Water Quality Assessment through PCA Analysis

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Abstract— This aim presents the first detailed geochemical data of water of the Jaguari stream, Lavras do Sul-RS. In this study we use Principal Component Analysis (PCA) to establish geochemical grouping that can be related back to likely mining, lithological and anthropic actives in the region. The results indicated that the high concentrations of Cu, Rh and Cd have a close relationship to local anthropic activities and lithological with geochemical changes seasonal fluctuations. The geochemistry results too indicated waters classified as soft and hard (total hardness range from 53.02 to 79.28 mg L^{-1}), neutral pH, and electric conductivity ranged from 157.1 to 184.9 μ s cm⁻¹. All measured values met the potability standards for human consumption established by Ordinance Nos. 2914 (2011), 36-GM/1990, and 1469/2000.

Keywords—Jaguari, PCA, Water.

I. INTRODUCTION

In the last few decades, the significant increase of metal extraction in Brazil has caused serious environmental problems. Effluents containing chemical compounds from mining are discharged into waterways without appropriate treatment. Lavras do Sul fits perfectly in this scenario, what makes this region is unique because it suffers from the effects of metals mining in its surroundings and has no sewage treatment of any kind, e.g. domestic or industrial.

The center-south region of Rio Grande do Sul, Lavras do Sul, provides a vast variety of lithologic types and, has an immense metallogenetic importance. This territory is known for its occurrence of mineralization, which combined with sulfites, produces base metals like gold (Au), copper (Cu), lead (Pb), zinc (Zn) and silver (Ag) [4].

The discovery of gold in this area was pioneered by miners arising from Minas Gerais, endorsed by the Portuguese crown, at the time fighting against the Spanish group, whom occupied the south of the country. Although the exploitation of this minerals only began at the end of the XIX century, postponed on account of unleashed strikes and social movements like the Farroupilha Revolution [4].

In this region, the mineralizations of gold and coppergold related to the Lavras do Sul Intrusive Complex and igneous rocks originated on the Hilário Formation (Fig. 1). The granitic rocks are composed of several minerals rich in alkali feldspar (KNaAlSi₃O₈), plagioclase (CaNa) Al(AlSi) Si2O₈), quartz (SiO₂) and micas (biotite and/or muscovite) witch accessory minerals as hornblende (Ca2Na (MgFe)₄ (AlFeTi) AlSi₈AlO₂₂ (OHO)₂) pyroxene (CaNa) (MgFeAlTi) (Si₂O₆), zircon and apatite. The mineralization in the granitic rocks have mineralogical prevalent iron disulfide-based on the mineralogical form of pyrite (FeS₂), and those embedded in andesitic and sedimentary rocks from the Hilário Formation have a copper dominant mineralogy [17]. Copper occurs in the form of sulfides, for example, chalcopyrite (CuFeS₂) and chalcocite (Cu₂S), in addition to carbonates in the form of copper hydroxide, like azurite (Cu₃(OH)CO₃. There is also a secondary mineralization in flood, as well as in water resources that roam the region that carry the primary mineralization [17] for example, Jaguari stream that is inserted in Santa Maria basin.

Metals are abundant in natural environments, its dissemination on water is constrained depending on the chemical variables that affect the hydric resource, specifically: flow, water composition and, the geological substrate. Accordingly, the metals can have lithogenic and anthropogenic sources depending on its natural origin. The natural origin, then, depends on the source material ally weathering rates, as well as the surrounding humans that can increase its concentration [5].

Many metals, in the right quantities, are essential to maintaining life [6]. Though, if it fluctuates or suffers unsteadiness, it can cause severe damage to the ecosystem. The universal solvent, water is very easily polluted, therefore becoming unfit for public consumption [7] by affecting human health through direct intake, food preparation, personal hygiene, agriculture or leisure activities [8]. Consequently, the knowledge of the water's chemical composition provides subsidies for the possible contamination of the water resource, once a certain capacity is exceeded the metal has the potential to leachate [9]. So, those concentrations of metals can be greater than authorized as they have a cumulative impact on the environment [10].

In order to improve the understanding of the water quality, assessment through the geochemistry analysis and quantification of metals and non-metals present in samples of the Jaguari stream on Lavras do Sul.

1.1 Study area

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Lavras do Sul is located in the Rio Grande do Sul State of Brazil, 342 kilometers from Porto Alegre, between Caçapava do Sul and Bagé, with access at BR-290, BR-392, and at RS-357 (Fig. 1). The municipal district of Lavras do Sul is located amongst the coordinates 30°48'46 "S and 53°53'42 "W, its altitude reach 277 meters, with an area of 2.600.611 km² and, in 2016, the population was estimated at 7,820 inhabitants [11].



Fig.1: Geological map of the region Lavras do Sul [12].

The study area is inserted in the Escudo Sul-riograndense, that represents Província Mantiqueira's southern portion [12], being constituted by both Archeans and Neoproterozoic lands (2.26 Ga, 535 Ma) [14], [15] and represented by igneous, sedimentary and metamorphic rocks. It presents a rocky soil, whose origin dates from the Pre-Cambrian. The local vegetation varies along the district, from mixed pastures to bushes, clean and even plain fields, with rice cultivations. The climate is subtropical humid, with four very defined seasons, in the summer the temperatures can arrive at 30°C, and in the winter, standards are from 6°C to 12°C, easily decreasing to 0°C with frequent occurrence of frosts. The rains are distributed regularly throughout the whole year, although drought periods eventually happen.

The Lavras do Sul Intrusive Complex is a circular body with dimensions of 216 $\rm km^2$. This body has

intrusive behavior in orthogneisses and pre-and sintectonic granitoids in the W-SW and N-NW portions. It is delimited to S-SE and NE by the Maricá Formation, whose contact is controlled by the São Domingos fault zone with direction NE-SW, and to the east by Hilário Formation [15].

The main body of the Lavras do Sul Intrusive Complex, Lavras granite, presents zonation of reverse facies between alkali-calcic (core) and alkaline facies. In the central portion are included biotite-granodiorite circumcised by hornblende-biotite monzogranite, which progresses to hornblende-biotite sienogranite. The edges are composed of biotite-hornblende sienogranite and alkaline-granite feldspar [16]. It is known that the deposit configuration of the area fits in the system of copper porphyries, in which porphyritic igneous rocks subjected to intense hydrothermal processes end up

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enriching themselves in sulphides. The Tapera monzonite (Fig. 1) is a half-moon shaped intrusion consisting of monzonite, monzonite, monzodiorite and diorite quartz. It has its limits comprised by the abundance of intermediate and acid dykes, which include the andesites belonging to Hilário Formation. The monzodiorite arroio dos Jacques (Fig. 1) is characterized as an elongated and narrow body located to the northeast, between the Tapera monzonite and the Lavras granite [16].

The mineralogy of these granitoids is composed of alkali feldspar (KNaAlSi₃O₈), plagioclase (Ca,Na) Al(Al,Si) Si₂O₈), biotite (K₂(Mg, Fe²⁺)₆₋₄(Fe³⁺,Al,Ti)₀₋₂Si₆₋ 5Al2-3O20(OH,F)4, quartz (SiO2) and oxides, witch accessory minerals as hornblende (Ca2Na (Mg,Fe)4 (Al,Fe,Ti) $AlSi_8AlO_{22}(OH,O)_2)$ pyroxene (Ca,Na) (Mg,Fe,Al,Ti) (Si₂O₆), zircon and apatite. The alkaline feldspar (possibly orthoclase) is euhedral, prismatic up to 1 cm in length, with a reddish-beige coloration and alteration for white mica and iron oxides. The plagioclase is euhedral, prismatic of up to 0.9 cm in length, with light to white beige coloration and alteration for kaolinite (Al₂Si₂O₅ (OH₄)) and/or gibbsite (Al (OH)₃). The biotite is anhedral, lamellar, with dimensions of up to 0.2 cm, black coloration and alteration for reddish oxides and metallic blacks. The quartz is anhedral, equidimensional up to 0.3 cm in length and colorless. The oxides are anhedral, black metallic, concentrated in fine textured aggregates.

Along the outcrops it is possible to observe the occurrence of differential changes in the rocks. These changes are marked by the filling of fractures of the rock with euhedral quartz, which forms pyramidal prisms of 0.5 cm in length. Along with this, there are films of pervasive iron oxide (probably hematite) and generalized changes to sericite and white micas. This configures the alteration processes responsible for argilization, chloritization and carbonation in the rocks.

II. MATERIALS AND METHODS

2.1 Sampling procedure and analysis The sampling place was strategically selected due to the proximity with areas of mineral exploitation (Fig. 2) and to reflect the condition of the environment in terms geochemical.

Bottles of polyethylene were used to collect the samples of water. Those flasks were previously decontaminated with nitric acid at 10% for 48 hours and, soon afterward, washed with distilled water and put to dry in the incubator (25°C). Thirteen samples of water were collected in the summer of 2017 (Fig. 2) and one of public distribution (P14). All of the samples were preserved and analyzed within seven days starting from the date of the compilation with standard criteria [18], [8]. The analyses were performed at the Laboratory of Chemistry of the Federal University of the Pampa - UNIPAMPA.



Fig.2: Map of location of the points of sampling of the stream Jaguari in the district of Lavras-do-Sul RS, Brazil.

Immediately after the samples were collected, the pH was checked by using a pH meter at the Laboratory.

The conductivity of the samples was measured by a GEHAKA CG1800 apparatus. The electric conductivity is a measure of the aqueous solution capacity to drive an electric current due to the ions presence. The higher the number of dissolved ions, the greater the electrical conductivity of the water. The electrical conductivity is an indirect measure of the pollutants concentration.

To determine the hardness of the samples, the EDTA served as titrant and the eriochrome-T as an indicator [1], [2]. The reagent's blank titration was done simultaneously using distilled/deionized water. The hardness levels were determined to verify any constraints on potability and, for human consumption. The hardness is one of water's natural characteristics and, it indicates the total concentration of alkaline earth ions in water. This property can be quantified when water comes into contact with rocks enriched with calcium and magnesium minerals, in which the calcium and magnesium salts dissolve. These salts excessively aggregate to the water composition, as bicarbonate (HCO³), nitrate (NO₃), chlorides (Cl) e sulfates (SO₄). Calcium analysis was performed using the same titrant of the total hardness and murexide indicator.

Approximately 50 ml was isolated from each sample for the Elemental Analysis by Energy Dispersive X-ray Fluorescence (EDXRF). The analyses of the chemical elements and their present amounts in the water occurred in the Laboratory of Mineralogy and Petrography (LMP -Unipampa). The Equipment model S1 Turbo SD was calibrated with a tension of 15 keV (Na to Sc) and 50 keV (Ti to U) with a current in the tube of 184 and 25 A respectively; and 120 s of real-time integration.

PCA was selected as the method as it is a multivariate statistical technique commonly used to investigate variability in large geochemical data sets [29]. All analyses were conducted using XLSTAT statistical software package, statistical analysis, 2018.

PCA is a method of variable reduction that produces a lower number of artificial variables, known as Principal Components (PCs). Each PC represents a certain amount of variability in the data, and the first two PCs usually answer for most of the variations inside of the whole group of data [29]. When using PCA, only the PCs with values > 1 are used, therefore they are responsible for most of the variation in the data.

RESULTS AND DISCUSSIONS

III.

The physico-chemical characteristics of the water are a reflection of the means by which they are percolated. Aside from the lithologic aspects, the existing amount of dissolved salts reflects the variation of geochemical behavior as a whole [21]. Thus, a close relationship is expected between the composition of the water and the rocks surrounding the investigated area, as well as of the influence anthropic activity.

The results presented in Table 1 correspond to the analyses to determine the total hardness, pH, conductivity, temperature, calcium and EDRXF.

The electric conductivity results at the chosen locations ranged from 157.1 to 184.90 μ S cm⁻¹ (Fig. 3A). Along these lines, levels above 100 μ S cm⁻¹ indicate impacted environments and high values sometimes indicate water traits [19]. Thus, these points may be more greatly impacted by the mining activity or perhaps this is a result of the predominant soil in the area, which contains a great number of minerals. Both calcium and magnesium have great mobility and are easily leached, and it is possible that their presence may lead to high conductivity at these points.

The hardness analysis results (Fig. 3B) indicate that Jaguari stream water is inferior to 75 mg L^{-1} CaCO₃, indicating soft waters [23] (Fig. 4). The presented data does not deviate from Rio Grande do Sul and Brazil's average hardness on urban and rural waters [20],[21].

The pH of the samples at temperatures from 17,20 to 21,30° C ranged from 7.75 to 8.62 (Fig. 3C), indicating alkaline waters. This may be due to carbonate dissolution from the nearby limestone extraction area collection and to the increased concentration of carbonates in the low-rainfall months when the samples were collected. The public distribution sample presented neutral pH (7,0).

The calcium levels ranged from a minimum of 10.83 mg L^{-1} in the T14 sample and, to a maximum of 41.31 mg L^{-1} in the P13 sample (Fig. 3D). At Jaguari stream, it varied between 18.27 and 41.31 mg L^{-1} . Comparing these results to those found by [22], where results show 1.07 mg L^{-1} and, also, [21] where the result show 11.20 mg L^{-1} both for the calcium, accordingly, the tenor of calcium calculated in this study was ~2.6 and ~2.5 times bigger.



Fig.3: A) Conductivity (μ S cm⁻¹), B) Total hardness (mg L⁻¹), C) Temperature (°C), and D) Calcium (mg L⁻¹) of the sample's unit showing that the P5 sample presented higher conductivity and temperature than the other water samples. The P1, P2, P3, P4 and P5 samples presented the highest values in terms of conductivity and temperature. The P3 sample showed the lowest total hardness along with T14.

The EDRXF analysis attested that the largest values are made of magnesium, varying between, 4.12 and 7.19% and correspond up to 39% higher than the public distribution sample results (T14). The high values of Cu, Rh, Ag, and Cd (up to 0.12, 6.56, 0.97, mg L⁻¹ respectively) draw awareness.

When there is Rh ingestion in large proportions, it can lead to the occurrence of carcinomas or cancer in individuals. This element has no biological role in human beings. Second [24], cadmium is a non-essential element and highly toxic to plants and animals. Prolonged exposure to this element has caused severe chronic effects, predominantly in the lungs and kidney. Exposure by inhalation causes emphysema and other chronic lung effects. According to [3], to be potable for human consumption the cadmium values cannot exceed 0.005 mg L⁻¹ and for Cu, it cannot exceed 2.0 mg L⁻¹.

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Samples	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	T14
Conductividy	184.90	183.40	171.80	170.50	184.30	157.10	158.60	159.50	164.50	165.30	165.70	166.10	166.20	149.8
Temperature	20.80	21.30	20.80	20.90	20.70	17.20	17.20	17.30	17.90	17.60	17.90	18.00	18.30	20.7
Ca	23.83	20.26	21.85	23.83	26.21	18.27	21.85	20.65	33.76	33.36	35.35	33.36	41.31	10.82
Total hardness	74.32	63.92	53.02	73.33	70.36	69.37	72.34	71.35	76.31	75.32	78.29	74.32	79.28	44
pH	7.95	8.52	8.62	8.55	8.58	7.81	7.82	7.79	7.75	7.79	7.84	7.83	7.77	7
Mg	6.41	4.42	4.54	5.36	4.26	5.71	4.12	6.90	4.82	6.78	7.19	5.30	4.77	4.35
Al	0.00	0.00	0.00	0.53	0.00	0.60	0.00	0.00	0.00	0.58	0.71	0.00	0.00	0.66
Si	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.18	0.01	0.00	0.00	0.00	0.00	0.39
к	0.18	0.20	0.26	0.23	0.23	0.26	0.30	0.27	0.31	0.24	0.25	0.28	0.26	0.056
Fe	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.01	0.02	0.00	0.00	0.00	0.00	0.01
Cu	0.10	0.10	0.10	0.10	0.10	0.08	0.12	0.07	0.08	0.00	0.07	0.06	0.07	0
Rh	1.15	1.12	1.14	1.13	1.16	5.94	6.56	6.50	5.49	6.25	6.23	5.99	6.23	0
Ag	0.00	0.00	0.00	0.00	0.00	0.90	0.00	0.00	0.91	0.00	0.00	0.00	0.00	0
Cd	0.00	0.78	0.82	0.92	0.00	0.00	0.00	0.91	0.00	0.97	0.00	0.00	0.00	0

As shown in Fig. 4, it is possible to observe a positive correlation linking the calcium values to the total hardness in water. That suggests a correlation between the

total hardness in the water and calcium-rich minerals of the study's area lithology. The equation shows that the coefficient for total hardness in the calcium is 0.9155 mg

L⁻¹. The correlation between the amount of calcium and the hardness was of r = 58% (Fig. 4). This confirms that the total hardness in Jaguari stream is mainly due to calcium bicarbonate and the dissolution of minerals originating from another calcium-rich minerals

dissolution from near lithologies. Thus, the mineral's dissolution during the process fluid/rock interaction is responsible for the calcium bicarbonate presence in shallow waters.



Fig.4: Relationship of calcium (mg L⁻¹) with the Total Hardness (mg L⁻¹). Classification of water as to its hardness in accordance with [23].

The analysis exhibits other elements in lower percentages and, or with less, such as silica, chlorine, and iron (Table 1).

Using the Pearson coefficient, it is possible to summarize the relationship between two variables. For a better analysis of the data, a statistical study was accomplished starting from the analysis of correlations, where values with a strong Pearson correlation were outstanding in the table [26]. The most common way to introduce and analyze groups of Bivariate Data is through X and Y axes, the correlation measures, the similarity among two different variables. Therefore, the value can be calculated accordingly to the equation (1).

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

where, Xi being the variable X value, Mx the average values of X, Yi the variable Y value, My the average values of Y, σx the X standard deviation and σy the Y standard deviation.

Table 2 shows strong positive correlations between electric conductivity and temperature (0.60), pH (0.76); calcium and total hardness (0.76); total hardness and K (0.67) and Rh (0.64); pH and Cu (0.68); and Rh and K (0.70). Also, demonstrate strong negative correlations between electric conductivity and Si (-0.65); temperature and K (-0.62), Rh (-0.97); Ca and (-0.66); total hardness and Si (-0.65); pH and Si (-0.66); Si and K (-0.62).

Table.2: Pearson's correlation matrix for the investigated parameters and elements

Variable	Conductivit	Temperatur	Са	Total	pН	Mg	Al	Si	K	Fe	Cu	Rh	Ag	Cd
	У	e	Cu	hardness										
Conductivity	1	<u>0.60</u>	0.17	0.22	<u>0.76</u>	-0.07	-0.46	<u>-0.65</u>	0.02	-0.46	0.52	-0.47	-0.28	0.14
Temperature	<u>0.60</u>	1	-0.40	-0.53	0.48	-0.40	-0.10	0.00	-0.62	-0.30	0.19	<u>-0.97</u>	-0.38	0.20
Ca	0.17	-0.40	1	<u>0.76</u>	0.05	0.26	-0.15	-0.66	0.55	-0.40	-0.02	0.55	0.00	-0.17
Total	0.22	0.52		1	0.11	0.45	0.14			0.05	0.00	0.64	0.14	0.14
hardness	0.22	-0.53	<u>0.76</u>	1	0.11	0.45	-0.14	<u>-0.65</u>	0.6 7	-0.05	0.26	<u>0.64</u>	0.14	-0.14
рН	<u>0.76</u>	0.48	0.05	0.11	1	-0.19	-0.35	-0.66	0.32	-0.21	<u>0.68</u>	-0.37	-0.18	0.45
Mg	-0.07	-0.40	0.26	0.45	-0.19	1	0.39	-0.03	0.12	-0.30	-0.30	0.42	-0.04	0.23
Al	-0.46	-0.10	-0.15	-0.14	-0.35	0.39	1	0.42	-0.39	-0.01	-0.54	0.01	0.11	0.05
Si	<u>-0.65</u>	0.00	<u>-0.66</u>	<u>-0.65</u>	<u>-0.66</u>	-0.03	0.42	1	-0.62	0.35	-0.55	-0.17	0.14	-0.11
Κ	0.02	<u>-0.62</u>	0.55	<u>0.67</u>	0.32	0.12	-0.39	-0.62	1	0.18	0.47	0.70	0.32	0.05
Fe	-0.46	-0.30	-0.40	-0.05	-0.21	-0.30	-0.01	0.35	0.18	1	0.19	0.15	0.45	-0.19
Cu	0.52	0.19	-0.02	0.26	<u>0.68</u>	-0.30	-0.54	-0.55	0.47	0.19	1	-0.12	0.09	-0.10

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Rh	-0.47	<u>-0.97</u>	0.55	<u>0.64</u>	-0.37	0.42	0.01	-0.17	<u>0.70</u>	0.15	-0.12	1	0.28	-0.16	
Ag	-0.28	-0.38	0.00	0.14	-0.18	-0.04	0.11	0.14	0.32	0.45	0.09	0.28	1	-0.30	
Cd	0.14	0.20	-0.17	-0.14	0.45	0.23	0.05	-0.11	0.05	-0.19	-0.10	-0.16	-0.30	1	

To gather water's chemical properties, it was applied the Principal Component Analysis (PCA) based on the correlation matrix between the components and padronized variables. The 11 PCs represent 100% of the variance in the obtained results (Table 3). The first three PCs have > 1, representing 80.83% of the variance (Table 3). The first and second main components are the result of the linear combination of 14 studied variables, and both explained 36.99% and 63.98% of the variance, respectively.

PC	Eigenvalue	Total variance%	Cumulative Eigenvalue	Cumulative %
1	4.07	36.99	4.07	36.99
2	2.97	26.99	7.04	63.98
3	1.85	16.85	8.89	80.84
4	0.82	7.50	9.72	88.34
5	0.49	4.49	10.21	92.83
6	0.39	3.57	10.60	96.41
7	0.20	1.80	10.80	98.20
8	0.09	0.83	10.89	99.03
9	0.06	0.59	10.96	99.62
10	0.03	0.30	10.99	99.92
11	0.09	0.07	11.00	100

Table 3: Eigenvalues of correlation matrix and related statistics

The PCA also produces Eigenvectors, also referred to as coefficients or main components loads (Fig. 5). They describe the relative significance of a component, for example, a chemical element and its variability amongst a group of data. The eigenvectors automatically calculate the punctuation for each PC. The values of the element charges determine the score from a sampling point. So that the grouping of elements of high charges provides high punctuations, and the grouping of low charge elements supplies low punctuations. In this regard, the number of calculated Eigenvectors will be equal to the number of used variables, which in this study is the number of chemical elements and analyzed parameters [29].



Fig.5: Multivariate analysis of geochemical characteristics of Jaguari stream water using PCA to extract the principal components.

For PC1 (36.99% variance) high scores are equivalent to elements of high charges (> 0.2), for example, temperature, Fe, Al and Si (Fig. 5). the lowest scores are equivalent to the lowest charges (< 0.19), such as conductivity, pH, the Cd observed in the anthropogenic contribution and Cu.

High scores for PC2 are related to strong positive charges (> 0.2) to the elements Fe, Ag, Ca, Mg, Rh, Al and K. Negative charges and low scores appear in Cd, Cu, pH and total hardness (Fig. 5).

IV. CONCLUSION

The water samples collected at Jaguari stream from Lavras do Sul-RS showed water's total hardness ranging from soft to intermediate. The Ph values indicated slightly alkaline to alkaline waters, with electrical ranging from 157.1 to 184.90 μ S cm⁻¹ and calcium levels fluctuate between 18.27 and 41.31 mg L⁻¹.

The multivariate statistical methods showed positive and negative correlations that can be interpreted as derived from interaction with the lithology (for instance, granite, volcanic) and anthropogenic activity.

The distribution of the scores for PC1 and PC2 shows that changes can happen in the geochemistry composition of the waters, principal to Cl, conductivity, temperature and, pH followed by Fe, Ag, Ca, Cu and K. This suggest lithological influence in the composition of the waters. The Cd was associated with anthropic interference because its correlation was secondary.

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