Mining's legacy: Unraveling the impacts of acid mine drainage on the rivers and streams of the Santa Catarina coal region, Brazil

O legado da mineração: desvendando os impactos da drenagem ácida de minas nos rios e córregos da região carbonífera de Santa Catarina, Brasil

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ABSTRACT
Acid Mine Drainage (AMD) is a major environmental concern associated with coal mining activities, leading to the deterioration of water quality and posing significant risks to aquatic ecosystems and human health. In this study, we analyzed the physicochemical parameters of water samples collected from rivers and streams affected by mining in the Santa Catarina coal region, Brazil, to assess the extent and severity of AMD impact. Our findings reveal a substantial increase in element concentrations, including Fe, Mn, Al, and major cations (Na, Mg, Ca, and K), with some values exceeding background levels by several orders of magnitude. The majority of the samples exhibited acidic pH values, with only 24% and 34% within the limits established by the Ministry of Health and the geochemical background, respectively. Strong correlations between physicochemical parameters, such as pH and EH, and between acidity, sulfate, and metals, highlight the role of pyrite oxidation and mineral dissolution in generating AMD. Although most samples presented values within the established limits for toxic metals (Cu, Cd, Pb, As, and Hg), high concentrations of Zn were observed, exceeding regulatory and background limits. The results of this study emphasize the need for continuous monitoring and assessment of water quality in the region and contribute to a deeper understanding of the extent and severity of AMD in the Santa Catarina coal region.
Keywords: Acid Mine Drainage, Santa Catarina carboniferous region, surface water resources contamination.

RESUMO
Este estudo examinou a Drenagem Ácida de Minas (DAM) em rios contaminados pela mineração de carvão no sul de Santa Catarina, Brasil. Os resultados indicam um aumento significativo na concentração de vários elementos, incluindo Fe, Mn, Al, e cátions principais, com alguns ultrapassando significativamente os níveis de *background* geoquímico da região. A maioria das amostras apresentou pH ácido, com apenas uma pequena porcentagem dentro dos limites estabelecidos pela legislação e pelo *background* regional. Evidenciou-se a ligação entre a oxidação da pirita, a dissolução de minerais e DAM através das fortes correlações entre parâmetros físico-químicos. Embora a maioria das amostras estivesse dentro dos limites para metais tóxicos (Cu, Cd, Pb, As, e Hg), altas concentrações de Zn excederam os limites regulatórios e de *background*. O estudo ressalta a importância do monitoramento contínuo da qualidade da água e aumenta a compreensão do alcance e severidade dos impactos da DAM na região.
Palavras-chave: Drenagem Ácida de Mina, Região Carbonífera de Santa Catarina, Contaminação dos recursos hídricos superficiais.

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1 INTRODUCTION

Coal mining has been an essential economic activity in the southern region of Brazil, particularly in the Santa Catarina State, accounting for 4.9% of the country's energy production (BRASIL - MINISTÉRIO de MINAS e ENERGIA, 2021). Despite its economic importance, coal mining activities can have significant adverse effects on the environment. Among the most concerning environmental issues associated with coal mining is the generation of Acid Mine Drainage (AMD). AMD poses considerable risks to water resources such as groundwater, streams, and rivers, potentially leading to long-term environmental degradation (CRAVOTTA, 1989; CRAVOTTA et al., 1999; GRAY, 1998; JOHNSON; HALLBERG, 2005; YANG et al., 2006).

The coal mining industry in Santa Catarina is characterized by the extraction of low-quality coal with high pyrite content, which exacerbates the impact on the region's environment (KALKREUTH et al., 2006; SILVA et al., 2009). Although the Brazilian government has made efforts to modernize the coal-mining sector, AMD remains a persistent concern. Thus, understanding the impact of coal mining on water resources in Santa Catarina is crucial for informing policy decisions and developing effective strategies to mitigate the adverse effects of AMD.

Previous studies have investigated the hydrogeochemical processes and environmental impacts associated with AMD in coal mining areas around the world (ALPERS; NORDSTROM, 1997; NORDSTROM, 1982, 2015; YOUNGER et al., 2002). However, the international scientific literature on these studies in the state of Santa Catarina coal region is still limited. The purpose of this study is to address this gap in the literature and examine the extent to which coal mining has affected the water resources in Santa Catarina state, comparing these results with regional background values of water resources. To achieve this, the objectives of the study are to: 1) Assess the physicochemical parameters of water samples collected from rivers and streams impacted by coal mining activities in the Santa Catarina coal region; 2) Compare the results of the water quality analysis with values from regional background and federal guidelines to determine the extent of alterations caused by AMD; and 3) Investigate the correlations between various physicochemical parameters to better understand the underlying processes and mechanisms associated with AMD in the study area.

2 STUDY AREA

The study area is located in the southern region of Santa Catarina and is composed of three watersheds: the Araranguá River Basin (BHRA), 3,025 km², the Tubarão River Basin (BHRT), 5,960 km², and the Urussanga River Basin (BHRU), 709 km² (Fig. 1). The surface areas impacted and the sources of Acid Mine Drainage contamination are located to the northeast of the BHRA, to the northwest of the BHRU, and to the southwest of the BHRT, as shown in detail in Figure 1.

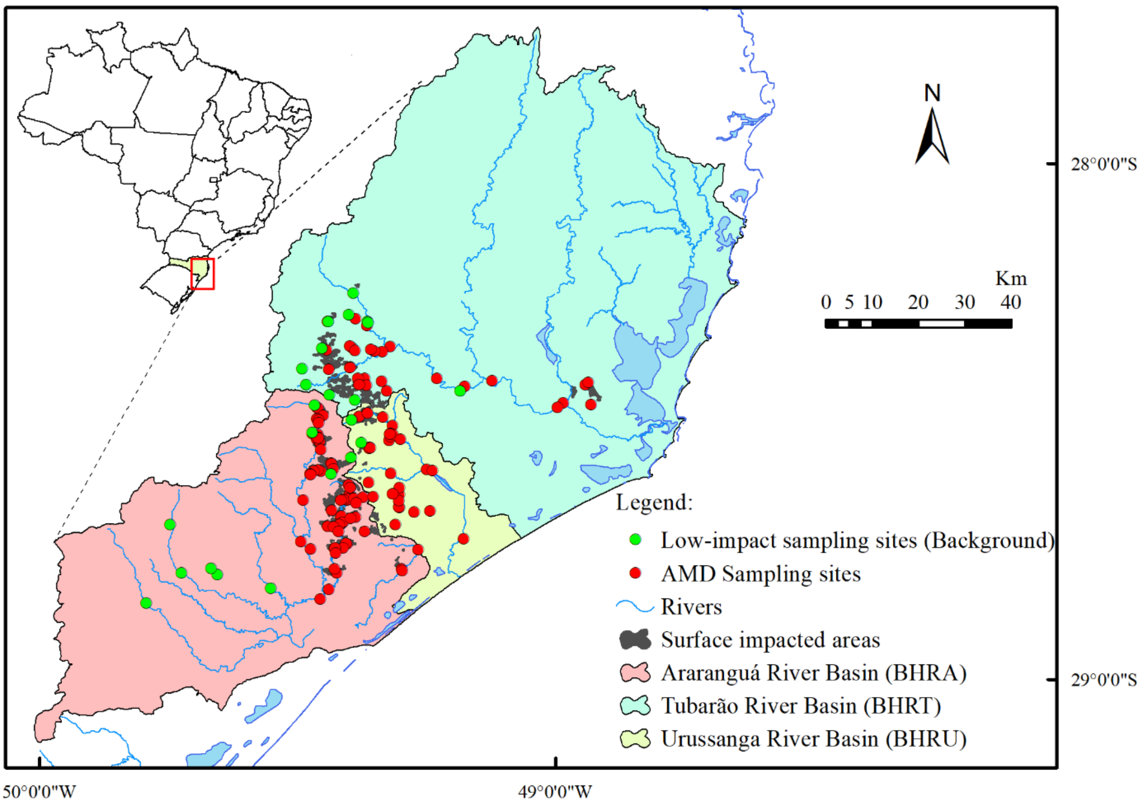

Figure 1 - Study area and sampling sites locations.

The climate of the study area is classified as humid subtropical (Cfa) according to the Köppen classification, characterized as mesothermal with no defined dry season and hot summers. The average annual temperature ranges from 16 to 20 °C, with an increase in the summer months (December to March). The average annual precipitation is around 1,630 mm, with an average of 500 mm of precipitation in the summer months, between December and March (GOTARDO *et al.* 2018).

2.1 HISTORY OF MINING AND WATER RESOURCES CONTAMINATION IN SANTA CATARINA

The region studied in southern Brazil has a history of coal mining that started in the late 19th century and intensified in the mid-20th century due to increased financial support from the federal government. The intensification of coal mining led to a decrease in the selectivity of mineral extraction and increased the amount of potentially contaminating material brought to the surface, causing environmental pollution. Mining activities occurred both on the surface and underground, causing negative impacts such as water and soil contamination and occupational health problems for workers (ALEXANDRE, 1999). The area was even designated a ''Critical National Area for Pollution Control and Environmental Conservation'' in the 1980s due to this critical situation.

The most significant and concerning impact was the contamination of water resources due to AMD and, despite 20 years of environmental reclaiming efforts, at least 1,241 km of streams are still affected by AMD in three watersheds (GTA, 2019).

The generation of AMD from coal mining can be attributed to the chemical reaction known as pyrite oxidation, which can be broken down into the following steps: in the first part of the reaction (Equation 1), solid pyrite is oxidized in the presence of water and atmospheric oxygen, generating ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}) and releasing H^+ ions. Then, ferrous iron is oxidized to ferric iron (Fe^{3+}), Equation 2, and this to ferric hydroxide ($Fe(OH)_3$), Equation 3 (SINGER; STUMM, 1970). The oxidation step to ferric iron occurs limitedly in abiotic environments, however, in environments with a pH between 2.8 and 3.2, this step can be accelerated by the action of bacteria that are naturally present in aquatic environments and that develop best in these pH conditions.

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$
$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \quad (2)$$
$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \quad (3)$$

In very acidic pH values (close to or below 2.3), hydrolysis (Equation 3) practically does not occur. This causes an increase in the concentration of Fe^{3+} in the environment, which oxidizes the pyrite, according to Equation 4 (DE MELLO *et al.*, 2014).

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad (4)$$

As a result, the generation of AMD contaminates the rivers of the region through the decrease of pH, acidification of the waters, and release of high concentrations of sulfate and metal ions, particularly iron, aluminum, and manganese. The release of aluminum and manganese ions occurs when the acidic conditions caused by the reactions above lead to the dissolution of other minerals present in the rocks and sediments (NORDSTROM; ALPERS, 1999). For instance, aluminum can be released from the weathering of aluminosilicate minerals like feldspars and clay minerals (BIGHAM; NORDSTROM 2000). Similarly, manganese can be released from the weathering of manganese-bearing minerals (LARSEN; MANN, 2005; PAUFLER *et al.*, 2019). The increased concentrations of these metal ions contribute to the toxicity of the contaminated water and further exacerbate the negative effects of AMD on aquatic ecosystems and water quality (CRAVOTTA; NANTZ, 2008).

3 METHODOLOGY

The approach used in this study involved gathering, organizing, and evaluating data collected over a three-year period by the Brazilian Geological Survey (SGB/CPRM) in the region. The data was classified, analyzed, and processed statistically with the aim of evaluating the impact of AMD.

3.1 FIELD MONITORING AND LAB ANALYSIS

The water samples from rivers and streams were collected between 2018 and 2020 along the studied area. In total, 652 surface water samples from three different monitoring projects carried out by the Brazilian Geological Survey were analyzed. Normally, sampling campaigns are carried out biannually; however, due to the COVID-19 pandemic, in 2020, only one campaign was conducted and the number of sampling sites was reduced. Most of samples are result of a continuous monitoring project, thus, the 652 samples are divided in 162 sampled sites. (Fig. 1). The duration of each campaign is approximately 4 months, spanning more than one season, which is why seasonal variations were not the focus of our analysis.

In contrast to the study conducted by Cardoso *et al*. (2022), the present research exclusively employed the samples collected from the sedimentary geology region. It's essential to clarify that the background values established by Cardoso *et al*. (2022) to the Santa Catarina coal region were substantiated by the sedimentary units of the Paraná Geological Basin. This selection was based on the fact that this region harbors the water resources that are impacted by AMD, and is also the region where the authors established the geochemical background.

All the samples were collected and analyzed following the SGB/CPRM default procedures, which is detailed in Cardoso *et al.* (2022). Table 1 presents the parameters and their corresponding units, as well as the analysis site, quantification limits, and analysis method used for each parameter.

Table 1 - List of analyzed parameters, quantification limits, and analysis methods of the samples used in the study.

Parameter	Unit	Analysis site	Quantification limits	Analysis method
pH	...	Field	0.1	AP-800 Probe
Redox potential (E_H)	(V)	Field	0.01	AP-800 Probe
Dissolved oxygen (DO)	(mg.L^{-1})	Field	0.01	AP-800 Probe
Electrical conductivity (EC)	µS.cm^{-1}	Field	0.1	AP-800 Probe
Acidity	mg. $CaCO_3$.L^{-1}	Laboratory	0.5	Potentiometric
Sulfate (SO_4^{2-})	(mg.L^{-1})	Laboratory	0.5	Gravimetric
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

3.2 CLASSIFICATION OF SAMPLING SITES

The long history of coal mining in the southern Santa Catarina, both on the surface and underground, makes it difficult to determine some of the monitored sites in the region that have been affected in some way by mining. These difficulties are mainly related to the determination of sources of contamination, as many degraded surface areas were later occupied for urban or industrial use, making their location difficult using satellite images. Additionally, there are hundreds of abandoned mine openings draining water from old flooded underground mines and contributing to the degradation of surface water resources. Many of these have already been registered, but it is likely that others are still without their locations determined.

The sampling sites for low-impact streams, were the same used on the study conducted by Cardoso *et al*. (2022), but restricted to locations within the sedimentary rocks area. For streams affected by AMD, the sampling sites were selected using GIS software with data obtained from polygons of impacted and explored areas both on the surface and underground, as well as available information on abandoned mine openings, and knowledge acquired by SGB/CPRM, which has been monitoring the region for over 15 years.

For sample classification, two categories were established: (I) streams in low-impact areas and (II), and streams affected by acid mine drainage (AMD streams). A total of 67 samples were classified as category I, while 585 samples were assigned to category II (Fig. 1).

3.3 STATISTICAL AND GRAPHICAL ANALYSIS

The initial evaluation of the database of AMD Streams took place through descriptive statistics. Values less than the quantification limit were replaced by half the value of that limit, following the practice proposed in previous studies in the literature (KEITH *et al.* 1983).

The descriptive statistics results were compared with reference values from Minister of Health's (MS) Decree No. 888/2021, National Environmental Council Resolution (CONAMA) No. 357/2005, and geochemical background limits of surface waters in the region defined by Cardoso *et al*. (2022) to assess the water quality standard for human consumption, classification of water bodies, and natural levels of chemical constituents in surface water. As the water resource classifications in the study area are not yet established, the results were compared to the parameters specified for class 2 rivers, as per Resolution guidelines. Furthermore, it should be noted that the Al, Fe, and Cu values reported in the resolution refer to the analysis of the dissolved fraction of the elements, whereas our study analyzed the total fraction.

The distribution analysis of the parameters between categories I and II, as well as the comparison with the geochemical background limits of the region, were performed using boxplot graphs (TUKEY, 1977).

The evaluation of the correlation of parameters was done using the non-parametric correlation matrix of Spearman (GLASSER; WINTER 1961). The Spearman correlation analysis is a non-parametric method used to evaluate the correlation between variables without assuming a specific distribution. This analysis can provide insights into how various parameters may be affected by the presence of AMD in the water.

4 RESULTS AND DISCUSSION

The obtained results are presented in the following sequence: descriptive statistics; comparative analysis of parameter distribution; and correlation analyses.

4.1 DESCRIPTIVE STATISTICS OF AFFECTED RIVERS AND STREAMS AND COMPARATIVE ANALYSIS

The collected samples from rivers and streams affected by mining were distributed as follows: 315 in BHRA, 132 in BHRT, and 138 in BHRU. Table 2 presents the statistical summary of the physicochemical variables, while Figure 2 displays the comparative distribution graphs (boxplots) between the two categories, incorporating the limit values of the geochemical. background. of. the region for added context.

Most of the samples for Cu, Cd, Pb, As, and Hg were below the analytical quantification limit for the method used, so these variables were excluded from the boxplot graphical analysis. Additionally, the DO variable was removed due to its sensitivity to both the water's chemical characteristics and the physical properties of the bedrock and flow speed.

Table 2 - Statistical summary with parameter results for mining-affected samples.

Vars	mean	SD*	median	min	max	Geochemical Background**	CONAMA 357	MS 888/21
pH	4.4	1.5	3.8	2.0	8.1	5.4 - 8.1	6 - 9	6 - 9.5
E_H	0.50	0.20	0.59	0.07	0.78	0.01 - 0.53	-	-
DO	6.5	2.4	6.9	0.0	13.9	-	5.0	-
EC	823	724	593	56	4287	153.7	-	-
Acid	203.1	351.9	73.6	<0.5	3022.0	13.6	-	-
SO_4^{2-}	346.3	504.4	174.5	<0.5	3678.1	29.4	250	250
Fe	30.90	82.43	6.14	<0.01	840.20	1.01	0.3	0.3
Mn	2.17	3.94	0.93	<0.002	37.90	0.06	0.1	0.1
Al	15.20	31.86	3.84	<0.01	316.00	0.01	0.1	0.2
Na	17.62	24.78	11.90	2.43	268.00	6.99	-	200
Mg	11.31	12.59	8.04	1.42	105.00	3.85	-	-
Ca	42.73	52.05	26.40	1.41	370.00	10.35	-	-
K	4.48	3.22	3.52	<0.07	23.20	1.69	-	-
Cu	0.014	0.083	<0.002	<0.002	1.180	<0.002	0.009	2
Cd	0.004	<0.002	<0.002	<0.002	<0.002	<0.002	0.001	0.003
Pb	<0.005	0.022	<0.005	<0.005	0.337	<0.005	0.01	0.01
Zn	0.411	0.818	0.119	<0.005	9.760	0.027	0.18	5
As	<0.002	<0.002	<0.002	<0.002	0.014	<0.002	0.01	0.01
Hg	<0.0003	<0.0003	<0.0003	<0.0003	0.0029	<0.0003	0.0002	0.001

*Standar Deviation; ** Cardoso *et a*l. (2022)

The maximum values of some elements were found to exceed the background values by several times. For example, Fe exceeded the background value by approximately 830 times (840.2 $mg.L^{-1}$ compared to 1.01 $mg.L^{-1}$ background), Mn by about 632 times (37.9 $mg.L^{-1}$ compared to 0.06 $mg.L^{-1}$ background), and Al by an astounding 31,600 times (316 $mg.L^{-1}$ compared to 0.01 $mg.L^{-1}$ background). Additionally, the maximum values for Na, Mg, Ca, and K exceeded their respective background values by 38, 27, 36, and 14 times. These significant increases in element concentrations emphasize the extent of the environmental impact caused by AMD in the region.

The pH, one of the main indicators of AMD, varied in these samples from 2.0 to 8.1, presenting acidic characteristics in most of the records. Considering the decree of the Ministry of Health and the resolution of CONAMA, only 24% of the samples were within the permitted range, which is above 6. Considering the geochemical background limits, pH above 5.4, only 34% of the samples had values within this limit. As pH is directly linked to the dissolution and mobilization of metals, it is one of the main monitoring variables in waters affected by AMD.

In addition to pH, acidity, sulfate, and iron are also direct indicators of pyrite oxidation, as presented in the equations previously shown. The distribution of samples from impacted streams in these three parameters was clearly different from the distribution of samples collected in less affected areas (Fig. 2). Considering the geochemical background limits for acidity, SO_4^{2-}, and Fe, only 22%, 11%, and 14% of the samples, respectively, were below the limit concentrations. It should be noted that the background limits for Fe in the region are higher than those established in the resolution and the decree, which set a limit of 0.3 $mg.L^{-1}$. If this limit is considered, the percentage of samples that fall within the authorized limit decreases to only 6%.

The mean redox potential (E_H) was 0.50 V, exceeding the regional geochemical background range of 0.01 - 0.53 V, suggesting an oxidizing environment likely influenced by AMD. This oxidative state can impact the geochemistry of the aquatic systems. According to Søndergaard (2009), while the oxidizing envi ronment typically favors the formation of insoluble iron compounds (Fe^{3+}), the high mean iron concentrations in the data suggest complex interactions, possibly involving sulfate. This oxidizing environment could also affect nutrient cycling, potentially impacting primary production and eutrophication (SØNDERGAARD, 2009). Furthermore, the high redox potential may influence the speciation and mobility of heavy metals in the water bodies (BOURG; LOCH, 1995).

The Dissolved Oxygen varied between 0 $mg.L^{-1}$ and 13.9 $mg.L^{-1}$, with most of the samples, 74%, within the limit established by CONAMA Resolution 357. According to the Food and Agriculture Organization of the United Nations (n.d.), the main source of dissolved oxygen in the water is the atmosphere, and the incorporation of this element into the water occurs through diffusion. Therefore, the high values of DO in the samples can be justified by the fact that most of the sampling sites are located at the headwaters of the watersheds and in places with higher slopes, increasing water movement and facilitating the process of diffusion.

Metals Mn and Al are commonly associated with AMD and can negatively impact the aquatic ecosystem and make water unsuitable for human consumption or agricultural use. For both metals, the maximum limit established by CONAMA Resolution and MS Decree is 0.1 $mg.L^{-1}$, resulting in 91% and 97% of the samples being non-compliant with the limits. Comparing with the more restrictive geochemical background limit, the percentage rises to 95% for manganese and 98% for aluminum. The visualization of the percentage of samples of Mn and Al above the geochemical background, as well as the comparison with the distribution of non-impacted samples, is shown in Figure 2.

Electrical Conductivity is typically high in AMD waters due to the elevated concentration of dissolved metals and minerals. The average EC was 823 $\mu S/cm^2$ with an SD of 724 $\mu S/cm^2$. 89% of the samples had a value above the maximum limit established in the geochemical background study of the region, a result that shows the proportion of alterations caused by AMD.

According to Bartos and Ogle (2002), Na, Mg, Ca, and K are known as major cations in water and are naturally present in rocks and soils. In the presence of AMD the concentration of these elements can increase due to the dissolution of minerals in rock formations. For these elements there is only the limit of the geochemical background established for the region, and the maximum limits established are, respectively: 6.99 $mg.L^{-1}$ (Na), 3.85 $mg.L^{-1}$ (Mg), 10.35 $mg.L^{-1}$ (Ca), and 1.69 $mg.L^{-1}$ (K). The percentage of samples above these limits was 57% for Na, 80% for Mg, 82% for Ca, and 86% for K, demonstrating that mineral dissolution by AMD, mainly from aluminosilicates and carbonates, is occurring in the region.

Due its toxicity, the elements Cu, Cd, Pb, As, and Hg are relevant in AMD studies. These elements are commonly found in AMD waters due to its occurrence in sulfide minerals. Different concentrations of these elements are reported in waters impacted by AMD in the literature (KIMBALL *et al*., 2002; CRAVOTTA, 2006; SHEORAN; SHEORAN, 2006; GALVÁN *et al*., 2012; MIGUEL-CHINCHILLA *et al.,* 2014; CARDOSO; FAN, 2021; CARDOSO *et al.*, 2024). However, most of the samples collected in the Santa Catarina coal region presented values within the standard for these elements. Considering the more restrictive CONAMA Resolution, 92% of the samples are within the established standards for Cu, 100% for Cd, 99% for Pb, 99% for As, and 96% for Hg. One of the factors that can contribute to the low concentrations found in these elements is the high content of quartz found in Brazilian coal, usually associated with low availability of these types of heavy metals (SILVA *et al*., 2011)

Just like Cu, Cd, Pb, As, and Hg, zinc can also be toxic when present in high concentrations. Unlike the previous elements, the values of Zn found in the samples from impacted sites were, for the most part, higher than the established limits. When compared to CONAMA Resolution, 40% of the samples were above the limit, whereas when compared to the background limit, 82% of the samples were higher. The concentrations of Zn suggest an effective dissolution of Zinc sulfides, particularly sphalerite (ZnS), which is particularly soluble in AMD waters, even across a broad pH range (EPA, 1980; SILVA, 2011).

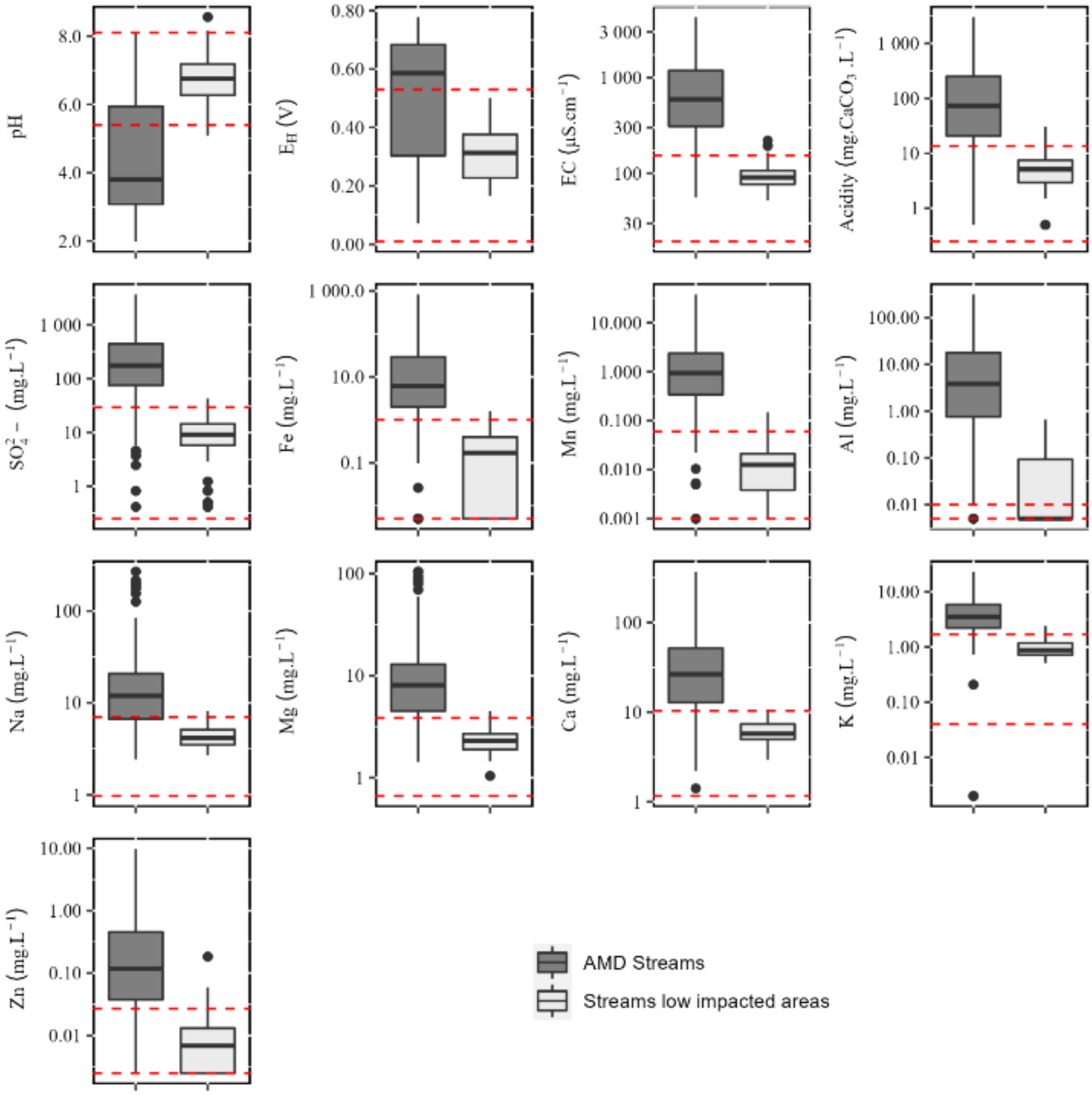

Figure 2 - Comparative boxplots presenting the distribution between groups samples from AMD Streams and Streams from low impacted areas. Dashed red lines indicate the limit values of the geochemical background of the region.

4.2 CORRELATIONS

To further understand the relationships between the various physicochemical parameters in the Santa Catarina coal region, we conducted a Spearman correlation analysis. The results of this analysis are presented in the correlation matrix below (Table 3). Several significant correlations can be observed between the physicochemical parameters. These correlations can help elucidate the mechanisms and processes occurring in the AMD-affected rivers and streams in the study area.

A strong negative correlation between pH and E_H (-0.88) was observed, which is consistent with the general understanding of AMD (BARNES; ROMBERGER, 1968). As pH decreases (acidic conditions), the redox potential (E_H) increases, facilitating the oxidation of sulfide minerals and the dissolution of heavy metals (NORDSTROM, 2011). This correlation supports the notion that AMD is driven primarily by the dissolution and mobilization of metals due to acidic conditions in the water.

Acidity, SO_4^{2-}, and Fe also showed strong positive correlations with E_H (0.77, 0.60, and 0.55, respectively) and strong negative correlations with pH (-0.85, -0.68, and -0.68, respectively). These relationships are consistent with the established understanding that the oxidation of pyrite leads to increased acidity, sulfate, and iron in AMD-affected waters (NORDSTROM; ALPERS, 1999).

Mn and Al exhibited strong positive correlations with acidity (0.87 and 0.93, respectively), SO_4^{2-} (0.89 and 0.83, respectively), and Fe (0.79 and 0.83, respectively). This suggests that the dissolution and mobilization of these metals are also related to pyrite oxidation and AMD processes (JOHNSON; HALLBERG, 2005).

Major cations, including Na, Mg, Ca, and K, displayed positive correlations with electrical conductivity (EC) (0.54, 0.90, 0.90, and 0.62, respectively). This supports the idea that increased EC in AMD waters is due to elevated concentrations of dissolved metals and minerals, which in turn results from mineral dissolution by AMD (YOUNGER et al., 2002).

The toxic elements Cu, Cd, Pb, As, and Hg did not show strong correlations with the other parameters, indicating that other factors cooperate in their behavior, in addition to the AMD processes in the study area. However, Zn exhibited strong positive correlations with acidity (0.91), SO_4^{2-} (0.83), Fe (0.81), Mn (0.86), and Al (0.93), which suggests that Zn's higher concentrations in the water samples could be attributed to sulfide oxidation and the dissolution sulfide minerals, such as ZnS, and aluminosilicates. Added to its availability is the fact that the electronegativity of Zn is lower than other metals, such as Cu, which has a preference for forming bonds and precipitating, leaving Zn in solution.

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

	pH	E_H	OD	CE	Acid	SO_4^{2-}	Fe	Mn	Al	Na	Mg	Ca	K	Cu
E_H	**-0.88**													
OD	0.19	-0.06												
CE	**-0.70**	**0.62**	-0.23											
Acid	**-0.85**	**0.77**	-0.30	**0.85**										
SO_4^{2-}	**-0.68**	**0.60**	-0.21	**0.94**	**0.85**									
Fe	**-0.68**	**0.55**	-0.30	**0.81**	**0.85**	**0.80**								
Mn	**-0.79**	**0.72**	-0.22	**0.87**	**0.87**	**0.89**	**0.79**							
Al	**-0.85**	**0.78**	-0.20	**0.82**	**0.93**	**0.83**	**0.83**	**0.86**						
Na	-0.10	-0.05	-0.40	**0.54**	0.30	0.48	0.42	0.32	0.22					
Mg	**-0.62**	**0.54**	-0.22	**0.90**	**0.76**	**0.90**	**0.74**	**0.89**	**0.74**	**0.53**				
Ca	**-0.55**	0.45	-0.17	**0.90**	**0.71**	**0.91**	**0.73**	**0.83**	**0.71**	**0.59**	**0.94**			
K	-0.38	0.24	**-0.56**	**0.62**	**0.58**	**0.56**	**0.56**	**0.51**	0.45	**0.68**	**0.59**	**0.56**		
Cu	0.13	0.16	0.04	0.06	0.11	0.04	0.06	0.14	0.08	-0.11	0.09	0.04	-0.06	
Zn	**-0.82**	**0.74**	-0.28	**0.81**	**0.91**	**0.83**	**0.81**	**0.86**	**0.93**	0.27	**0.76**	**0.71**	0.49	0.10

5 CONCLUSIONS

This study conducted a comprehensive analysis of the physicochemical parameters of water samples collected from rivers and streams affected by mining in the Santa Catarina coal region. Our findings indicate that the waters in the area are significantly impacted by AMD, with high concentrations of acidity, sulfate, and metals such as Fe, Mn, and Al.

The remarkable exceedances of maximum element concentrations over their respective background values further emphasize the severity of AMD impact on the water quality in the region. For instance, the maximum values of Fe, Mn, and Al exceeded their background values by 830, 632, and 31,600 times, respectively, while major cations like Na, Mg, Ca, and K also showed exceedances several times above their respective background values.

The pH values of the samples were generally acidic, with only 24% and 34% falling within the limits established by the Ministry of Health and the geochemical background, respectively. These acidic conditions promote the dissolution and mobilization of metals, which are key indicators of AMD.

The observed correlations between physico-chemical parameters support the notion that AMD is the primary driver of water quality degradation in the study area. The strong negative correlation between pH and E_H, along with the positive correlations between acidity, sulfate, and metals (Fe, Mn, and Al), highlight the role of pyrite oxidation in generating AMD. Additionally, the dissolution of carbonates and aluminosilicates contributes to increased concentrations of major cations such as Na, Mg, Ca, and K.

Although most samples presented values within the established limits for toxic metals like Cu, Cd, Pb, As, and Hg, high concentrations of Zn were observed, with 40% and 82% of samples exceeding the limits set by CONAMA Resolution and the geochemical background, respectively. The high levels of dissolved oxygen in the samples indicate that increased water movement and turbulence at the sampling sites likely facilitate the diffusion of oxygen into the water, contributing to the oxidation processes.

The significant alterations in the geochemical composition of the water, as evidenced by our findings, can have detrimental effects on aquatic ecosystems, water usability for human consumption, and agricultural activities. The acidic nature and high mineral content of this water also present challenges for industrial use, potentially damaging machinery and infrastructure if preemptive measures are not taken. The adverse effects extend to livestock, where the consumption of contaminated water can lead to health issues. Given these circumstances, communities within the Santa Catarina coal region find it unfeasible to utilize local water resources impacted by AMD. As a result, there is a shift towards sourcing water from other watersheds, underscoring a pressing need for comprehensive management strategies and specific guidelines to safeguard and rehabilitate water quality for safe usage across all sectors.

The results of this study not only highlight the importance of continuous monitoring and assessment of water quality in the region but also contribute to a understanding of the extent and severity of AMD in the Santa Catarina coal region.

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