Geochemical Conditioning Factors Acting in the South Mesoregion of Santa Catarina State, Brazil: Influence of the Carboniferous Basin

Fatores Geoquímicos Condicionantes Atuando na Mesorregião Sul do Estado de Santa Catarina: Influência da Bacia Carbonífera

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ABSTRACT

This research uses Principal Components Analysis (PCA) to synthetize information about low density geochemistry survey of the South Mesoregion of Santa Catarina State (Brazil), where a coal mining region is inserted. The sampling survey includes 74 samples from stream sediments, taken with a sample density near of 1/150 km^2. The sediments were sieved at <80# mesh, submitted to extraction by HNO_3/HCl (3:1) and analyzed by ICP for 53 elements. Up to 47 parameters were selected for PCA analysis after normalization and correlation analysis. The three main components explained 72.7% of the total variance. The first and second components reflected the lithotypes and the third component portrays the anthropic influence of coal mining.

Keywords: regional geochemistry, bottom sediments, acid mine drainage.

RESUMO

Esta pesquisa utiliza Análise de Componentes Principais (ACP) para sintetizar informações sobre levantamento geoquímico de baixa densidade na Mesorregião Sul do Estado de Santa Catarina, onde está inserida uma região de mineração de carvão. A amostragem inclui 74 amostras de sedimentos de corrente, tomadas com uma densidade amostral próxima de 1/150 km^2 e peneiradas em tamanho de malha <80 # para análise após extração por HNO_3 / HCl (3:1) e analisados por ICP para 53 elementos. Destes, 47 parâmetros foram selecionados após análise de normalização e correlação. Os três componentes principais explicaram 72,7% da variância total. O primeiro e o segundo componentes refletiram os litotipos e o terceiro componente retrata a influência antrópica da mineração de carvão.

Palavras-chave: geoquímica regional, sedimentos de corrente, drenagem ácida de mina.

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1 - INTRODUCTION

Until the 1980s, coal mining in Santa Catarina (SC) occurred without any environmental control or concern. In the 1990s, the Santa Catarina Carboniferous Basin had 5,500 ha (55 km^2) of areas degraded by coal exploitation (JICA, 1998 [1]). In 2000, a judicial sentence condemned the Union, the Coal Mining Companies and the Santa Catarina State to recover some of the impacted areas, which initiated the Environmental Recovery Project for Degraded Areas by Coal Mining.

Currently, the coal mining activity takes place subject to environmental licensing, which prioritizes making the coal industry viable in a self-sustainable way, combining coal activities with environmental recovery.

To identify the natural geochemical substrate, a low-density regional scale geochemical survey was carried out by the Geological Survey of Brazil (SGB-CPRM) in the South Mesoregion of Santa Catarina, where coal mining areas are located.

2 – OBJECTIVES

The objective of this work was present the geochemical behavior of stream sediments since the spring of superficial water resources until the mouth of the hydrographic regions. For this purpose, it was present a part of multivariate statistical treatment, ordering the variables into main components that synthesize active and founding processes of the geochemical substrate. More details of these results can be found in the Informe Técnico-Científico de Prevenção de Desastres e Ordenamento Territorial of SGB-CPRM.

2.1. Case Study

The study area is in the South Mesoregion of Santa Catarina State (10.827 km^2), where there are two hydrographic regions and the Carboniferous Basin (Figure 1).

The Extreme-South hydrographic region is formed by Mampituba (1.250 km^2), Araranguá (2.956 km^2) and Urussanga (676 km^2) basins, while the South region includes Tubarão (4.734 km^2) and Duna (1.211 km^2) basins.

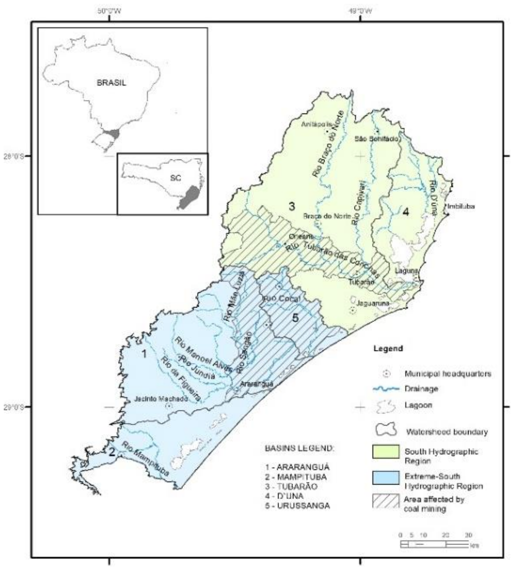

Figure 1 - Study area.

A current estimation of the affected by Acid Mine Drainage (AMD), considering only the sub-basins from their headwaters until the major river mouths, is about 2.745 km^2 (Figure 1). These areas are inserted in three hydrographic basins of Araranguá, Urussanga and Tubarão rivers, which together make up 8.366 km^2. The greatest environmental impact is located in the Central-East of the study area, which completely comprises Urussanga river basin.

According to Wildner et al. (2014) [2], the study area is located on the Santa Catarina Shield grouped in the Granitic-Gneissic Complex. They are foliated granitoids, late to transcurrent, belonging to the Intrusive Paulo Lopes Suite, which predominate in the northern portion of the study area (Figure 2).

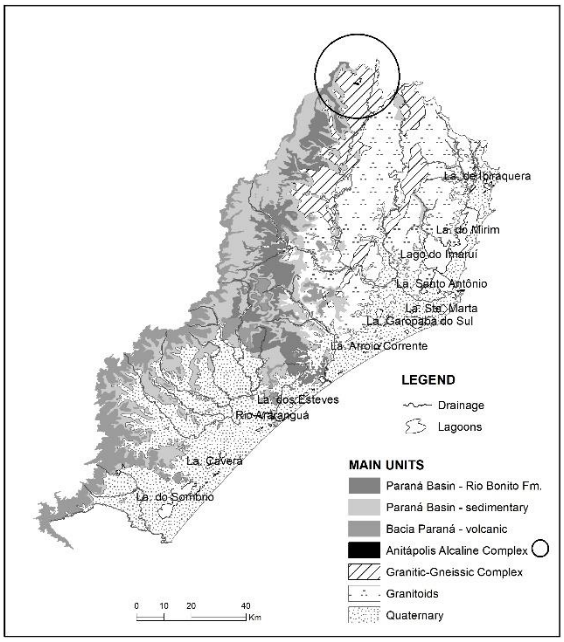

Figure 2 - Simplified Geology. Modified of Wildner et al. (2014).

Intrusives in the Granitic-Gneissic Complex and partly contemporary, dating from the Neoproterozoic, the granitoids suites Pedras Grandes and Cambirela are considered consanguineous (calcium-alkaline or alkaline) also due the existing isotopic data (SILVA; LEITE, 2000) [3].

The Anitápolis Alkaline Complex is a small body of approximately 6 km^2 located in the extreme North of the area. It is composed by basic-ultrabasic alkaline rocks, which intruded the calcic-alkaline granitoids of Pedras Grandes Suite (KAHN, 1988) [4].

Also registered hydrothermal fluorite veins mineralization, in the mid and high stretches of Tubarão river basin. The ore is embedded between the granitoids Pedras Grandes and the basal unit of Paraná river Basin (DARDENNE; SAVI, 1984) [5]. Sedimentary rocks of Paraná Basin are located at the West and South edges of the basement and predominating in the Central-East portion of the area. These rocks are covered by basic volcanic rocks at the high-relief of the Serra Geral, across the West quadrant. This sedimentary basin consists of continental deposits and shallow platforms of the Paleozoic-Mesozoic period, and comprises a sedimentary-magmatic package, with a maximum total thickness of around seven thousand meters (MILANI et al., 2007) [6]. The coal lithology is part of Rio Bonito formation in Paraná Basin.

3 - MATERIALS AND METHODS

74 samples of bottom sediments were collected at representative locations of hydrographic sub-basins at average 1 sample every 146 km², covering an area of influence of approximately 10.827 km^2. The stream sediments were collected in the active drainage channel, below the water level, in sub-rectilinear stretches, in a compound of a 10m strip along the drainage, upstream of the access, sieving samples in situ, with <32 mesh (0,5 mm) nylon sieve.

The samples were dried at 55°C and later sieved at <80 mesh (0,177 mm) fraction, prior to extraction with aqua regia (HNO_3/HCl - 3:1) (USEPA, 2007) [7], which aims to determine the availability and mobility of metals.

ICP-OES or ICP-MS chemical analysis were performed, comprising 53 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr), by SGS GEOSOL. Depending on the bond strength of the chemical elements to the crystalline matrix, the results of extraction with aqua regia approached partial or total concentrations.

Data processing involved statistical analysis (quartiles, percentiles, histograms, boxplots, geostatistics and multivariate), where the Principal Component Analysis (PCA) was the main objective of this work. A multivariate analysis indicates simpler patterns than individual analysis of each element, explaining them in a smaller number of variables called factors, or components. The PCA data preparation requires data normalization keeping outliers values due to the low sample density. The selection of variables was carried out by means of correlation analysis, removing weaker correlated data which does not provide valuable information. The PCA method calculates a correlation matrix using all sample variables, resulting in a new set of artificial variables called eigenvalues. The eigenvalues indicate the contribution of each variable to the total variation in the set. The loadings express the influence of each variable within the factors, and the scores express the influence of an eigenvector in a specific sample, allowing the spatial mapping factor in individual samples.

The analysis was performed using the Geosoft Target 9.8.1 software, based on an original data matrix with 74 samples and 47 variables (chemical elements).

4 - RESULTS

With PCA, the most relevant components were obtained in the first dimensions, or so-called main axes. The relationships of the data set were obtained considering a minimum significance (1.0) in each component, indicated by the eigenvalue (Table 1).

Table 1 - Eigenvalues and cumulative values.

PC	Eigenvalue	% cumulative
1	20.097	42.8
2	9.363	62.7
3	4.704	72.7
4	2.04	77
5	1.947	81.2
6	1.26	83.9
7	1.058	86.1
8	1.018	88.3

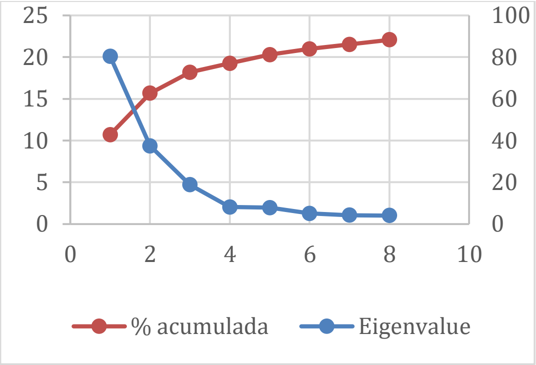

Figure 3 - Eigenvalues and cumulative graph.

Table 2 – Loadings and scores of PC1, PC2 and PC3.

PC1	LOADINGS	SCORES	PC2	LOADINGS	SCORES	PC3	LOADINGS	SCORES
U	0.912	-0.955	**V**	0.899	0.948	**Fe**	0.823	-0.615
Ce	0.876	-0.936	**Cu**	0.858	0.834	**Al**	0.814	-0.257
Tl	0.869	-0.932	**Ga**	0.854	0.739	**Sb**	0.732	-0.834
Rb	0.866	-0.93	**Sc**	0.853	0.741	**As**	0.724	-0.837
Yb	0.853	-0.86	**Ti**	0.824	0.892	**Mo**	0.693	-0.781
La	0.84	-0.917	**Co**	0.797	0.859	**P**	0.647	-0.417
Y	0.839	-0.858	**Mg**	0.707	0.782	**Ag**	0.639	-0.516
Be	0.834	-0.913	**Zr**	0.625	0.789	**S**	0.577	-0.711
Lu	0.833	-0.845	**Ni**	0.602	0.769	**Zn**	0.525	-0.413
Th	0.796	-0.892	**Sr**	0.58	0.761	**Hg**	0.412	-0.411
Tb	0.784	-0.885	**Hf**	0.571	0.751			
Cs	0.758	-0.871	**Mn**	0.536	0.678			
Sn	0.744	-0.863	**In**	0.49	0.611			
Bi	0.649	-0.806	**Ba**	0.471	0.667			
Pb	0.626	-0.791	**Cr**	0.359	0.524			
K	0.463	-0.681						
Li	0.438	-0.662						

The first principal component (PC1) has the largest eigenvalue, and the following components gradually decrease eigenvalues. The other components (eigenvalues <1.0) were rejected, and the main components were recalculated using Kaiser's Varimax scheme. It is noteworthy that the first three components explain 72.7% of the total variance (Figure 3). The result of PCA can be represented by the scores of the first three main components (PC1 - PC3), viewed in 2D (Figure 4), or even in 3D three-dimensional space (Figure 5).

According to the exposed data, Axis 1 represents PC1 high negative eigenvectors of U, Ce, Tl, Rb, Yb, La, Y, Be, Lu, Th, Tb, Cs, Sn, Bi, Pb, K and Li. Axis 2 represents PC2 high positive eigenvectors with V, Cu, Ga, Sc, Ti, Co, Mg, Zr, Ni, Sr, Hf, Mn, In, Ba and Cr. Axis 3 represents PC3 high negative eigenvectors with Fe, Al, Sb, As, Mo, P, Ag, S, Zn and Hg.

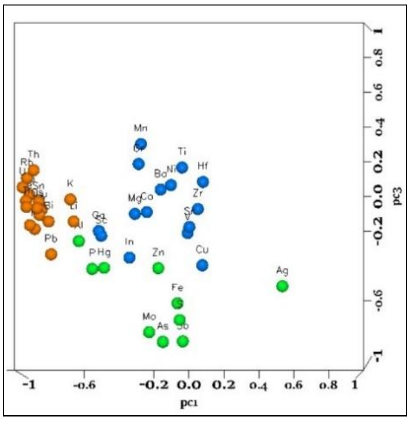

Figure 4 - Scores PC1 x PC2.

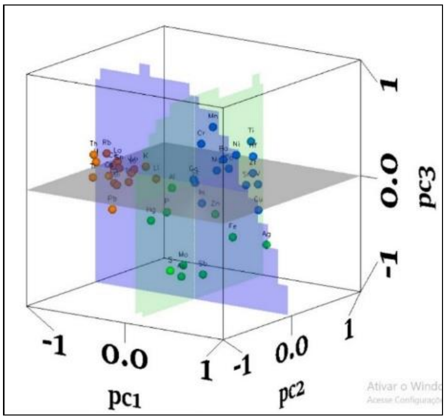

Figure 5 - Scores PC1 x PC2 x PC3.

The research omitted lower components due to their low significance and focused on relevant components. The distribution of the main components (PC1 to PC3) in the area and a brief description of these are presented below.

PC1 - U, Ce, Tl, Rb, Yb, La, Y, Be, Lu, Th, Tb, Cs, Sn, Bi, Pb, K and Li.

Essentially lithologic component, represented by naturally high levels of U, Tl, Rb, Be, Th, Cs, Sn, K and Li in the North, originating from the crystalline basement; slightly increased background contents of Rare Earth Elements - ETR (Ce, La, Yb, Y, Lu and Tb), both in the North and in the South (Figure 6).

Possibly anthropic contents of Bi and Pb in Tubarão and Duna river basins, based on the fact that both form sulfides, possibly present in the fluorite veins, explored in Tubarão and Urussanga basins.

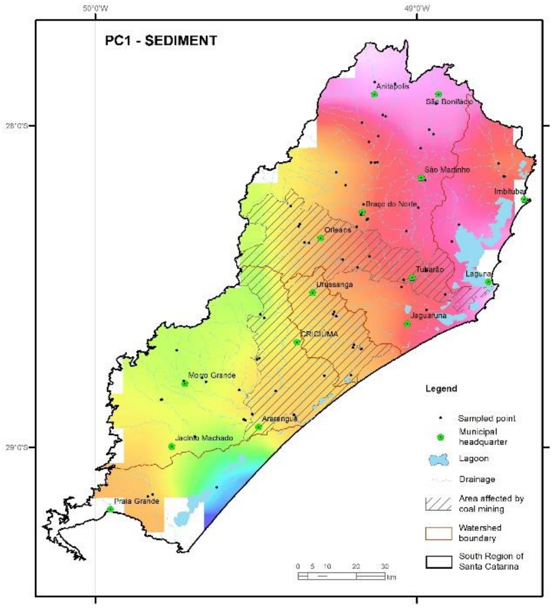

Figure 6 - PC1 spatial distribution.

PC2 – V, Cu, Ga, Sc, Ti, Co, Mg, Zr, Ni, Sr, Hf, Mn, In, Ba e Cr.

Represents lithologic influence of basic rocks in the South, in Mampituba and Araranguá river basins and, secondarily, of the basic-ultra-basic rocks in the North, in Tubarão basin. There are also localized enrichments of Ni, In and Ba, in the middle stretches of Urussanga and Araranguá basins (Figure 7). These are supposed to be anthropic, because the springs have a lower content, and these enrichments are punctual, downstream of the mined areas.

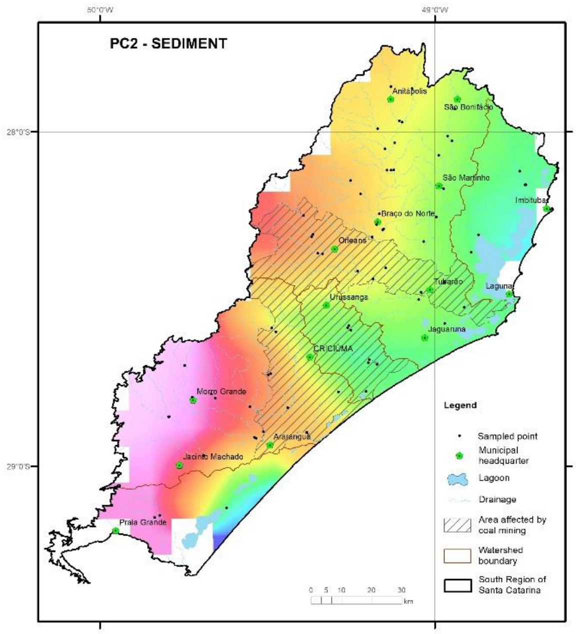

Figure 7 - PC2 spatial distribution.

Naturally high levels of V, Cu, Ga, Sc, Ti, Co, Mg, Zr, Ni, Mn, In and Cr, occur from the sources in the tholeiitic basalts of Serra Geral (Mampituba and Araranguá basins).

Due to the Acid Mine Drainage (AMD), part of these metals are leached locally and are slightly concentrated in the middle section (V, Cu, Ga, Sc, Ti, Mg), as well as at the river mouth of Araranguá (Co, Ni, In).

The Urussanga basin, despite having occurrences of basic rocks, is depleted in almost all elements of basic provenance (V, Cu, Ga, Sc, Ti, Co, Ni, Mg, Cr).

PC3 – Fe, Al, Sb, As, Mo, P, Ag, S, Zn e Hg.

Resulting from the anthropic influence of coal mining in the Central-East area in Urussanga basin and part of Araranguá and Tubarão basins (Figure 8).

Due to the environmental impact caused by AMD, there is an enrichment of elements with probable anthropic origin (Sb, As, Ag, Hg), the enrichment of Fe and S in the whole area affected by AMD, the depletion of some elements in the mined areas (Al, P) and their appearance downstream (Al, P, Mo, Zn).

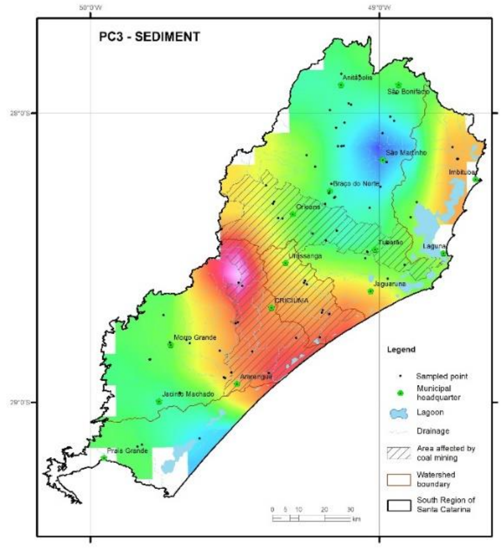

Figure 8 - PC3 spatial distribution.

In Urussanga basin, of lesser extent and totally circumscribed in the impacted area, most elements are concentrated at the river mouth (Fe, Al, Sb, As, Mo, Ag, S, Zn, Hg).

5 - CONCLUSIONS

There are marked differences in the geochemical substrate of the Extreme-South and South regions of Santa Catarina. There are reflected in the two main components (PC1 and PC2), essentially litholic, representing the naturally high levels of acidic plutonic rocks in the Southern basins (Tubarão and Duna basins), and basic volcanic in the Extreme-South (Mampituba and Araranguá basins).

The Central-East portion, where Urussanga basin is located, has both influences cited above regarding geology. However, Paraná basin units are predominant and the impact of coal extraction activity, which is manifested by leaching most of the natural chemical elements derived from rocks and concentrating anthropic elements influenced by mining (PC3).

It is not unwittingly that the elements naturally present are leached from the area impacted by AMD. Various minerals that have less resistance than pyrite, such as gypsum, calcite, fluorite, apatite, and feldspar, can be attacked by AMD, which explains why the Central-East portion was depleted in several chemical elements.

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