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# Surface water resources of Santa Catarina state's southern region – geochemical background of the coal mining territory

## *Recursos hídricos superficiais da região sul de Santa Catarina – background geoquímico da região afetada pela mineração de carvão*

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## ABSTRACT

In the environmental reclaiming process, it is essential to distinguish between chemical elements concentrations that occur naturally in water resources (geochemical background), from those originated from anthropogenic activities. Despite the environmental efforts that have been carried out for more than two decades in the southern Brazilian region impacted by coal mining, its geochemical background is still not completely known. Filling this environmental knowledge gap was the objective of this work, which systematically analyzed the results of monitoring efforts carried out by the Geological Survey of Brazil (SGB/CPRM) across three years. Quality parameter distributions of rivers and streams unaffected by anthropogenic impact were analyzed. The database was used to perform principal component analysis (PCA) and cluster analysis, and to define the background values, which was done through the boxplot and ± 2 MAD (Median Absolute Deviation) methods. The results of multivariate statistical analyses clustered the monitoring sites into two groups, one related to the sedimentary rocks of the Paraná Basin and another to the crystalline basement rocks. The sedimentary group had a greater correlation with the parameters Eh, $SO_4^{2-}$, Ca, Mg, EC, Mn, Acidity, Zn and Na; while, and the crystalline rocks group were better correlated with pH, Cu, Al, K, and Fe. The results of the geochemical background were similar for both methods, with values of pH, Fe, Al, and Mn being slightly different from those defined in Brazilian legislation (CONAMA 357/05 and MS 888/21).

**Keywords:** Geochemical background; Surface water resources; Santa Catarina carboniferous basin.

## RESUMO

A diferenciação entre concentrações naturais de espécies químicas presentes nos recursos hídricos, *background* geoquímico, daquelas encontradas em locais contaminados é fundamental em projetos de recuperação de áreas degradadas. Apesar das ações de melhoria ambiental que vem sendo realizadas por mais de duas décadas na região de Santa Catarina impactada pela mineração de carvão, seu *background* geoquímico ainda não é plenamente conhecido. O preenchimento dessa lacuna de conhecimento foi objetivo deste estudo, que analisou os resultados de campanhas de monitoramento realizadas pelo Serviço Geológico do Brasil SGB/CPRM durante três anos. A distribuição de parâmetros de qualidade dos rios e córregos não afetados por contaminações antrópicas da área de estudo foi analisada. Este banco de dados foi utilizado para realização de análises de componentes principais (ACP) e de *cluster*, e na definição dos valores de *background*, que foi feito pelos métodos de *boxplot* e mediana ± 2 MAD (*Median Absolute Deviation*). As análises estatísticas multivariada convergiram para o agrupamento dos locais de coleta em dois grupos, um relacionado às rochas sedimentares da Bacia do Paraná, com maior correlação com os parâmetros Eh, $SO_4^{2-}$, Ca, Mg, EC, Mn, acidez, Zn, e Na, e outro às rochas do embasamento cristalino, correlacionadas com pH, Cu, Al, K, e Fe. O resultado do *background* geoquímico foi similar para ambos os métodos, com valores de pH, Fe, Al, e Mn levemente diferentes daqueles definidos nas normas CONAMA 357/05 e Portaria MS 888/21.

**Palavras-chave:** *Background* geoquímico; Recursos hídricos superficiais; Bacia carbonífera de Santa Catarina.

## INTRODUCTION

The extraction of mineral substances is an economic activity that happens around the world, with records showing some cases of areas that have been mined for over a thousand years (Runnells et al., 1992; Sarmiento et al., 2009). If not treated properly, mining waste can present health hazards both to people as well as to the environment (Runnells et al., 1992). One of the main environmental problems that stems from mining, specifically related to sulfide minerals, is Acid Mine Drainage (AMD), which can contaminate surface and groundwater resources (Cravotta, 1989; Cravotta et al., 1999; Gray, 1998; Gray & Member, 1996; Yang et al., 2006).

It is important to have the knowledge of the geochemical background of water resources in environmental remediation and reclaiming efforts of mining areas (Matschullat et al., 2000) that is, knowing what is the natural concentration of the elements present in the location being investigated. According to Mast et al. (2007), despite mining affecting the quality of a region's waters, the weathering of mineralized rocks in mineral provinces can naturally be a source of water resource contamination by way of metals and acidity. In these regions, the reference values for water resource quality parameters, as defined in legislation, do not always reflect the local reality and, if they are taken into consideration, they might hinder the remediation/reclamation goals for these places. Thus, the differentiation of water contamination caused by natural rock weathering, from that engendered by mining activities should be an elemental objective in environmental remediation and reclamation projects of degraded areas (Nordstrom, 2015).

In Brazil, coal is found in the States of Rio Grande do Sul, Santa Catarina and Paraná. Specifically in the southern region of Santa Catarina, coal extraction activities began at the end of the 19th Century, intensifying around the middle the 20th Century through the mechanization of the mines (Alexandre, 1999). The increase in coal extraction around that period, coupled with negligence and lack of government control, resulted in a series of environmental damages. These impacts are observed in the explored sites, in those with irregular coal refuse disposal and, primarily, in the region's water resources. Scientific research in the region featuring subjects related to these impacts has been carried out since the 90's (Alexandre, 1999; Alexandre & Krebs, 1995; Cardoso & Fan, 2021; Freitas et al., 2017; Gothe, 1993; Ilha, 2019; Leyen, 2019; Lattuada et al., 2009; Simão et al., 2019; Volpato et al., 2017). Among the existing work in the literature, the research by Simão et al. (2019) is of particular note, establishing the geochemical background for pH, sulfate, iron and manganese values of the water springs in the municipality of Criciúma, a breakthrough in the understanding of these variables in the region.

Given the history of environmental damage in the region, the Public Prosecutor's Office started a Public Civil Suit (ACP), popularly known as the Coal ACP. This lawsuit resulted, through the Federal Court, in the indictment of private companies and the Federal Government itself, binding them to recover the degraded areas, as well as the region's water resources. The dimension and complexity of the existing environmental damage, with at least 1.241,3 km of the rivers compromised by AMD (Fórum ACP Carvão, 2019), pushed back the timescale for environmental reclamation and its implementation is still underway.

In 2022, over two decades of environmental mitigation and improvement actions in the affected basins have elapsed, and quantifying the quality of water resources is still essential. However, the natural concentration of chemical species in superficial water resources in a condition prior to the impact (geochemical background) for the entire mined area still remains to be known in its totality, which impairs defining realistic goals for the environmental reclamation of the region. Establishing these values is not just an operational challenge, but a scientific challenge as well, since it relies on the interpretation of hydrochemical analysis results, given the region's complex hydrological and hydrogeological context. Especially with regard to understanding the processes that occur in its natural waters.

Following this line, the present research seeks to fill this knowledge gap, starting off from the analysis of a database with 3 years worth of surface water monitoring, having the goal of defining background values for surface water resources across the entire region affected by coal mining in the south of Santa Catarina of the following variables: pH, Redox potential (Eh), Electrical conductivity, Acidity, $SO_4^{2-}$, Fe, Mn, Al, Na, Mg, Ca, K, Cu, Cd, Pb, Na, As and Hg. We strived to relate the characteristics of the background to the region's geology. In addition, the background data was cross-checked with the quality reference values that were adopted in Brazilian legislation, such as contamination thresholds, aiming to highlight differences between what would be natural waters according to the legislation in comparison to the values verified in the field.

## MATERIAL AND METHODS

The methodology of this research consisted of compiling, systematizing and analyzing data from three years of monitoring performed by the Geological Survey of Brazil (SGB/CPRM) in the region. The data was classified, analyzed and statistically processed in order to obtain the background values, according to scientific standards of previous works (Aboubakar et al., 2021; Dung et al., 2013; Ismaiel et al., 2018; Sequeira et al., 2020; Simão et al., 2019).

A detailed explanation of the study area and methodological steps follows.

### Study area

The study area is located in the southern region of the State of Santa Catarina and is composed by three river basins (Figure 1): Araranguá River Basin (BHRA), 3025 $km^2$, Tubarão River Basin (BHRT), 5960 $km^2$, and Urussanga River Basin (BHRU), 709 $km^2$. The main sources of AMD contamination: surface impacted areas and abandoned mine openings with AMD outflows, are located North/Northeast of BHRA, to the Northwest of BHRU and Southwest of BHRT, as in the detail of Figure 1.

In the Köppen climate classification, the study region's climate falls under Humid subtropical (Cfa); mesothermal, with no defined dry season and Hot summer. The average annual temperature is between 16 and 20°C, with an increase during the Summer months (Pandolfo et al., 2002). The annual average for

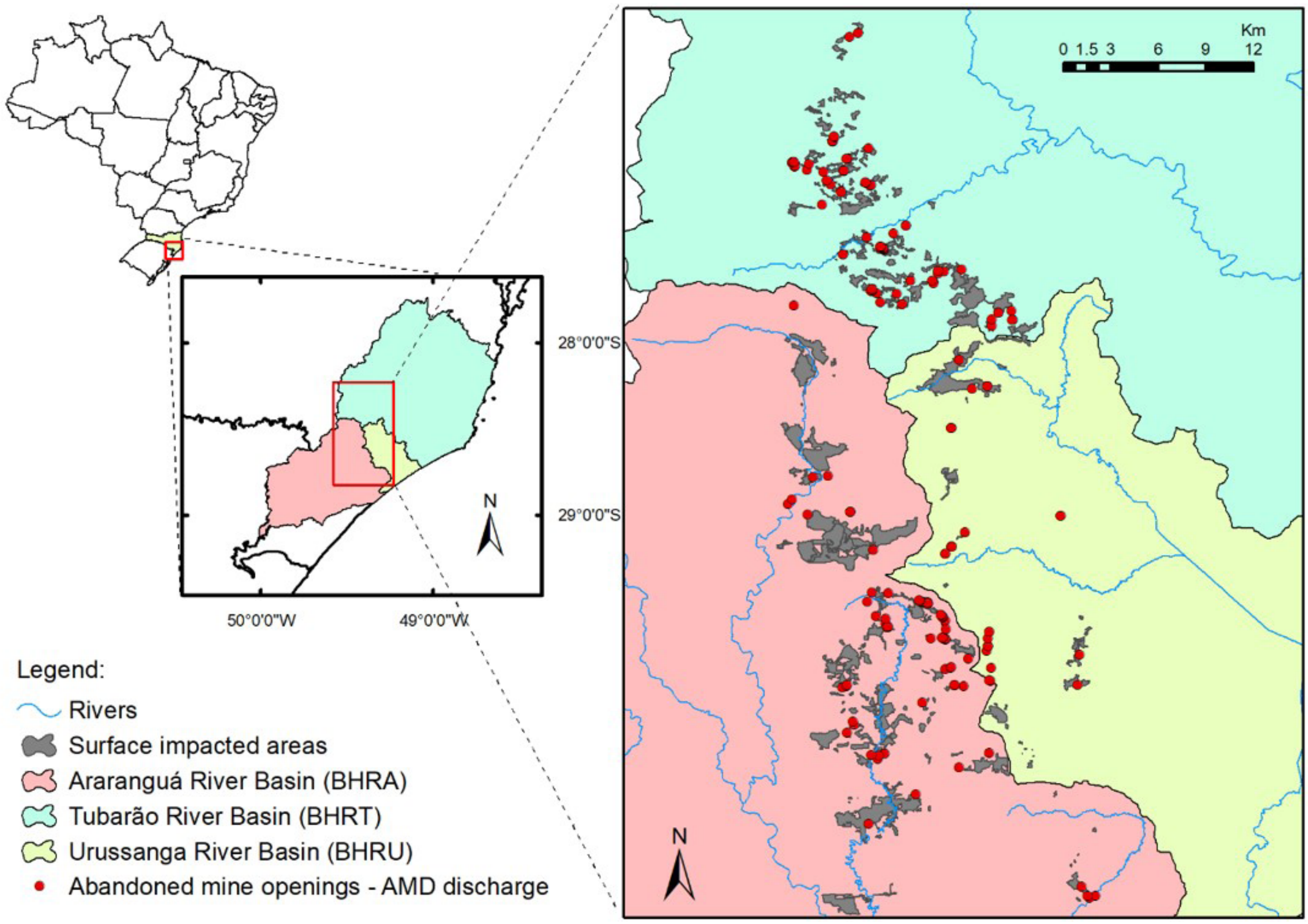

**Figure 1.** Study area location.

precipitation is around 1,630mm, with a 500mm average during the Summer months (Gotardo et al., 2018 ).

## Geology

According to Silva & Leite (2000), the study area has, as its foundation, units in the Catarinense Shield that are grouped together under Granite-Gneiss Complex (Complexo Granítico-Gnáissico). They are foliated, syn to late-transcurrent granitoids, which predominate the Northern portion (Figure 2).

The granitoids of the Pedras Grandes and Cambirela suites are intrusive and partly contemporary, and can be grouped due to the petrographic homogeneity, field characteristics and existing isotopic data.

The Anitápolis Alkaline Complex, a small basic-ultrabasic alkaline massif of approximately 6km$^2$ with a small expression in the extreme North of the area, intruded the calc-alkaline granitoids of the Pedras Grandes Suite (Kahn, 1988).

Fluorite hydrothermal mineralizations are recorded in the North, in the upper and middle segments of the Tubarão Basin. The ore is slotted in Pedras Grandes Suite's granitoids and in Paraná Basin's basal units (Dardenne & Savi, 1984).

At the basement's Western and Southern edges, and predominantly in the Central-East portion, there are sedimentary rocks of the Paraná Basin, consisting of continental deposits and shallow shelf, which had its implantation in the Paleozoic-Mesozoic period (Milani et al., 2007). The outcropping package in the study area corresponds to the Gondwana I Supersequence (predominantly Paleozoic) where South Santa Catarina's coal deposits are found. Subordinately, there are Botucatu Formation's arenite exposures and Serra Geral Formation's magmatites, with essentially basic volcanics, positioned in the highest elevations of the terrain.

Figure 2 groups the sedimentary units of Paraná Basin, with the exception of the Rio Bonito Formation, highlighted for containing the coal layers.

Occupying a wider strip to the south of the study area, the Coastal Plain is formed by a Cenozoic sedimentation, developed during the Quaternary, which encompasses sedimentary deposits of the continental (alluvial fans); transitional (fluvial-lagoon and coastal, related to the evolution of two sandy barriers, one Pleistocene and the other Holocene); and marine (fluvio-deltaic-marine) types.

According to the hydrogeological map of the state of Santa Catarina (Machado, 2013), occur in the region the hydrostratigraphic units related to (i) fractured aquifers corresponding to the crystalline basement; (ii) aquifers with intergranular porosity enlarged by fracturing, represented by sedimentary rocks of the Paraná basin; (iii) fractured aquifers corresponding to the volcanic rocks by Serra

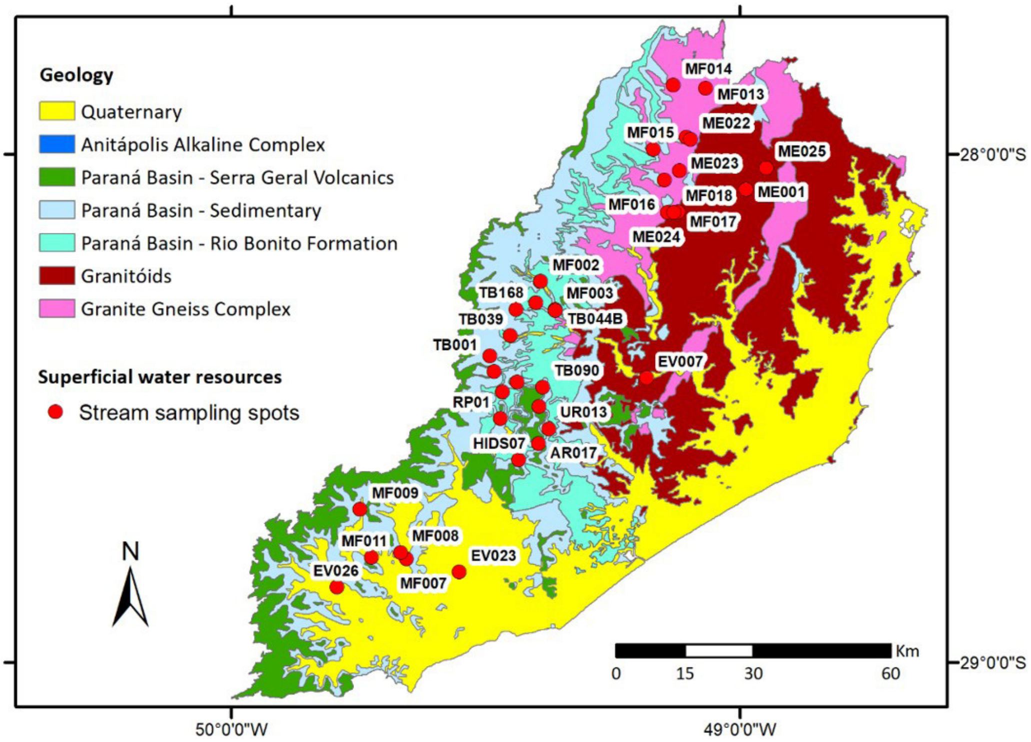

**Figure 2.** Geology of the study area and location of the stream sampling spots.

Geral formation; and (iv) unconfined aquifers related to Cenozoic coastal aquifer systems.

## Monitoring and analyses

The surface water samples that were utilized are located upstream of sites with anthropic activity (mining, agriculture, urban area, etc.). The monitoring campaigns of these samples were performed between the years of 2018 and 2020. In total, 85 surface water samples were analyzed for this research, they were from three different monitoring projects carried out in the study watersheds, all performed by the Geological Survey of Brazil (SGB/CPRM). A sum of 21 samples from the "Low-density geochemistry of Southern Santa Catarina" (Geoquímica de baixa densidade da região Sul Catarinense) project, 12 samples from the "Environmental Reclamation of the Santa Catarina Carboniferous Basin" (Recuperação Ambiental da Bacia Carbonífera de Santa Catarina) project and 52 samples pertaining to the project "Environmental Indicators in the Carboniferous Region" (Indicadores Ambientais da Região Carbonífera), conducted by the SGB/CPRM as a result of the Coal Public Civil Suit (Fórum ACP Carvão, 2019). Since the monitoring is continuous, the amount of samples collected in the last two projects (64) is spread across 14 checkpoints, so, taking into account the checkpoints of project "Low-density geochemistry of Southern Santa Catarina", makes a total of 35 sampled spots (Figura 2).

The monitoring carried out in the three projects followed the same procedure (detailed in the next paragraphs), with the most important AMD parameters as reference. Thus, the parameters of pH, Redox Potential (EH), Dissolved Oxygen (DO) and electrical conductivity (EC) were measured on site using the Aquaread multiparameter probe, model AP-800 (Aquaread, 2017). At each site, samples were collected manually by inserting high-density polyethylene bottles directly into the streams, at the points with the highest flow, just below the water surface, and in the flow direction. Two bottles were collected at each site for lab analysis: one container without preservation, for physico-chemical analysis, and the other with 2% HCl, for analysis of metals. Once collected, the samples were sent to the Mining Pollution Control Center laboratory (Centro de Controle de Poluição Mineral - CECOPOMIN) of the SGB/CPRM. At the lab, the samples were filtered with a Millipore®, 0.45 μm pore size. Analytical methods used were defined by the Standard Methods for the Examination of Water and Wastewater (American Water Works Association, 1998). The samples' quality control was undertaken following SGB/CPRM's standards. Table 1 displays the Parameters and their units, Analysis site, Quantification limits and Analysis method.

The Redox potential values measured on site were corrected based on the reference electrode in the probe, of the AgCl type (Aquaread, 2017).

## Descriptive statistics and correlations

The initial assessment of the database was done through descriptive statistics. The values smaller than the quantification limits were replaced by half the limit's value, following the practice proposed in previous studies in the literature (Keith et al., 1983).

The results of the descriptive statistics were compared to the reference values of Decree (Portaria) nº 888, from 2021, by the Ministry of Health (MS); and the CONAMA Resolution nº 357,

**Table 1.** Relation of the analyzed parameters, quantification limits and analysis methods for the study samples.

| Parameter | Unit | Analysis site | Quantification limits | Analysis method |
|---|---|---|---|---|
| pH | ... | Field | 0.1 | AP-800 Probe (*Aquaread*) |
| Redox potential ($E_H$) | (V) | Field | 0.01 | AP-800 Probe (*Aquaread*) |
| Dissolved oxygen (DO) | $(mg.L^{-1})$ | Field | 0.01 | AP-800 Probe (*Aquaread*) |
| Electrical conductivity (EC) | $\mu S.cm^{-1}$ | Field | 0.1 | AP-800 Probe (*Aquaread*) |
| Acidity | $mg.\ CaCO_3.L^{-1}$ | Laboratory | 0.5 | Potentiometric tritation |
| Sulfate ($SO_4^{2-}$) | $(mg.L^{-1})$ | Laboratory | 0.5 | Gravimetric analysis |
| Total Iron (Fe) | $(mg.L^{-1})$ | Laboratory | 0.01 | ICP OES* |
| Total Aluminium (Al) | $(mg.L^{-1})$ | Laboratory | 0.01 | ICP OES* |
| Total Manganese (Mn) | $(mg.L^{-1})$ | Laboratory | 0.002 | ICP OES* |
| Sodium (Na) | $(mg.L^{-1})$ | Laboratory | 0.07 | ICP OES* |
| Magnesium (Mg) | $(mg.L^{-1})$ | Laboratory | 0.01 | ICP OES* |
| Calcium (Ca) | $(mg.L^{-1})$ | Laboratory | 0.025 | ICP OES* |
| Potassium (K) | $(mg.L^{-1})$ | Laboratory | 0.07 | ICP OES* |
| Copper (Cu) | $(mg.L^{-1})$ | Laboratory | 0.002 | ICP OES* |
| Cadmium (Cd) | $(mg.L^{-1})$ | Laboratory | 0.002 | ICP OES* |
| Lead (Pb) | $(mg.L^{-1})$ | Laboratory | 0.005 | ICP OES* |
| Zinc (Zn) | $(mg.L^{-1})$ | Laboratory | 0.005 | ICP OES* |
| Arsenic (As) | $(mg.L^{-1})$ | Laboratory | 0.002 | HVG ICP OES** |
| Mercury (Hg) | $(mg.L^{-1})$ | Laboratory | 0.0003 | ICP OES* |

*Inductively Coupled Plasma Optical Emission Spectrometry. **Hydride Coupled Plasma Optical Emission Spectrometry.

from 2005. The MS Decree lays out the water quality standards for human consumption, while the CONAMA Resolution outlines a classification of the water bodies and environmental guidelines for its framing. Due to the water resource configurations analyzed in this research not being defined in a basin plan in the CONAMA Resolution, the results were compared to the parameters of Class 2 rivers, as advised by the ruling. The Al, Fe and Cu values featured in the Resolution correspond to the analysis of the dissolved portion of the elements.

After descriptive statistical analysis, the median values of the parameters were used in the samples of the spots that have a historical time series of sampling, so as to enhance the robustness of the results. Spearman's nonparametric correlation matrix was the basis for evaluating the correlation of the parameters (Glasser & Winter, 1961).

## Multivariate statistical analyses

The multivariate statistical analyses were performed with the median value of the parameters with historical time series, as previously described. The selection of the variables for insertion in the analyses was made with the results of the correlation matrix as a basis. The parameters that did not display a gaussian distribution were normalized through logarithmic transformation. All the variables were then standardized for adjustment of their orders of magnitude.

Cluster analyses of the samples were carried out through hierarchical and non-hierarchical clustering. The hierarchical methods that were employed are: Single linkage, Complete linkage, Ward's method, Average linkage and Centroid method; while k-means was the non-hierarchical method (Murtagh, 1985). The use of different methods had the aim of giving support and consistency to the final result of the clustering.

The generated clusters were plotted onto the area's geology map in order to identify the correlations between the clusters' characteristics and the geological aspects. As per Mast et al. (2007), the degree of alteration to the bedrock and to its associated minerals are the main controlling factors of the region's geochemical background.

Principal Component Analysis (PCA) was used to verify the interrelations between the study variables (Venables & Ripley, 2002). The results of the cluster analysis and PCA were integrated so as to explain the generated clusters based on each component's significance.

## Establishing the background

The water quality data that precede the historical mining activities are usually not available, which makes differentiating dissolved constituent concentrations in the water of mined sites, from those that were not mined, a challenging task (Nordstrom, 2015). Runnells et al. (1992) proposed three methods for estimating the background values in mined areas: historical document analysis, comparison to the natural concentration in unmined areas, and theoretical geochemical modeling.

This study employed the method of comparison to the natural concentration in unmined areas. The database was defined based on cluster analyses and PCA. Two statistical methods were applied to the selected database for the detection of extreme values, or outliers: the boxplot method and the ± 2 MAD method (Tukey, 1977). For both methods, the data series of normalized variables was used, as described in the previous item and as recommended by Reimann et al. (2005).

The boxplot method splits the data's ordered list of values in four equal parts. With the median as a basis, the upper quartile (Q3) and the lower quartile (Q1) are drawn, these quartiles define the central box, which contains 50% of the data. The inner fence is defined as the central box extended 1.5 times the box's length towards the maximum, from the upper quartile, and to the minimum, from the lower quartile. The whiskers are traced at the inner fences' extremes, and any value outside the whiskers' interval is defined as an outlier (Reimann et al., 2005). This boxplot analysis is also known in some Portuguese language literature as "mustaches diagram" ('diagrama de bigodes').

The ± 2 MAD method utilizes the dataset's median and the median absolute deviation, or MAD. MAD, in statistics, is a robust measure of a univariate sample, defined as:

$$MAD = b M_i\left(\left|x_i - M_j\left(x_j\right)\right|\right) \quad (1)$$

Where *b* is a constant linked to the data's assumption of normality, with a value of 1,4826, $x_j$ is the *n* of original observations and $M_i$ is the series's median (Leys et al., 2013; Rousseeuw & Croux, 1993).

The background results defined by both methods were compared to the reference values of Portaria nº 888, 2021, by the Ministry of Health (MS) and the CONAMA Resolution nº 357, 2005.

## RESULTS AND DISCUSSION

Following are the results obtained in the ensuing order: (i) descriptive statistics and correlation analyses; (ii) multivariate statistical analyses and relation with the study area's geology; and (iv) establishment of background values.

### Descriptive statistics and correlations

The result of descriptive statistics of the field and laboratory data for all samples is featured on Table 2. Out of the total amount of samples, 28 were collected at BHRA, 48 at BHRT and 9 at BHRU.

The pH of these spots varied from 5.1 to 8.6, and 83% of the samples were within the range of CONAMA nº 357's guidelines: between 6 and 9. The Redox potential values (ORP) were all positive and remained between 0.17 and 0.50, indicating an environmental predominance of oxidizing conditions.

Dissolved Oxygen (DO) varied between 5.2 and 13.2 mg.L$^{-1}$, with all samples remaining within CONAMA's minimum limit for Class 2 Rivers. Considering Class 1 rivers, whose threshold is 6 mg/L OD, most samples were also charted, at 93%.

The electrical conductivity (EC) rested between 39 and 220 39 e 220 μS/cm$^2$, with the median and the mean placing respectively at 88.4 μS/cm$^2$ and 83.0 μS/cm$^2$. The larger EC values were observed in samples that also possessed elevated magnesium, calcium and sodium values; the correlations between these parameters and CE were all significant: Na: 0.54, Mg: 0.75 and Ca: 0.73 (Table 3).

All samples remained within the limits of CONAMA Resolution's Class 2 values for sulfate, which is 250 mg.L$^{-1}$. The maximum concentration that was found was 112.8 mg.L$^{-1}$, that is, 45% of the reference value. Sulfate also displayed a positive correlation with Mn (0.61) and Mg (0.57), as shown in Table 3.

The mean concentration values for Fe and Al were the only to surpass the resolution's limits. However, in both cases the median remained below this limit, which denotes that the mean values of these variables were affected by outliers. In the case of iron, the outliers refer to three spots with values above 1.2 mg.L$^{-1}$, while for aluminium there were four values with concentrations above 1.0 mg.L$^{-1}$. The nonparametric correlation matrix showed that the correlation between these two parameters is the second most significant across all analyzed parameters, with r = 0.76.

All cadmium, arsenic and mercury samples presented values below the equipment's quantification limits.

**Table 2.** Statistic summary with results of the parameters.

| Parameter | Average | SD* | median | minimum | maximum | CV**(%) | CONAMA 357 | MS 888/21 |
|---|---|---|---|---|---|---|---|---|
| pH | 6.8 | 0.7 | 6.8 | 5.1 | 8.6 | 10.2 | 6 a 9 | 6 a 9.5 |
| Eh | 0.32 | 0.09 | 0.32 | 0.17 | 0.50 | 27.1 | - | - |
| DO | 8.1 | 1.3 | 8.1 | 5.2 | 13.2 | 16.7 | 5.0 | - |
| EC | 88.4 | 36.4 | 83.0 | 39.0 | 220.0 | 41.2 | - | - |
| Acid | 5.9 | 5.5 | 4.5 | <0.5 | 30.2 | 94.2 | - | - |
| $SO_4^{2-}$ | 10.9 | 9.1 | 8.6 | <0.5 | 42.8 | 83.4 | 250 | 250 |
| Fe | 0.34 | 0.43 | 0.23 | <0.01 | 2.53 | 127.7 | 0.3 | 0.3 |
| Mn | 0.02 | 0.02 | 0.01 | <0.002 | 0.15 | 133.4 | 0.1 | 0.1 |
| Al | 0.16 | 0.56 | <0.01 | <0.01 | 4.40 | 341.5 | 0.1 | 0.2 |
| Na | 4.33 | 1.33 | 3.86 | 2.61 | 8.14 | 30.7 | - | 200 |
| Mg | 2.17 | 0.80 | 2.12 | 0.51 | 4.49 | 36.7 | - | - |
| Ca | 5.55 | 1.83 | 5.41 | 2.08 | 10.70 | 33.0 | - | - |
| K | 1.05 | 0.49 | 0.92 | 0.38 | 3.45 | 46.8 | - | - |
| Cu | 0.007 | 0.030 | <0.002 | <0.002 | 0.256 | 413.1 | 0.009 | 2 |
| Cd | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | - | 0.001 | 0.003 |
| Pb | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | - | 0.01 | 0.01 |
| Zn | 0.012 | 0.022 | 0.005 | <0.005 | 0.184 | 186.3 | 0.18 | 5 |
| As | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | - | 0.01 | 0.01 |
| Hg | <0.0003 | <0.0003 | <0.0003 | <0.0003 | 0.002 | - | 0.0002 | 0.001 |

*Standard Deviation. **Coefficient of variation.

## Multivariate statistics and relations with geology

As cadmium, lead, arsenic and mercury values were below equipment's quantification limits, presenting a zero standard deviation, they were not used in multivariate statistical. The DO variable was also removed, bearing in mind that this parameter is influenced not only by the water's chemical characteristics but also by the physical characteristics of the bedrock and the flow speed.

Hierarchical and non-hierarchical cluster analyses were carried out with different amounts of clusters. The result of the analyses converged when the samples were sorted into two clusters. Out of the six methods that were used, only Complete Linkage did not present the same result, deviating from the others in the charting of a single sample.

Figure 3 features the result of cluster analysis, plotted onto the area's geological map. The clusters were divided in a spatially consolidated manner, one of them resting in the central and southwestern part, while the other is found only in the northern portion of the study area (Figure 3). By analyzing the contribution areas of the samples spots and the locations of the springs that supply water to these rivers and streams, it is noticed that such cluster division reflects the differences in the chemistry of the weathering in the area's geological formations; Paraná Basin's sedimentary rocks are found in the central and southwestern regions, while crystalline basement rocks predominate in the north.

Figure 3 displays a proper response to the clustering of spots by similarity, with the exception of a single spot (MF014), located north of the map; this spot presented a differing cluster

**Table 3.** Spearman's nonparametric correlation matrix (r values below -0,5 and above 0,5 are bold.).

| | pH | $E_H$ | DO | EC | Acid | $SO_4^{2-}$ | Fe | Mn | Al | Na | Mg | Ca | K | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $E_H$ | **-0.55** | | | | | | | | | | | | | |
| DO | 0.19 | -0.26 | | | | | | | | | | | | |
| EC | -0.08 | -0.10 | -0.47 | | | | | | | | | | | |
| Acid | -0.43 | 0.09 | -0.26 | 0.34 | | | | | | | | | | |
| $SO_4^{2-}$ | -0.16 | 0.17 | -0.40 | 0.32 | 0.36 | | | | | | | | | |
| Fe | -0.13 | -0.10 | 0.09 | -0.01 | 0.25 | -0.06 | | | | | | | | |
| Mn | -0.31 | 0.21 | **-0.59** | 0.32 | 0.46 | **0.61** | 0.34 | | | | | | | |
| Al | 0.05 | -0.21 | 0.49 | -0.33 | 0.07 | -0.27 | **0.76** | -0.08 | | | | | | |
| Na | -0.08 | -0.31 | -0.27 | **0.54** | 0.19 | 0.10 | 0.30 | 0.42 | 0.02 | | | | | |
| Mg | -0.34 | 0.18 | **-0.65** | **0.75** | **0.61** | **0.57** | 0.02 | **0.64** | -0.36 | 0.39 | | | | |
| Ca | -0.07 | 0.04 | -0.37 | **0.73** | 0.38 | 0.31 | -0.23 | 0.19 | -0.46 | 0.22 | **0.80** | | | |
| K | -0.09 | -0.22 | 0.30 | -0.16 | 0.02 | -0.41 | **0.66** | 0.05 | **0.55** | 0.36 | -0.23 | -0.33 | | |
| Cu | 0.35 | -0.40 | 0.31 | -0.11 | -0.27 | -0.24 | 0.22 | -0.29 | 0.28 | 0.29 | -0.42 | -0.32 | 0.37 | |
| Zn | -0.16 | 0.02 | 0.12 | 0.12 | 0.41 | 0.01 | 0.19 | 0.26 | 0.18 | 0.06 | 0.30 | 0.30 | 0.11 | -0.30 |

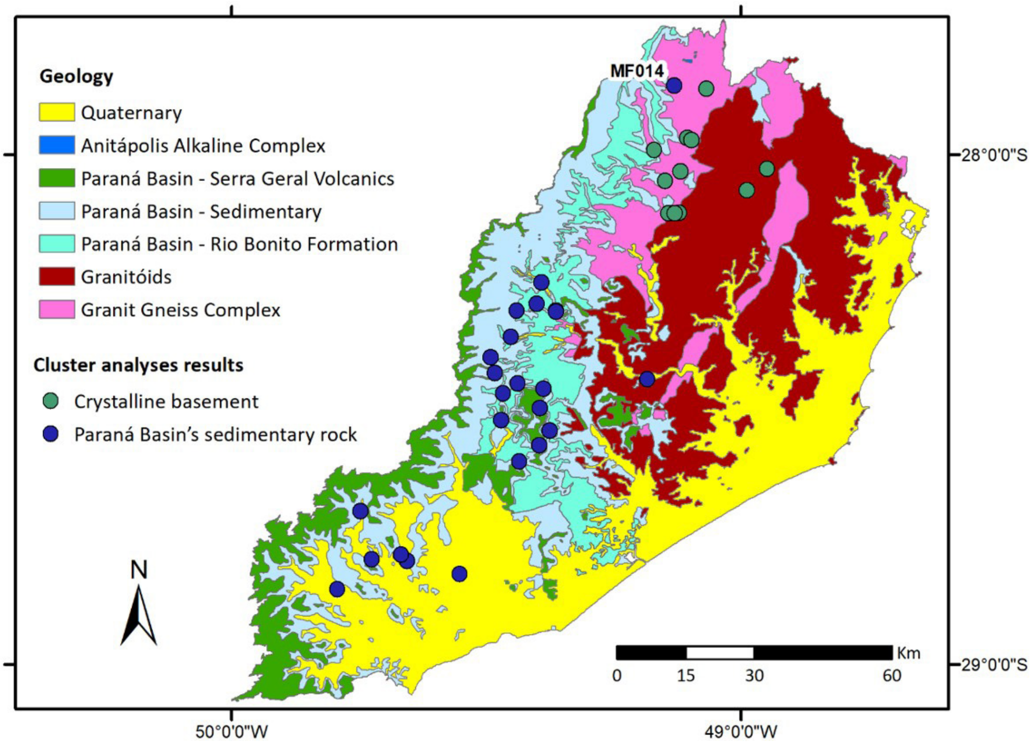

**Figure 3.** Results of the samples' cluster analyses sorted into two clusters.

similarity from its surrounding spots. This apparent discrepancy can be attributed to local geological constraints. While the cluster that surrounds it bears a chemical signature related to the crystalline basement, this spot displays a signature that, in cluster analysis, correlates it to the samples of Paraná Basin's sedimentary rock context. A hypothesis that may explain such a result is the influence of the Anitápolis Alkaline Complex, which occurs near the sampled location.

The result of the interrelations between the variables, which were analyzed through PCA, is featured on Figure 4. Figure 4a shows the chart with the first two principal components (PC), PC 1 explains 31% of the data variance, while PC2 explains 21%. The samples were colored according to the two clusters generated during analysis. This figure verifies that the result of PCA corroborates the results from the cluster analyses, with the samples that were collected from the sedimentary basin on the left side of the graph, and the crystalline basement samples on the right.

The graph featured on Figure 4b shows the significance of each variable within the principal components. Considering the results displayed on Figure 4a-4b, one verifies that the sedimentary basin samples are positively correlated to the variables: $E_H$, $SO_4^{2-}$, Ca, Mg, EC, Mn, acidity, Zn e Na, which are also positively correlated with each other, Mg and Ca being the most representative in the set. On the other hand, the set with the crystalline basement samples relates to higher pH, Cu, Al, K and Fe values, the first three variables being more strongly associated to the set's characteristics. These results reflect the soil's chemical composition in each region. The leaching of soils of granitic origin mainly involves the elements originating from feldspar and aluminosilicate weathering (K, Al, Na, Cu). While the soils of the rocks from Paraná Basin (basalt, siltstone and shales), predominantly involve elements that originate from the weathering of clay-minerals (Fe, Mg, Ca, K) (Lepsch, 2010; Lepsch, 2016).

Sample MF014, which during cluster analysis was ascribed to the sedimentary basin set, also presented indefinite results in PCA. As shown in Figure 4a, this sample is located in the intermediate area between the two sets composed by the analysis.

## Establishment of background values

Due to the low amount of samples classified in the crystalline basement set, the geochemical background was established only for the set of samples from the sedimentary basin, a section that encompasses all the areas that were impacted by the production chain of coal mining activities. The MF014 sample spot, whose analysis did not allow us to define its classification, was also excluded from the background analysis. After the removal of these spots, the final set of clusters from the sedimentary basin counted with 73 samples.

Table 4 presents the results of the dataset of the surface water resource checkpoints from the sedimentary basin's cluster of spots: descriptive statistics, lower and upper background limits established by the Boxplot and ± 2 MAD methods, defined background limits and the values from CONAMA Resolution 357/2005, class 2 rivers, and MS Portaria 888/2021 for comparison. The background results for the lower limit that lied below the quantification limits were replaced by each parameter's Limit value.

The two methods used to establish the background presented close values for most parameters, supporting the approaches that were used. For lower background limits, the ± 2 MAD method generated values equal to or higher than those defined by the Boxplot method. For upper limits, the Boxplot method presented higher values for 8 parameters, the ± 2 MAD method for 5 values, and values were below the limit of detection with both methods for the other 5. The background limits that were determined for the region (the highlighted values on Table 4) were defined based

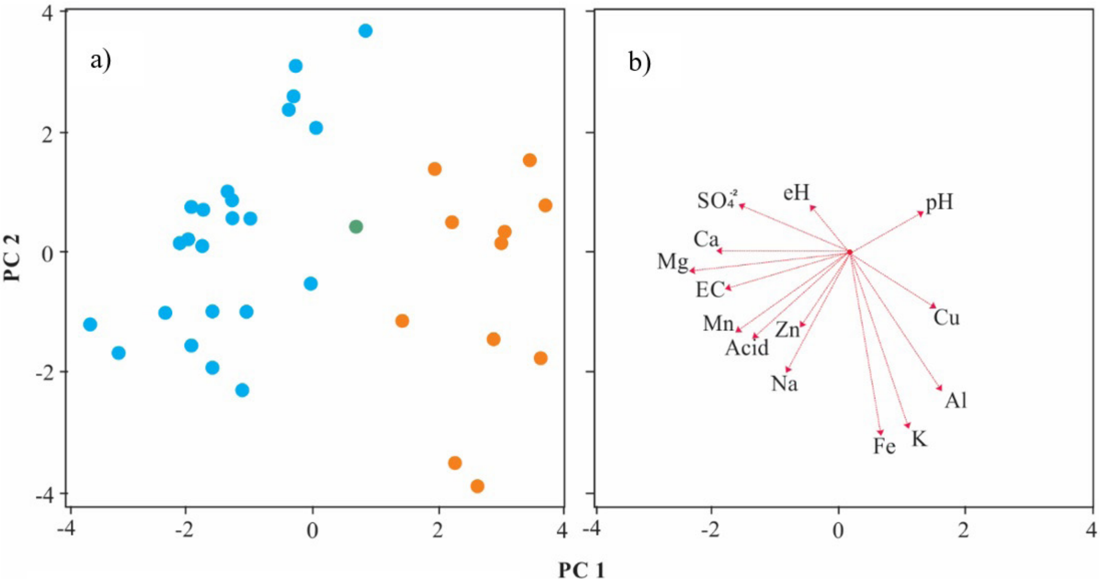

**Figure 4.** Results of Principal Component Analysis (PCA), a) graph with the first two principal components (PC) sorted by the resulting clusters of the cluster analysis (blue: sedimentary basin, red: crystalline basement); b) significance of each variable within the principal components 1 (PC1) and 2 (PC2).

**Table 4.** Background results of surface water resources of the sedimentary basin's cluster points (n = 73). Descriptive statistics and the lower and upper background limits, which were established through two methods: Boxplot and ± 2 MAD, as well as the defined methods are presented.

| | | **Descriptive statistics** | | | | **Background values** | | | | | | **CONAMA 357 Resolution** | **MS Portaria 888/21** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **Boxplot** | | **Median ± 2 MAD** | | **Defined Limits** | | | |
| | | **Mean** | **Median** | **Min** | **Max** | **Lower Limit (Q1-1,5 IQR)** | **Upper Limit (Q3+1,5 IQR)** | **Lower Limit (median -2 MAD)** | **Upper Limit (median + 2 MAD)** | **Lower** | **Upper** | | |
| pH | .... | 6.73 | 6.75 | 5.1 | 8.6 | 5.1 | 8.3 | 5.4 | 8.1 | **5.4** | **8.1** | 6 a 9 | 6 a 9.5 |
| $E_H$ | (V) | 0.32 | 0.32 | 0.17 | 0.5 | 0.01 | 0.61 | 0.11 | 0.53 | **0.01** | **0.53** | - | - |
| EC | (μS.cm$^{-1}$) | 94.9 | 89 | 40.8 | 220 | 19.5 | 159.3 | 51.5 | 153.7 | **19.5** | **153.7** | - | - |
| Acidity | (mg. CaCO$^3$.L$^{-1}$) | 6.3 | 4.9 | 0.5 | 30.2 | <0.5 | 13.6 | 1.2 | 19.2 | **<0.5** | **13.6** | - | - |
| $SO_4^{2-}$ | (mg.L$^{-1}$) | 11.9 | 9.9 | 0.4 | 42.8 | <0.5 | 29.4 | 2.3 | 41.7 | **<0.5** | **29.4** | 250 | 250 |
| Fe | (mg.L$^{-1}$) | 0.3 | 0.18 | 0.01 | 1.6 | <0.01 | 1.01 | <0.01 | 3.27 | **<0.01** | **1.01** | 0.3 | 0.3 |
| Mn | (mg.L$^{-1}$) | 0.02 | 0.01 | 0.001 | 0.15 | <0.002 | 0.06 | <0.002 | 0.194 | **<0.002** | **0.06** | 0.1 | 0.1 |
| Al | (mg.L$^{-1}$) | 0.06 | <0.01 | 0.01 | 0.66 | <0.01 | 0.22 | <0.01 | 0.01 | **<0.01** | **0.01** | 0.1 | 0.2 |
| Na | (mg.L$^{-1}$) | 4.42 | 3.92 | 2.61 | 8.14 | 0.97 | 7.58 | 2.2 | 6.99 | **0.97** | **6.99** | - | 200 |
| Mg | (mg.L$^{-1}$) | 2.38 | 2.23 | 1.4 | 4.49 | 0.66 | 3.89 | 1.29 | 3.85 | **0.66** | **3.85** | - | - |
| Ca | (mg.L$^{-1}$) | 5.9 | 5.54 | 2.94 | 10.7 | 1.16 | 10.39 | 2.97 | 10.35 | **1.16** | **10.35** | - | - |
| K | (mg.L$^{-1}$) | 0.97 | 0.87 | 0.38 | 2.41 | 0.04 | 1.83 | 0.45 | 1.69 | **0.04** | **1.69** | - | - |
| Cu | (mg.L$^{-1}$) | 0.007 | <0.002 | <0.002 | 0.256 | <0.002 | <0.002 | <0.002 | <0.002 | **<0.002** | **<0.002** | 0.009 | 2 |
| Cd | (mg.L$^{-1}$) | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | **<0.002** | **<0.002** | 0 | 0.005 |
| Pb | (mg.L$^{-1}$) | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | **<0.005** | **<0.005** | 0.01 | 0.01 |
| Zn | (mg.L$^{-1}$) | 0.013 | 0.007 | 0.003 | 0.184 | <0.005 | 0.027 | <0.005 | 0.117 | **<0.005** | **0.027** | 0.18 | 5 |
| As | (mg.L$^{-1}$) | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | **<0.002** | **<0.002** | 0.01 | 0.01 |
| Hg | (mg.L$^{-1}$) | <0.0003 | <0.0003 | <0.0003 | <0.0003 | <0.0003 | <0.0003 | <0.0003 | <0.0003 | **<0.0003** | **<0.0003** | 0.0002 | 0.001 |

on the more conservative figures, from the point of view of environmental contamination, for the two methods that were used.

When compared to the CONAMA Resolution and the MS Decree, the values of some quality parameters lie outside the boundaries of these regulations; that is, in the natural environment, the water may be found unfit for some of its intended uses. The lower background limit for pH, for example, was below the limit for both regulations, which is 6. Through the Boxplot method the figure was 5.1 while through ± 2 MAD, it was 5,4. Iron was another case of a background value appearing above the regulations' limits in both methods. While the upper limit is 0.3 mg.L$^{-1}$, the encountered background values were 1,01 mg.L$^{-1}$ and 3,27 mg.L$^{-1}$ , for Boxplot and MAD, respectively.

Aside from pH and iron, the aluminium and manganese parameters also had background values outside the bounds established by the CONAMA Resolution and the MS Decree. In both cases, however, only one of the methods extrapolated these limits. The manganese, for whom the resolution and decree outlined a limit of 0.1 mg.L$^{-1}$, had its background value through Boxplot at 0.06 mg.L$^{-1}$, yet the ± 2 MAD found an exceeding value of 0.194 mg.L$^{-1}$. The same happened for aluminium, whose legal value is 0.1 mg.L$^{-1}$ in the Resolution and 0.2 mg.L$^{-1}$ in the MS Decree, yet the encountered parameters were 0.01 mg.L$^{-1}$ through ± 2 MAD and 0.22 mg.L$^{-1}$ through the Boxplot method.

The obtained background results bring forth a contribution for the understanding of the region's water resources since it makes clear that many of the parameters that were evaluated naturally feature concentrations that surpass the figures established by water usage legislation concerning their suitability for the intended purposes. The surface waters from sedimentary basin of Santa Catarina State presented a restriction due to its quality in the iron, manganese and pH parameters, despite not being impacted by coal mining. However, it is important to stress that the degradation stemming from coal mining is not at all confused with natural conditions in terms of concentration.

Such non-compliance to legislation may have a geogenical relation to the rocks that make up the region's substrate and its respective soils originating from weathering. The region's soils are predominantly composed of these types: Red-Yellow Argisol (Argissolo Vermelho-Amarelo), Humic Cambisol (Cambissolo Húmico) and Haplic Cambisol (Cambissolo Háplico) (Embrapa, 2006), rich in elements such as iron and manganese, in addition to being naturally acidic. Environmental diagnostic studies performed by the Geological Survey of Brazil (SGB/CPRM) in the surroundings of the region's degraded areas (Instituto de Pesquisas Ambientais e Tecnológicas, 2010) found the same types of soil, which still matched the aluminium (alumínico) character, a condition where the soils presents larger concentrations of this element.

In other studies, authors also found naturally acidic rivers with high concentrations of metals related to geological environments (Kwong et al., 2009; Mast et al., 2008; Nordstrom, 2015; Runnells et al., 1992; Verplanck et al., 2009). According to Eppinger & Fuge (2009) the acidity may be naturally present in some types of geological environments, such as areas with pyritic shale, active volcanoes, regions with hot springs in terrestrial or underwater environments, undisturbed mineral deposits and saline lake systems, or with groundwater. For Nordstrom (2015) the presence of acidity in natural environments, such as those mentioned, occurs because the same microbiological and geochemical conditions present in the AMD phenomenon are also present in these locations, with the difference that mining accelerates the process.

Specific geochemical and pedological surveys can help in the understanding of the origin of the acidity and the slightly elevated concentrations of metals in the region's rivers. Among geochemical research, we cite the inverse geochemical model work, which is based on mineralogy and water quality data (Alpers & Nordstrom, 1997).

## CONCLUSION

This study delved into analyses related to the qualities of surface water resources in Southern Santa Catarina, focusing on basins impacted by coal mining in a pioneering manner. Quality parameters distribution of the rivers and streams unaffected by anthropic contamination in the study area was analyzed. The geochemical background of surface waters was established in the region where mining activities occurred, a factor that may help in setting more realistic goals for the environmental reclamation of the region's degraded areas.

The cluster analyses' results converged to the sorting of the samples into two sets. It was verified that these clusters reflected the differences in the geological formations of the region in which they are located, one of them related to Paraná Basin's sedimentary rocks, the other to the crystalline basement rocks. Principal Component Analysis results corroborated the cluster analyses, in addition to rendering further information regarding the affinity of the variables to each group. The sedimentary basin's samples had the biggest correlation to the Eh, $SO_4^{2-}$, Ca, Mg, EC, Mn, acidity, Zn and Na parameters; while the crystalline basement samples better correlated pH, Cu, Al, K e Fe.

The background of surface waters was generated through two methods: Boxplot and median ± 2 MAD, both with similar results for most parameters. For the upper limits, the Boxplot method generated higher values for 8 parameters; the median ± 2 MAD method had values below the limit of detection for 5 out of 5 for both methods. The background limits that were established for the region were determined based on the more conservative figures, from the point of view of environmental contamination, for the two methods that were used. When compared to the CONAMA Resolution 357/2005 and the MS Portaria 888/2021, it was found that the values of the lower pH limit were below both regulations' limits. Fe displayed a background value above the regulations in both methods that were used. The Mn and Al parameters also had values beyond that which was determined by the Resolution and the Portaria for only one of the background methods. The reference values of the aforementioned regulations are related to the toxicological unsuitability of the water, that is, the waters in the study area may be naturally unsuitable for some intended uses, even if they are not impacted by AMD. However, it is essential to mention that, although there is a correlation between the parameters that cause water unsuitability and those related to the impact caused by coal mining, the orders of magnitude of the mean and median values make it clear that these different types of concentrations can be clearly differentiated in the waters.

The geochemical background results obtained in the present study show that the waters of the basins in question may possess waters unsuitable for some of the intended uses, even without being impacted by coal mining. The speculation is that such apparently anomalous concentrations have a profound geogenic relationship, that is to say, the concentrations of the analytes of interest reflect the characteristics of the region's geological substrate and the soils that result from the weathering of these rocks. Given these results, we indicate that the exact origin of the values will be the subject of a targeted subsequent study.

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