd	nd	150	nd	nd	20	80	1,50	0,5	nd	nd	11	nd
		B	43,30	0,76	7,81	4,14	0,07	1,93	0,44	2,06	nd	nd	nd	nd	nd	nd	nd	200	nd	200	nd	nd	20	80	1,50	nd	0,6	nd	nd	nd
2	11	T	43,00	1,00	9,67	2,96	0,03	3,63	0,17	3,15	0,3	nd	nd	nd	100	nd	nd	nd	300	340	20	nd	50	30	1,50	0,4	nd	10	nd	nd
		B	36,70	0,94	9,65	3,38	0,02	3,81	0,11	3,16	0,1	nd	nd	nd	100	nd	nd	nd	100	340	20	nd	50	40	1,50	0,4	nd	10	11	nd
	12	T	47,10	1,08	9,58	3,25	0,06	3,19	0,39	3,62	0,0	nd	nd	nd	100	nd	nd	nd	200	300	20	10	20	50	1,30	0,3	nd	10	nd	nd
		B	49,40	1,18	9,75	3,19	0,05	4,77	0,29	3,83	0,1	nd	nd	nd	100	nd	nd	nd	100	250	20	nd	20	20	1,10	nd	nd	10	6	nd
	13	T	44,20	0,94	11,10	3,19	0,08	2,01	0,24	3,84	0,3	nd	nd	nd	100	nd	nd	nd	200	260	30	10	60	40	1,40	0,3	nd	10	nd	nd
		B	46,60	1,00	11,90	3,63	0,05	2,55	0,25	3,84	0,1	nd	nd	nd	100	nd	nd	nd	200	280	nd	nd	30	20	1,30	nd	0,5	10	nd	10
	14	T	41,80	1,39	7,44	4,77	0,16	5,54	0,73	2,59	0,1	nd	nd	nd	100	nd	nd	300	200	160	10	nd	30	70	1,40	0,3	nd	nd	nd	nd
		B	44,60	1,50	8,36	5,61	0,17	3,63	0,47	2,63	0,1	nd	nd	nd	100	nd	nd	300	200	150	10	nd	10	60	1,20	nd	nd	10	nd	nd
	15	T	43,10	1,71	9,67	8,74	0,16	4,97	0,56	1,74	0,1	nd	nd	nd	100	nd	nd	100	300	400	10	nd	10	20	1,30	0,3	nd	nd	9	10
		B	43,60	1,86	11,40	7,14	0,13	2,94	0,58	1,86	0,2	nd	nd	nd	100	nd	nd	nd	300	120	10	nd	10	20	1,40	0,3	nd	nd	11	10
	16	T	37,70	1,38	9,98	6,41	0,11	4,03	1,90	2,03	0,2	nd	nd	nd	100	nd	nd	300	400	800	nd	nd	10	130	1,20	0,3	nd	nd	nd	10
		B	40,10	1,52	11,30	8,29	0,15	3,12	1,89	2,20	0,0	nd	nd	nd	100	nd	nd	100	200	90	10	nd	10	60	1,40	nd	nd	nd	11	10
	17	T	37,60	1,29	7,85	5,87	0,17	2,92	1,68	1,73	0,2	nd	nd	nd	100	nd	nd	200	400	90	nd	nd	30	140	1,60	0,5	nd	nd	nd	10
		B	40,20	1,47	9,46	6,40	0,17	4,07	1,88	2,15	0,1	nd	nd	nd	100	nd	nd	nd	100	90	nd	nd	10	60	1,10	0,2	nd	10	8	10
	18	T	30,20	1,25	8,28	10,40	0,23	5,48	1,34	2,19	0,4	nd	200	nd	100	nd	nd	400	nd	110	10	nd	10	140	1,20	nd	nd	10	nd	10
		B	34,50	1,27	11,60	10,80	0,23	7,35	1,02	2,26	0,2	14	100	nd	100	nd	nd	200	200	20	nd	nd	10	50	1,00	nd	nd	nd	8	10
	19	T	45,80	1,58	8,40	7,74	0,14	3,23	0,54	2,90	0,1	nd	100	nd	200	nd	200	nd	200	40	10	nd	20	20	1,00	nd	nd	nd	10	nd
		B	44,60	1,59	9,09	8,41	0,15	2,29	0,48	2,90	0,3	nd	nd	100	200	nd	100	nd	300	40	10	nd	20	20	1,10	nd	nd	nd	10	10
	20	T	44,40	1,36	8,98	8,87	0,21	4,99	0,73	2,90	0,0	nd	100	100	100	100	200	nd	400	30	nd	nd	20	30	1,10	0,2	nd	nd	9	10
		B	45,40	1,52	8,69	8,58	0,17	4,40	0,58	3,20	0,1	nd	100	100	100	300	100	100	200	40	nd	nd	20	30	1,20	nd	nd	nd	10	10

nd = below the equipment limit; T=top (0 m); B=base (30 cm),

The Cd may be associated with phosphate fertilizers (1-170 $mg.kg^{-1}$) (GUILHERME et al, 2005), being weathered by water and deposited in sediments (BELLUTA et al, 2008). An anthropogenic source that improperly discards pieces of equipment such as batteries can also be held responsible for this containment (MARTIN; GRISWOLD, 2009).

Thus, Pearson's correlation coefficient was used to relate the elements to the lithology of the study area, enabling the knowledge of which elements are in fact the source material and which elements are present due to anthropic intervention.

Correlation tables were generated for profile 1 and profile 2 (Table 2). For a better analysis of the correlations values with strong Pearson correlation (>0,7) was highlighted in the table (MUKAKA, 2012). Using Pearson coefficient, it is possible to summarize the relationship between two variables. The most common way to present and analyze bivariate data sets is through the X and Y axes, the correlation measures the similitude between two different variables. Thus, the value can be calculated according to equation (1).

$$\rho = \frac{\frac{1}{n}\sum(Xi - Mx)(Yi - My)}{\sigma x \ \sigma y} \qquad (1)$$

Where, Xi is the variable X value, Mx the mean of X values, Yi is the variable Y value, my the mean of Y values, σx the standard deviation of X and σy the standard deviation of Y.

This coefficient varies between values from -1 to +1. Samples that correlate linearly with each other have a value closer to

1 in a module. The correlation concept refers to a numerical association between two variables, not necessarily implying a cause and effect relationship.

In table 2 is possible to observe the positive correlations in profile 1 between the elements Si-Pd (0.730), Pd-Ca (0.802), Zr-Nb (0,764), Nb-Y (0,704), Sr-Pd (0,932), and, Cd-Pd (0,816). In profile 2 the positive correlations are between the elements Mn-Fe (0.873), K-Nb (0.720), Ca-Sr (0,712), Ni-Cr (0,702), Zr-Nb (0,825), Zr-Y (0.819), Rh-Cd (0,741), and, V-Sr (0,773).

Table 2 – Pearson correlation for elements investigated in profile 1 and 2

	ProfileL 1				Profile 2					
Element	Pd	Zn	Cd	Ce	Cu	Ni	Zn	Cr	Cd	Ce
Si	0,730	0,002	-0,634	-0,419	-0,355	0,252	0,229	0,200	-0,128	0,226
Ti	-0,684	0,174	-0,041	0,005	0,372	0,245	0,318	0,160	-0,297	0,396
Al	-0,866	0,364	-0,376	0,184	-0,251	-0,229	-0,228	-0,198	0,019	0,324
Fe	-0,806	0,051	0,284	0,377	0,681	0,377	0,226	0,269	-0,501	0,295
Mn	-0,110	-0,104	0,281	-0,102	0,641	0,300	0,069	0,226	-0,426	-0,054
Mg	0,066	-0,314	-0,226	-0,026	0,594	-0,017	-0,312	0,140	-0,391	-0,084
Ca	0,802	-0,091	0,293	-0,043	0,042	-0,138	-0,158	-0,086	-0,058	-0,219
K	-0,740	0,284	-0,767	0,038	-0,343	0,161	0,079	0,166	-0,071	0,028
Cu	-	-	-	-	1	0,154	0,028	0,275	-0,295	0,061
Ni	-	-	-	-	0,154	1	0,327	0,702	-0,329	0,349
Zn	-0,962	1	-0,148	-0,086	0,028	0,327	1	-0,098	-0,426	0,302
Cr	-	-	-	-	0,275	0,702	-0,098	1	-0,158	0,249
Pb	-0,577	0,066	0,000	-0,131	0,307	0,591	0,553	0,378	-0,457	0,163
V	0,577	-0,296	0,108	-0,722	0,390	-0,215	-0,256	-0,057	0,000	-0,714
S	ND	0,049	0,012	-0,011	-0,217	0,279	0,063	0,056	0,229	-0,005
Zr	-0,992	0,254	-0,546	-0,076	-0,491	-0,418	-0,321	-0,291	0,522	-0,229
Nb	-0,980	0,256	-0,519	0,109	-0,351	-0,341	-0,035	-0,344	0,337	-0,087
Mo	ND	0,044	-0,464	0,133	-0,254	-0,140	-0,111	-0,098	0,168	0,0
Rb	0,229	0,208	0,070	-0,003	-0,358	-0,071	-0,056	-0,050	0,558	-0,032
Sr	0,932	-0,092	0,292	-0,075	0,104	-0,280	-0,280	-0,171	0,221	-0,664
Cd	0,816	-0,148	1	0,131	-0,295	-0,329	-0,426	-0,158	1	-0,177
Rh	0,577	-0,035	0,320	0,341	-0,357	-0,340	-0,409	-0,268	0,741	-0,185
Pd	1	-0,962	0,816	-0,988	-0,623	-0,343	-0,272	-0,241	0,170	-0,153
Y	-1,000	0,326	-0,156	0,529	0,061	0,349	0,302	0,249	-0,177	1
Ce	-0,988	-0,086	0,131	1	0,277	0,343	-0,068	0,241	-0,170	0,099

Pd and Rh are elements of the platinum group, being considerably resistant to weathering. Thus, they concentrate in soil due to the weathering of soluble components or by aggregation of secondary minerals. The correlation observed in both profiles is consistent with the lithologies of the study area (GRAZIA; PESTANA, 2008) and common in regions where Cu, Pb and Zn mineralizations occur (CAMPOS et al, 2005).

In order to investigate possible harmful concentrations to human health, the soil samples were compared with the guideline values of alert, reference and soil intervention (Table 3), which is based on the guideline values of Brasil (2009), but an updated data version. This table regulates the concentrations of soil chemical contents with tolerable and risks values to human health. In this study, the intervention values referred to in the tables and literature are from agricultural data rather than residential, since the study area is rural, with land use predominantly for agricultural purposes.

Table 3 - Guidance values in ppm for soils (CETESB, 2017)

Value	Cu	Ni	Zn	Cr	Pb	Cd	Mo	As
Reference	35	13	60	40	17	<0.5	<4	3.5
Alert	60	30	86	75	72	1.3	5	15
Intervention	760	190	1900	150	150	3.6	11	35

In profile 1, the guidance values from Table 3 are exceeded for Zn, Pb, and Cd, these high levels may be the result of the presence of sulfide mineralizations (RIEUWERTS et al, 2006) present in the region (GRAZIA; PESTANA, 2005). These values do not pose risk to the population, as they are within the acceptable levels of concentration. For Mo the risk values were exceeded in samples 4 and 6, that may be related to the strong retention of Mo by iron and aluminum oxides (BARROW, 1970), abundant elements in the area. However, as these high values appear only at the top, they may have migrated and concentrated at these sites eventually, not being a risk factor.

The Cd content may also indicate human activities, because in some samples it presented a higher concentration at the top, possibly due the use of agrochemical or fertilizers, since the study area is placed in a rural location. The element Cd can accumulate in the human body and induce renal dysfunction, bone diseases and deficiency in reproductive function, aside from the possibility of acting as a carcinogen in humans. The presence of Cd in food products is the main source of Cd intake by man (MARTIN; GRISWOLD, 2009), so if this element is present in the soil it can bioaccumulate in the vegetables and/or infiltrate in bodies of water.

Most of the studies that compare Mn levels in soils with and without human activity showed that there is no difference in the content of this element due to human activity, considering this fact as the abundance and intense dynamics of Mn, which has many states of oxidation in the soil (BURT et al, 2003). These considerations can be extended to Fe due to the similarities between these two elements. This may explain the inexistence of guiding values of these metals in soils defined by environmental agencies. Knowing the contents of Mn and Fe is important because it indirectly indicates the content of other heavy metals.

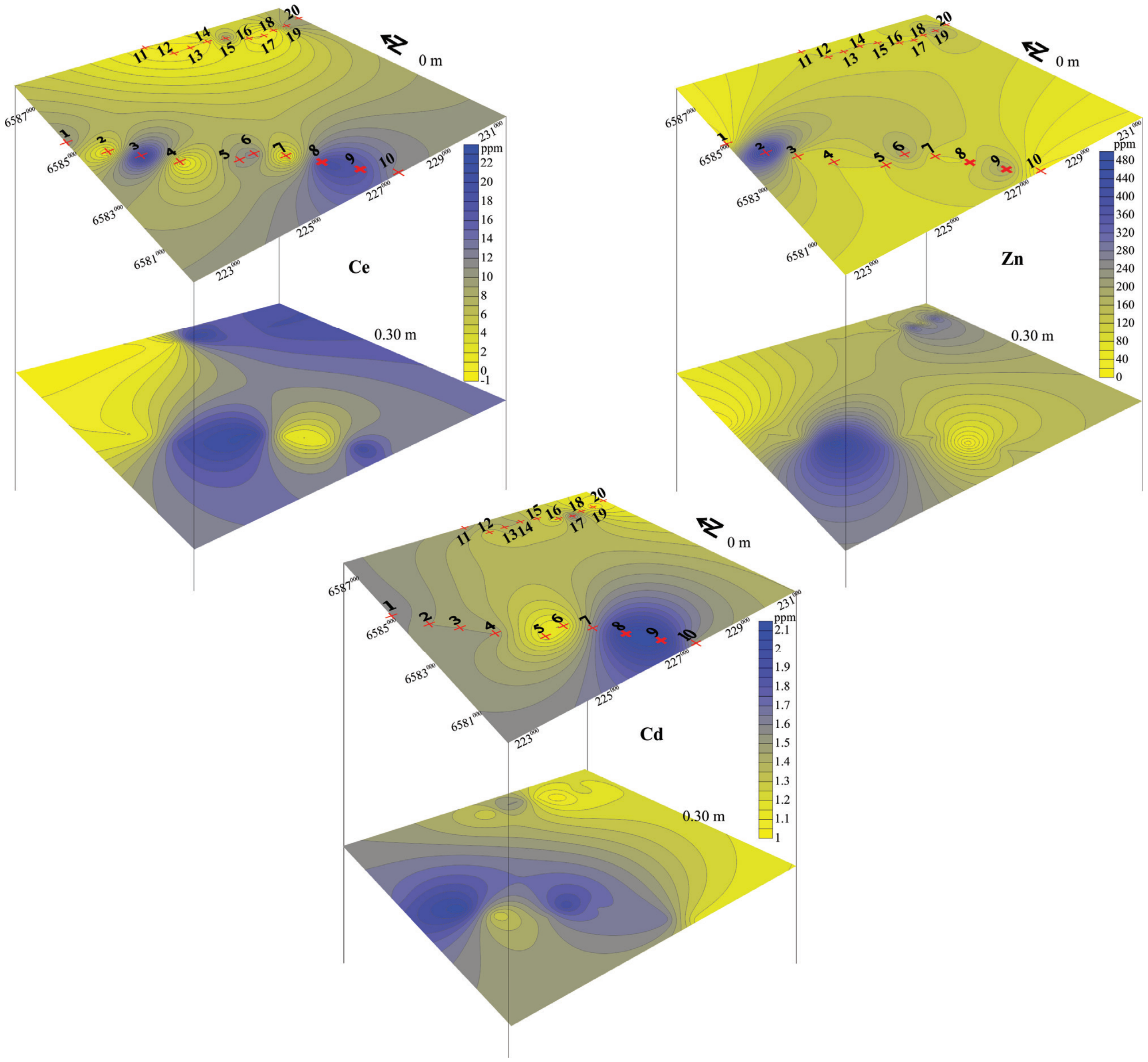
In profile 2, the guiding values from table 3 are exceeded for Cu, Zn, Pb, Cr, Mo, and Cd, possibly due to the sulfides mineralizations. Risk values are observed for Cr in sample 20 and Pb for samples 19 and 20. A hypothesis for the high value of Cr in the soil is that the behavior of this element is similar to Al, and can substitute it in aluminosilicates, despite having a larger atomic radius.[34.] It is noteworthy that the study area has considerable concentrations of Al. Because it is an isolated fact and not throughout the profile, this concentration does not indicate a significant risk to human health.

Figure 3 shows the behavior of Cd, Zn and Ce in the study area at points 1 to 20 at depth from 0 to 30 cm. All sample points present values higher than the allowed by CONAMA resolution n°420 (BRASIL, 2009), which establish 0,5 mg.kg^{-1} of Cd as the highest value allowed. At 0 cm depth, the highest values are found in the Southern region of the cartogram. For 30 cm depth, the highest values are found in the South and West portion, where the points 1 to 4 and 7 to 10 are located. The lowest values are found in the Northern and Northeast region.

All the sampled points, except for the surface samples (0 cm) from points 1 and 10, exceed the values established by the Conama Resolution n°420 (BRASIL, 2009), which establishes the maximum value for Zn of 60 mg.kg^{-1} in soils. At 0 cm of depth, the highest values are found in the western region of the cartogram (Figure 3). At 30 cm of depth, the highest values are found in the southwest and northeastern regions.

At 0 cm depth the highest values of Ce are found in the western and southern regions of the cartogram and, only on samples 2 and 4 were not detected the presence of this element. At 30 cm depth the highest values are found in the southwestern, southeast and northeast regions of the cartogram (Figure 3), although the lowest values are found in the northwestern and southern regions. At that depth just, the sample point 13 did not show concentration for Ce, this element usually goes together with Fe and Al and it is not associated with Pd. Ce is a Rare Earth Element (REE) and has the ability to replace Ca in mineral structures, due their ionic radius similarity. Then, the amount of Ce may be related to the REE in the soil, and, consequently, to be accumulated over the years.

Figure 3 - Concentrations of Zn, Ce and Cd in the study area at 0 to 30 cm depth



5 Conclusions

The sampled soil showed high concentration values of Cu, Pb and Zn, which are considered outside the standards established by Brasil (2009). Possibility, these results are due, in part, to natural geological sources, such as the sulfide mineralization in the region of Lavras do Sul.

An unexpected result of this study was that the Cd values are high concentration and are considered outside the standards established by Brasil (2009). The study area is rural and the Cd values can be associated to human intervention, through the use of fertilizers and agrochemicals. The Cd can cause a wide range of acting as a carcinogen in humans. If this element is present in the soil it can bioaccumulate in the vegetables and/or infiltrate in streams and point to the need for further studies to better characterize the possible sources responsible for values higher than those standards established by Brasil (2009).

Alert values are observed for Cr in one sample (sample 20) and Pb in two samples (19 and 20). Because it is an isolated fact and not throughout the profile, this concentration does not indicate significant risks to human health.

Samples were compared using multivariate statistical methods, which indicate a commonality in chemical signature between the profile 1 and 2. The most discriminating variables were Si-Pd, Pd-Ca, Zr-Nb, Nb-Y, Sr-Pd, Cd-Pd, Mn-Fe, K-Nb, Ca-Sr, Ni-Cr, Zr-Nb, Zr-Y, Rh-Cd, and, V-Sr. The variations in the chemical signatures are interpreted as being derived from the interaction with the lithology.

At depth 0 cm the highest values of Ce are found in the Western and Southern regions of profile 1. For Zn the largest value is restricted to sample 2 in the Western region of profile 1 and for Cd the highest values are concentrated in the Southern region of profile 1. The profile 2 does not present anomalous values for these three elements in surface. For the depth 30 cm the highest Ce values are distributed in both profile 1 and profile 2 in the N-NE, S-SE-SW and W regions. The highest Zn values are observed in the SW and NE regions in both profiles, and the highest values of Cd are concentrated in the southern region of profile 1.

The advantages of using the EDXRF method are diverse, including the variety of elements analyzed, the speed of the process and the relative low cost. For a generalist investigation of which elements are present in a given sample, this technique proves to be quite effective, both for speed and for relative low cost.

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