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UNDERSTANDING AND ASSESSING COAL MINING IMPACTS: A MULTIFACETED STUDY OF ACID MINE DRAINAGE ON WATER RESOURCES IN THE SANTA CATARINA COAL REGION, SOUTHERN BRAZIL

PORTO ALEGRE

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Tese de Doutorado apresentada ao Programa de Pós-graduação em Recursos Hídricos e Saneamento Ambiental do Instituto de Pesquisas Hidráulicas da Universidade Federal do Rio Grande do Sul, como parte dos requisitos para a obtenção do título de Doutor em Recursos Hídricos e Saneamento Ambiental.

Orientador: Prof. Dr. Fernando Mainardi Fan

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“We do not inherit the earth from our ancestors;
we borrow it from our children.”

(Autor desconhecido)

RESUMO

Esta pesquisa explora os complexos processos de contaminação de recursos hídricos pela Drenagem Ácida de Minas (DAM) na região de mineração de carvão do estado de Santa Catarina, Brasil. O objetivo da pesquisa é não somente compreender os processos subjacentes que contribuem para este importante problema ambiental, mas também avaliar criticamente as estratégias atuais de recuperação ambiental e desenvolver modelos eficazes de monitoramento. A investigação inicial é direcionada para entender a eficácia das estratégias atuais de recuperação ambiental implementadas na região. Através do monitoramento da qualidade da água e avaliação do impacto das antigas atividades de mineração nos recursos hídricos locais, o estudo apresenta uma imagem mista. O método de recuperação ambiental foi eficiente na neutralização da acidez da água na maioria dos recursos hídricos superficiais da área. No entanto, não foi eficaz na neutralização do curso d'água a jusante, sugerindo que a qualidade da água continua comprometida em termos de pH e acidez. Esta herança da mineração de carvão na região ressalta a necessidade de mais trabalho para remediar completamente os impactos desta atividade. Este estudo define as bases para as investigações subsequentes, estabelecendo um contexto mais amplo para entender os mecanismos de contaminação e recuperação na região. Com base nesse entendimento, o segundo estudo busca estabelecer o *background* geoquímico natural dos recursos hídricos superficiais da região afetada. Distinguir entre concentrações de elementos de ocorrência natural e aquelas resultantes de atividades antropogênicas é fundamental para avaliar a extensão da contaminação e a eficácia dos métodos de recuperação. Esta investigação revela que os valores de referência geoquímicos naturais na região desviam dos valores esperados estabelecidos pela legislação brasileira para alguns parâmetros. A formação geológica única e a dinâmica hidrológica da região resultam em concentrações naturalmente mais altas de certos elementos químicos nos corpos d'água, elucidando uma informação crítica para avaliar com precisão os impactos ambientais e informar estratégias de mitigação. O terceiro estudo analisa os impactos da DAM na qualidade da água. Através da análise de parâmetros físico-químicos de amostras de água coletadas de rios e córregos afetados, é avaliada a extensão e a gravidade do impacto da DAM. O estudo revela a gravidade do impacto da DAM, refletida nas notáveis superações das concentrações máximas de elementos em relação aos respectivos valores de background geoquímico. Por exemplo, os níveis máximos de Fe, Mn e Al excederam seus valores de referência em 830, 632 e 31.600 vezes, respectivamente. Isso não apenas destaca os impactos duradouros da mineração de carvão nos recursos hídricos, mas também ressalta a necessidade de monitoramento e avaliação contínuos da qualidade da água dos recursos hídricos da região. O quarto estudo busca desvendar as correlações significativas entre os parâmetros típicos de monitoramento da DAM na região carbonífera de Santa Catarina. Ao investigar o comportamento geoquímico dos elementos na presença de DAM, como pH, potencial redox e concentrações de ferro, manganês e alumínio, várias correlações fortes são descobertas. Essas correlações estão intimamente relacionadas à solubilidade, especiação e mobilidade de metais pesados na água, revelando os mecanismos hidroquímicos relacionados à contaminação por DAM. Com esse entendimento mais aprofundado da interação entre os parâmetros geoquímicos, é desenvolvido um novo modelo de regressão para possibilitar o monitoramento eficaz e contínuo da DAM nas águas superficiais da região. Esse modelo tem potencial para ser uma ferramenta valiosa, podendo fornecer dados em tempo real sobre a qualidade da água e facilitando uma resposta rápida às mudanças na dinâmica da DAM. Além disso, o desenvolvimento desse modelo resulta em uma estratégia de monitoramento mais econômica, uma contribuição para a gestão dos recursos hídricos na região. Em conclusão, esta pesquisa avança nossa compreensão científica dos impactos ambientais das atividades de mineração de carvão na região sul de Santa Catarina, Brasil. Ao elucidar os mecanismos de contaminação por DAM e a eficácia das estratégias de recuperação na mitigação desses impactos, ela destaca a necessidade crucial de monitoramento regular e abrangente dos recursos hídricos em áreas afetadas pela mineração. Apesar das melhorias na qualidade dos recursos hídricos superficiais devido aos esforços de recuperação, a pesquisa ressalta a necessidade de ações adicionais para amenizar os impactos da DAM nos recursos hídricos. Além disso, a pesquisa enfatiza a importância de compreender o contexto geoquímico local para uma avaliação mais precisa da extensão e gravidade dos impactos da DAM. Os insights obtidos desta pesquisa não apenas têm relevância para a região de Santa Catarina, mas também para outras áreas que lidam com as consequências ambientais das atividades de mineração de carvão. Espera-se que as descobertas desta pesquisa estimulem mais investigações científicas nessa área crucial e informem abordagens mais eficazes para a recuperação ambiental. A jornada para um futuro sustentável para a região de mineração de carvão de Santa Catarina é longa e desafiadora e que só será alcançada por meio de pesquisa contínua e compromisso de todos os entes envolvido neste processo.

Palavras-chave: Drenagem Ácida de Minas (DAM), *Background geoquímico,* Recuperação ambiental, Impactos da mineração de carvão, Monitoramento da qualidade da água.

ABSTRACT

This research delves into the complex processes of water resource contamination by Acid Mine Drainage (AMD) in the coal mining regions of Santa Catarina, Brazil. The objective of the research is not only to understand and communicate the underlying processes contributing to this pressing environmental issue, but also to evaluate current environmental reclamation strategies and develop effective monitoring models. The initial investigation is targeted towards understanding the efficacy of current environmental reclamation strategies implemented in the region. Through water quality monitoring and gauging the impact of past mining activities on local water resources, the study paints a mixed picture. The environmental reclaiming method was efficient in neutralizing water acidity in most of the surface water resources of the area. However, it was not effective in neutralizing the downstream water course, suggesting that the water quality remains compromised in terms of pH and acidity. This legacy of the region's coal mining history underscores the need for further work to fully remediate the impacts of past mining activities. This finding lays the groundwork for the subsequent investigations, setting a broader context for understanding the mechanisms of contamination and reclamation in the region. Building on this understanding, the second study dives into establishing the natural geochemical baseline of the impacted region. Distinguishing between naturally occurring element concentrations and those resulting from anthropogenic activities is critical in evaluating the extent of contamination and effectiveness of reclamation methods. This investigation reveals that the natural geochemical background values in the region deviate from the expected values established by Brazilian legislation. The unique geological formation and hydrological dynamics of the region result in naturally higher concentrations of certain chemical elements in the water bodies, elucidating a critical piece of information for accurately assessing environmental impacts and informing mitigation strategies. The third study takes a closer look at the impacts of AMD on water quality. Through the analysis of physicochemical parameters of water samples collected from affected rivers and streams, the extent and severity of AMD impact is assessed. The study reveals the severity of AMD's impact, which is reflected in the remarkable exceedances of maximum element concentrations over their respective background values. For example, the maximum levels of Fe, Mn, and Al exceeded their background values by 830, 632, and 31,600 times, respectively. This not only highlights the enduring impacts of coal mining on water resources but also underscores the need for continuous and comprehensive monitoring and assessment of water quality. The fourth study seeks to unravel the significant correlations between typical monitoring parameters of AMD in the coal region of Santa Catarina. Investigating the geochemical behavior of elements in the presence of AMD, such as pH, redox potential, and concentrations of iron, manganese, and aluminum, several strong correlations are uncovered. These correlations are related to the solubility, speciation, and mobility of heavy metals in the water, presenting the hydrochemical mechanisms associated with AMD contamination. With this understanding of the interaction between geochemical parameters, a new regression model is developed to enable continuous monitoring of AMD in the region's surface water. This model can be an effective tool, providing real-time data on water quality and facilitating rapid response to changes in AMD dynamics. In addition, the development of this model presents a more cost-effective monitoring strategy, a contribution to water resource management in the region. In conclusion, this research Thesis advances our scientific understanding of the environmental impacts of coal mining activities in the Santa Catarina region of Brazil. By interpreting the mechanisms of AMD contamination and the effectiveness of reclamation strategies in mitigating these impacts, it shines a spotlight on the critical need for regular monitoring of water resources in mining-impacted areas. Despite improvements in the quality of surface water resources due to reclamation efforts, the research highlights the need for further action to alleviate the impacts of AMD on water resources. Moreover, the research call attention to the importance of understanding the local geochemical background for a more accurate assessment of the extent and severity of AMD impacts. The insights gleaned from this research not only hold relevance for the Santa Catarina region but also for other areas dealing with the environmental consequences of coal mining activities. It is hoped that the results of this research will stimulate further scientific investigations in this area and inform more effective approaches to environmental reclamation. The journey towards a sustainable future for the Santa Catarina coal mining region is long and challenging and will only be achieved through continuous research and the commitment of all those involved in this process.

Keywords: Acid Mine Drainage (AMD), Geochemical background, Environmental reclamation, Coal mining impacts, Water quality monitoring.

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CHAPTER 1

Introductory Chapter

1.1 Introduction

Mining plays a crucial role in the economic growth of many countries but poses significant environmental risks, especially in the coal sector (BIAN et al., 2010; RATHORE; WRIGHT, 2007). A principal concern is Acid Mine Drainage (AMD), a global problem affecting both surface and groundwater (GRAY, 1996; CRAVOTTA, 1989). AMD emerges from the oxidation of sulfide minerals, notably pyrite, and is characterized by low pH and high concentrations of sulfates and metals (NORDSTROM, 1982; DOULATI ARDEJANI et al., 2011). This phenomenon has been studied across continents, including Asia (JUNG; THORNTON, 1997; LEE; CHON; JUNG, 2001; LIN et al., 2005; OUYANG et al., 2015; PARK et al., 2019; RAMBABU et al., 2020; TAO et al., 2012; WANG et al., 2021), Oceania (LOTTERMOSER; ASHLEY; LAWIE, 1999; WRIGHT; PACIUSZKIEWICZ; BELMER, 2018), Europe (HAIGH; KILMARTIN, 2015; OLÍAS et al., 2006; SÁINZ et al., 2002; SRACEK et al., 2010), Africa (OCHIENG; SEANEGO; NKWONTA, 2010; RÖSNER; VAN SCHALKWYK, 2000), North America (BURROWS; PETERS; CRAVOTTA, 2015; KIMBALL et al., 2002), and Latin America (PRIETO; DUITAMA, 2004), such as Brazil (CAMPANER; LUIZ-SILVA; MACHADO, 2014; CASAGRANDE; MOREIRA; TARGA, 2019). The global context of AMD brings us to the particular case of Santa Catarina, Brazil, where coal mining's environmental legacy has uniquely marked the region's water resources.

In Santa Catarina, coal mining was a driver of economic development, but the industry's environmental legacy has left its mark on the region's water resources. The contamination of surface and groundwater by AMD has led to extensive degradation of the region's water resources, soil, fauna, and flora (ALEXANDRE, 1999; POMPÊO et al., 2004; RAVAZZOLI, 2013; RYBICKA, 1996; SILVA et al., 2011). Abandoned mines have left a legacy of pollution, including the release of acidic and metal-laden waters, rich in heavy metals such as iron, manganese, and aluminum, into rivers and streams. This poses a severe risk to aquatic ecosystems, human health, and agriculture in the region. In response to these challenges, environmental reclamation efforts have been decreed by Federal laws to address the impacts of abandoned coal mining in the region (RAVAZZOLI, 2013).

Over the past two decades, as a result of initial court rulings, there has been a growing recognition of the need for concerted action to address the environmental issues associated with coal mining in Santa Catarina. As a result, a series of environmental reclamation efforts have been initiated, aimed at mitigating the impacts of mining activities and restoring the region's water resources (INVERNIZZI, 2010). These efforts, which have their methods proposed by the Technical Advisory Group (GTA), have included the implementation of measures such as the reclamation of degraded areas, revegetation, closure of abandoned mine openings, and the treatment of contaminated water (GONÇALVES, 2008; BRASIL, 2008).

Water resource monitoring in the three watersheds affected by coal mining - Araranguá, Tubarão, and Urussanga rivers - has been carried out since the beginning of the 2000s. The most recent environmental monitoring report, the 16th report, indicates that the coal region of Santa Catarina has 5,739 hectares of degraded areas, 822 abandoned mine openings, and 1,241 km of impacted rivers in the three watersheds (GTA, 2019). Although the latest reports have shown an improvement in the quality of the region's surface water resources, questions remain about the efficiency of reclaiming individual areas and the impact on groundwater (GTA, 2019; KIMBALL et al., 2002; HAIGH; KILMARTIN, 2015).

Despite its national recognition and monitoring, more in-depth scientific discussions about the region's water resource contamination and the environmental reclaiming efforts being undertaken are still limited. In this context, scientific understanding of the contamination processes occurring in the region is also limited. Recognizing these challenges, this Thesis, comprising four research articles, aims to delve deeper into the complexities of coal mining's environmental impact in Santa Catarina. It seeks to address specific scientific questions and explore the region's unique characteristics, contributing to a broader understanding of coal mining's legacy in the area.

The research seeks to address specific scientific questions, such as whether the reclaimed areas have achieved effective control of contamination in surface water resources, whether the natural water quality of the region is consistent with the expected values established by Brazilian legislation, and what the representative local values are if they differ. It also explores statistical differences between parameters of contaminated areas and background values, and the significant correlations between typical monitoring parameters of AMD, and how these correlations can be utilized for effective monitoring strategies.

The specificity of the study lies in its focus on the Santa Catarina coal mining region, with insights that can hold relevance for other areas with the environmental aftermath of coal mining activities. By understanding the local geochemical background, assessing the extent and severity of AMD impacts, and devising effective strategies to restore the local water resources within these degraded zones, the study also compares the results with regional background values, proposing improved monitoring strategies and providing a viable tool for assessing the effectiveness of reclamation efforts in the region.

1.2 Objectives

1.2.1 Main objective

The main objective of this Thesis is to conduct a multifaceted investigation into the processes of contamination of surface water resources by AMD in the coal mining region of Santa Catarina, Brazil, thereby expanding knowledge and fostering discussions surrounding environmental processes related to this issue.

1.2.2 Specific objectives

The objective will be achieved through the following topics, listed as specific objectives:

- Evaluating environmental reclamation efforts: Assess the effectiveness of existing reclamation strategies in improving water quality and mitigating the impacts of past mining activities on local water resources.
- Establishing the geochemical background: Identify the natural geochemical baseline for the affected region, distinguishing between naturally occurring element concentrations and those resulting from anthropogenic activities.
- Investigating the impacts of AMD on water quality: Analyze the physicochemical parameters of water samples collected from rivers and streams affected by mining to assess the extent and severity of AMD impact.
- Exploring the significant correlations between typical monitoring parameters of AMD, understanding the hydrochemical motivations behind these correlations.
- Determining how to utilize these correlations for effective monitoring strategies.

1.2.3 Scientific questions

The following scientific questions are addressed in this work:

- Have the reclaimed areas achieved effective control of contamination in surface water resources? (Chapter 2).
- Is the natural water quality of the region consistent with the expected values and those established by Brazilian legislation? If not, what are the representative local values, and why do they differ? (Chapter 3).
- Besides numerical values, are there any other statistical differences between parameters of contaminated areas and background values? (Chapter 4).

- Is there a significant correlation between typical monitoring parameters of AMD in contaminated areas? What are the hydrochemical motivations for this in the coal region of Santa Catarina? How can these correlations be utilized for monitoring strategies? (Chapter 5).

By addressing these interconnected topics, the Thesis seeks to not only enhance our understanding of AMD contamination mechanisms but also contribute to the broader scientific discussions and promote the development of sustainable practices.

1.3 Contextual overview of AMD generation and environmental reclamation

1.3.1 What is AMD

This Thesis is concerned with the study of reclaiming degraded landscapes, particularly those adversely impacted by coal mining, a process known for leading to AMD generation.. These studies aim to understand the mechanisms of AMD formation and its implications in reclamation of degraded areas. The discussion that follows elaborates on the genesis of AMD and its environmental consequences, with a particular focus on southern Santa Catarina State, a historical hub of coal mining in Brazil. Moreover, it delves into the reclamation techniques currently in practice, as well as their effectiveness. In doing so, this Thesis endeavors to contribute to a more comprehensive and effective approach to the reclamation of the areas degraded by coal mining and its associated environmental challenges.

Acid Mine Drainage refers to the formation and outflow of acidic water from metallic or coal mines as a consequence of geochemical reactions between water and rocks bearing sulfur-bearing minerals (CRAVOTTA et al., 1999; CRAVOTTA, 1989; GRAY, N. F., 1998; SINGER; STUMM, 1970; YANG et al., 2006). It is pertinent to understand that this phenomenon is not limited to regions actively engaged in mining and also extends to deserted mines. Often, these abandoned sites continue to pose a significant risk due to the continuous process of natural weathering, which facilitates the exposure of sulfide-rich deposits to atmospheric oxygen and water, leading to oxidation and subsequent hydrolysis reactions. The context of coal mining bears specific mention in this regard, as it involves the extraction of large volumes of rock and earth, thereby increasing the likelihood of AMD formation due to the exposure of pyrite (FeS^2) and other sulfide minerals (GRAY, 1998; JOHNSON; HALLBERG, 2005; QURESHI; MAURICE; ÖHLANDER, 2016).

The generation of Acid Mine Drainage from coal mining can be primarily attributed to the chemical reaction known as pyrite oxidation. This complex process can be broken down into several steps. Initially, 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 (Reaction 1.1). Subsequently, ferrous iron is oxidized to ferric iron (Fe^{3+}) (Reaction 1.2), which further reacts to form ferric hydroxide ($Fe(OH)_3$) (Reaction 1.3) (SINGER; STUMM, 1970). The oxidation step to ferric iron is limited in abiotic environments; however, in environments with a pH between 2.8 and 3.2, this step can be accelerated by bacteria naturally present in aquatic environments that thrive in these pH conditions.

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1.1)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \quad (1.2)$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \quad (1.3)$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad (1.4)$$

The chemical reactions described above lay the groundwork for understanding the broader environmental impacts of AMD. In very acidic pH values (close to or below 2.3), hydrolysis (Reaction 1.3) practically does not occur, leading to an increase in the concentration of Fe^{3+} in the environment. This Fe^{3+} further oxidizes pyrite, as shown in Reaction (1.4) (DE MELLO; DUARTE; LADEIRA, 2014). As a result, the generation of AMD contaminates the rivers of the region, leading to a decrease in pH, acidification of the waters, and the release of high concentrations of sulfate and metal ions, particularly iron, aluminum, and manganese.

1.3.2 Impacts of AMD on the Environment

This process leads to the formation of sulfuric acid, the main culprit of the acidification of water bodies around mining sites. At the outset, it is crucial to comprehend that the AMD phenomenon is not a localized environmental challenge. Instead, it has widespread effects that begin at a molecular level, gradually escalating to influence entire ecosystems (YOUNGER; BANWART; HEDIN, 2002).

One of the first noticeable indicators of AMD is the rust-colored deposits it leaves behind (Figure 1.1). These deposits, characterized by their high iron content, are typically found in streams and on rocks around mining sites. The distinctive coloration is due to the formation of iron hydroxides, a product of iron reacting with oxygen in water under acidic conditions (SILVA; WOLLENSCHLAGER; OLIVEIRA, 2011). Over time, these iron hydroxide deposits can choke stream beds, leading to a degradation of aquatic habitats and a decline in the associated biodiversity (LOTTERMOSER, 2010).

However, the ramifications of AMD extend beyond the visible iron deposits. It also instigates significant alterations in soil quality, with pervasive implications for terrestrial ecosystems. The influx of AMD into the soil triggers a series of deleterious processes, including a decrease in soil pH and heavy metal pollution (LIAO et al., 2016). The acidification process also sets the stage for nutrient leaching, depleting the soil of essential nutrients and reducing fertility. This degradation of soil quality often renders the lands unsuitable for traditional uses such as agriculture, forestry, or wildlife habitats (LIAO et al., 2016; SHEORAN; SHEORAN, 2006).

Moreover, AMD does not only affect terrestrial ecosystems, but also significantly impacts aquatic environments. Changes in water chemistry can disrupt delicate ecological balances, causing a decline in species richness and abundance. Aquatic ecosystems, particularly freshwater systems, are especially vulnerable to AMD. The high acidity and metal concentrations characteristic of AMD can be lethal to many forms of aquatic life, including fish, invertebrates, and microbial communities (CRAVOTTA; NANTZ, 2008; FREITAS et al., 2017; GRAY, 1997).

Fig. 1.1. Rust-colored deposits from AMD in riverbed (Source: Author).

Another point of concern is the contamination of surface water and groundwater resources by the mobilization of heavy metals associated with AMD. Elements such as arsenic, lead, and mercury, which are often found in association with sulfide minerals, can be released into the environment through the acid dissolution process (SOLÀ et al., 2004). These toxic heavy metals pose a significant risk to both human and ecological health. They have the potential to bioaccumulate in organisms and magnify up the food chain, ultimately reaching birds, mammals, and potentially humans who consume contaminated organisms. Bioaccumulation and biomagnification of these heavy metals can lead to a range of health problems, including neurological disorders, reproductive issues, and in severe cases, mortality (ALI; KHAN; ILAHI, 2019; LOTTERMOSER, 2010).

1.3.3 Reclamation and Mitigation Techniques

Recognizing the multifaceted impacts of AMD, mining companies have implemented comprehensive environmental reclamation techniques aimed at preventing, minimizing, or treating AMD. One of the most common techniques for treating AMD in water is alkaline addition. This involves adding alkaline materials such as limestone or lime to neutralize the acidity of the water. Alkaline addition can be done in several ways, including passive treatment systems, active treatment systems, and in-situ treatment. Another technique for controlling AMD is biological treatment. This involves using microorganisms to remove heavy metals from the water. Biological treatment can be done in several ways, including constructed wetlands and bioreactors. Physical treatment methods are also commonly used to control AMD pollution, these methods include sedimentation ponds, settling tanks, and filtration systems (AKCIL; KOLDAS, 2006; SKOUSEN et al., 1998).

Among the techniques for preventing AMD is the encapsulation of waste rock and tailings with non-reactive or low-reactivity material. By reducing the exposure of sulfur-bearing minerals to atmospheric oxygen and water, this technique significantly diminishes the potential for AMD formation (KUYUCAK, 1999; SAHOO et al., 2013; SKOUSEN et al., 1998).

Other preventive strategies include the use of oxygen barriers or physical barriers; they can be dry or wet and work limiting the oxygen diffusion or water infiltration, thereby inhibiting the oxidation of sulfide minerals. An additional method involves the application of alkaline materials such as limestone to waste rock and tailings. This process aims to neutralize the acidic conditions that drive AMD generation, thus reducing the solubility and mobility of metals (SAHOO et al., 2013; SKOUSEN et al., 1998).

Furthermore, re-vegetation efforts are commonly employed as part of the reclamation process. By stabilizing the land surface and improving its aesthetic appeal, vegetation serves not only to enhance the landscape after mining but also to provide a degree of passive water treatment. Plants can reduce surface runoff, increase evapotranspiration, and stimulate biogeochemical processes that can mitigate the impacts of AMD (KUYUCAK, 1999; SKOUSEN et al., 1998).

1.3.4 From Legacy to Remediation: The Journey of Environmental Reclamation in Santa Catarina's Coal Region

As mentioned earlier, the decline of the coal industry in Santa Catarina left a legacy of abandoned mines that scarred the region, generating AMD and contaminating both surface and groundwater resources. The declaration of Santa Catarina's coal region as a nationally significant pollution hotspot by the Federal government in 1980 marked a key moment in the environmental history of the area.

In response to the severe environmental issues and court rulings, environmental reclamation efforts were implemented. These efforts, proposed by the Technical Advisory Group, included the use of techniques such as: (i) encapsulation, when coal waste is present; (ii) techniques for closing underground mine openings, as a way to reduce the emergence of contaminated groundwater on the surface; and, (iii) for strip mined areas, dry cover techniques (physical barriers) to prevent infiltration of rainwater and oxygen contact with the waste rock.

Figure 1.2 illustrates the primary steps of the dry cover technique employed for the reclamation of degraded areas in Santa Catarina State: a) Cleaning the area and removing the limited number of exotic tree species that can thrive in this soil; b) Dismantling the piles left by the dragline; c) Conducting earthmoving activities and leveling the ground to ensure a stable surface; d) Introducing a new layer of soil by applying clayey material; e) Establishing drainage systems to channel rainwater; and f) Initiating re-vegetation.

In the 1990s, the scientific community embarked on preliminary research into environmental pollution in the region, primarily presented in the form of technical reports. These early studies frequently saw collaborations with government agencies (ALEXANDRE; KREBS, 1995; ALEXANDRE, 1999; GOTHE, 1993). Subsequently, various research pieces connected to AMD in the region have been published, each contributing in different ways to our understanding of the situation. These contributions range from the modeling of AMD contamination sources (GOMES; MENDES; COSTA, 2011), evaluating toxicity in water resources (LATTUADA et al., 2009), to investigating and proposing treatments for affected sediments (FREITAS et al., 2017; VOLPATO; MENEZES; SILVA, 2017). Further advancements have been made in tailings desulfurization methods (DO AMARAL FILHO et al., 2017), in the adsorption of heavy metals from coal AMD (NÚÑEZ-GÓMEZ et al., 2019), and in analyzing groundwater conditions (SIMÃO et al., 2019). Strategies for the integrated management of contaminated areas have also been proposed (GOUVÊA, 2023).

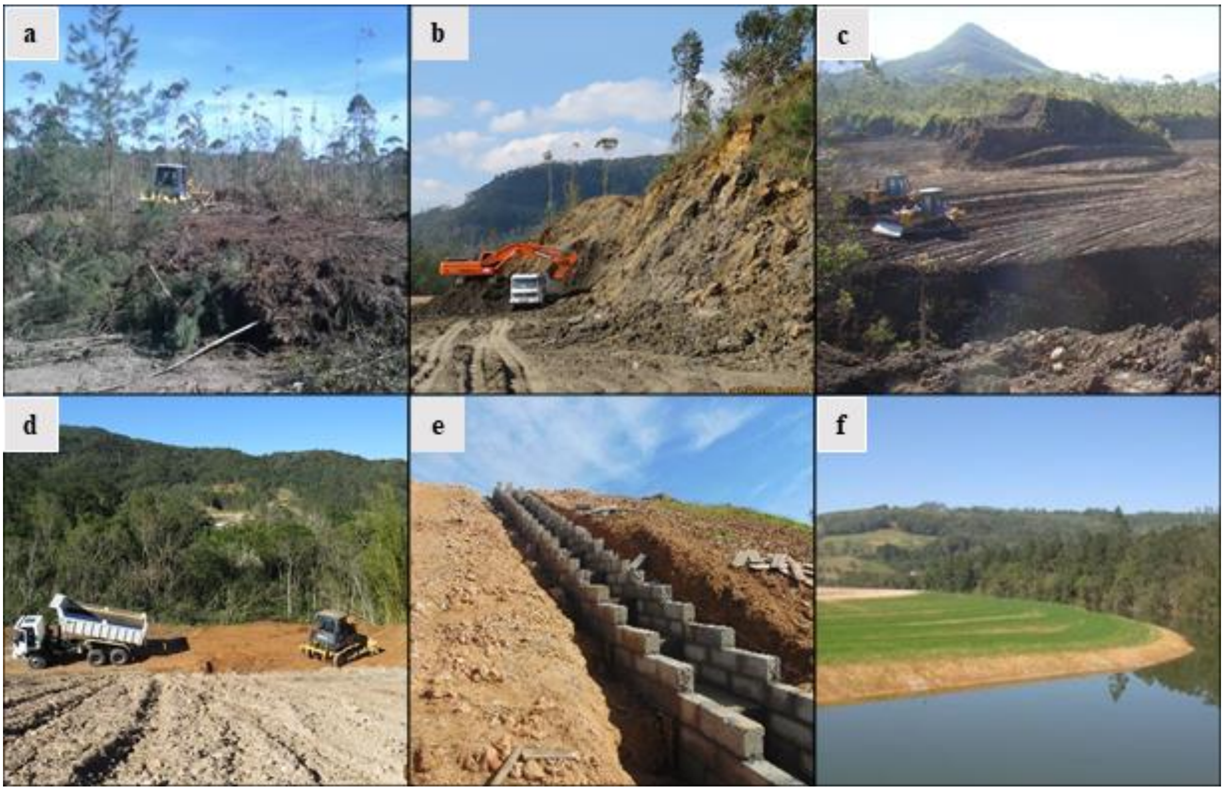

Fig. 1.2. Schematic representation of the sequential steps involved in the dry cover technique for the reclamation of degraded areas in Santa Catarina State. a) Area cleaning and exotic species removal; b) Dismantling of dragline piles; c) Earthmoving and ground leveling for stability; d) Application of clayey material to form a new soil layer; e) Establishment of drainage systems; and f) Initiation of re-vegetation.

Each of these studies has enriched our understanding of the environmental consequences in the affected areas. Yet, a broad-based investigation that evaluates environmental reclamation efforts, distinguishes the region's natural geochemical background, and assesses AMD's impact on water quality, while exploring the relationships between common AMD monitoring parameters, remains to be conducted. This all-encompassing approach is essential for devising effective strategies to restore the local water resources within these degraded zones. Thus, the goal of this thesis is to address this knowledge gap by providing a comprehensive exploration of these under-researched aspects of acid mine drainage and its mitigation in Santa Catarina.

1.3 Thesis organization

This Thesis is organized into six core chapters, with the first setting the stage for our investigation and the sixth encapsulating the conclusions drawn from the body of work. The intermediary chapters, each dedicated to a unique study, unfold a narrative that systematically addresses the objectives and scientific questions of this research. This structure allows for each chapter to build upon the findings of the preceding one, thereby deepening our understanding of the environmental challenges posed by coal mining activities in Santa Catarina (Figure 1.3).

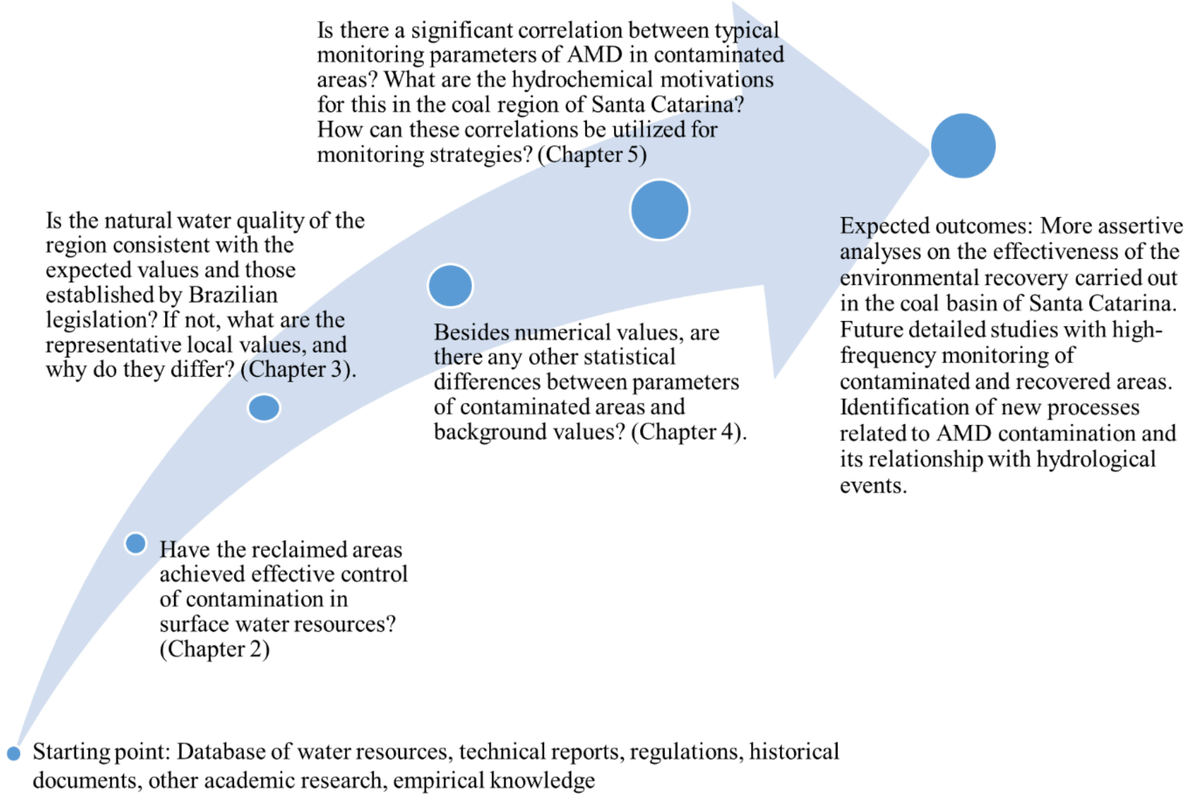

Fig. 1.3. Chronology of the scientific questions that originated the research throughout the Thesis.

Chapter 2, titled "A first evaluation of water resource conditions after an environmental reclamation effort at a former degraded coal mining area in Southern Brazil", serves as a point of departure from the introductory chapter. With the initiation of environmental reclamation efforts, a pressing question arose: had these reclaimed areas effectively achieved contamination control in surface water resources as necessitated by the lawsuit? This chapter presents a case study investigating this question. Through a comprehensive water monitoring plan, we scrutinize the groundwater and surface waters of the area, assessing the effectiveness of the reclamation methods and identifying potential causes for the observed contamination.

Our inquiry in Chapter 2 revealed a need for more representative information on the hydrogeochemical backgrounds of the region's waters for a more accurate evaluation of the reclamation methods and contaminated areas. This led to the formulation of Chapter 3: "Surface water resources of Santa Catarina state’s southern region – geochemical background of the coal mining territory". This chapter is devoted to differentiating between natural concentrations of chemical elements and those introduced through anthropogenic activities, thereby providing a comprehensive understanding of the geochemical background of the region's waters.

The results obtained in Chapter 3 highlighted certain geochemical background values of the region that were outside the established limit when compared with the current legislation. This prompted us to ask: how do these background values compare with the values found in waters contaminated by mining? The pursuit of an answer to this question forms the foundation of the Chapter 4: "Mining's legacy: Unraveling the impacts of acid mine drainage on the rivers and streams of the Santa Catarina coal region, Brazil". This chapter delves into the extent and severity of AMD impacts on the region's rivers and streams. Through the analysis of physicochemical parameters, we unveil the environmental repercussions of mining-related contamination and underscore the significance of continuous monitoring and assessment of water quality.

Chapter 4's exploration of the differences between geochemical background values and the values in contaminated waters yields significant insights, but also raises further questions. Notably, it becomes clear that there's a relevant correlation between typical parameters of acid mine drainage (AMD) monitoring in contaminated areas. This raises intriguing questions for Chapter 5: what are the hydrochemical motivations for these correlations in the coal region of Santa Catarina, and how can these correlations be utilized to enhance monitoring strategies?

Chapter 5, titled "A decade-long journey shed light on chemical composition and field determination of acid mine drainage in Santa Catarina, southern Brazil," addresses these questions. The chapter capitalizes on the correlations discovered in the previous chapter and uses them to propose improved monitoring strategies. By comparing field and laboratory measurements we propose a regression model for continuous, low-cost monitoring of contaminated water sources. This chapter emphasizes the importance of high-frequency monitoring in understanding the behavior of water sources affected by AMD and in developing effective mitigation strategies.

Chapter 6, the concluding chapter, synthesizes the findings from all previous chapters and articulates the implications of this work. It brings forward the lessons learned, addresses the initial research questions, and delineates future research directions. The knowledge and insights gained from this research are not confined to Santa Catarina but can hold relevance for other regions dealing with the environmental aftermath of coal mining activities.

Overall, this Thesis endeavors to enhance our understanding of the environmental challenges posed by coal mining activities in Santa Catarina. By examining the effectiveness of reclamation strategies and investigating the dynamics of water contamination, this work aims to contribute to the broader scientific discourse and inform more effective approaches to environmental reclamation. This progression from chapter to chapter, from identifying to analyzing the problem, mirrors the journey that we, as researchers, undertook. Each chapter represents a step forward, building on the knowledge of the previous chapters to deepen our understanding of the complex environmental legacy of coal mining in Santa Catarina, Brazil.

CHAPTER 2

A first evaluation of water resource conditions after an environmental reclamation effort at a former degraded coal mining area in Southern Brazil

This chapter presents a research previously published at Environmental Monitoring and Assessment Journal: CARDOSO, A. T.; FAN, F. M. A first evaluation of water resource conditions after an environmental reclamation effort at a former degraded coal mining area in Southern Brazil**. Environmental Monitoring and Assessment**, [s. l.], v. 193, n. 10, p. 1–16, 2021. https://doi.org/10.1007/s10661-021-09393-4

Abstract - In southern South America, Brazil, in the state of Santa Catarina, the neglect and lack of environmental supervision during coal mining caused the contamination of surface and groundwater by Acid Mine Drainage (AMD). By the force of the local law, environmental reclamation actions in these abandoned areas have been carried. A scientific work of monitoring and assessment of the water resources within these areas has never been developed, as the efficacy of the reclamation strategies has never been discussed. This work aims to fill this gap by presenting and analyzing the environmental reclamation strategy of a former degraded coal mining area and its impacts on local water resources. The water monitoring plan in Area IV's was carried out in groundwater and in lentic (ponds) and lotic (rivers) environments of surface waters, fourteen monitoring campaigns were conducted. The results showed that upstream and downstream river points have different water qualities, with the downstream points having poorer water quality, still affected by past mining activities. From the surface water perspective, the reclaiming method adopted was effective in three of the four ponds, presenting problems only in the downstream one. Two hypotheses were proposed, the first hypothesis is that contamination happens due to leaching of the material that still remains on the ponds' banks into the water. Another hypothesis is that the contamination comes from the upstream groundwater inflow into the pond, which runs through the entire area before reaching the pond. Those results serve to further access the actual monitoring perspectives as well as to better develop future reclaiming strategies.

Keywords: Coal mine, Acid Mine Drainage, Environmental reclamation, Water resources monitoring and assessment, Southern Brazil.

2.1 Introduction

Mining is important for the economic growth of many countries, however its pollution capacity is higher when compared to other activities. Coal mining in particular can cause a number of impacts on the environment (BIAN et al., 2010; QURESHI; MAURICE; ÖHLANDER, 2016; RATHORE; WRIGHT, 2007). The severity of these impacts depends on factors such as geological conditions, whether the mine is active or abandoned, and the mining methods (BELL et al., 2001).

The main environmental impact of coal mining is the contamination of nearby water resources by Acid Mine Drainage (AMD) (CRAVOTTA et al., 1999; CRAVOTTA, 1989; GRAY, 1998; YANG et al., 2006). According to Gray (1996), AMD is the main environmental contamination problem in the world, capable of affecting both surface and groundwater.

AMD results from the oxidation of sulfide minerals, usually pyrite, being removed from the interior of the earth by mining activities and exposed to oxygen and atmospheric water (CRAVOTTA, 1989). Pyrite oxidation involves several redox reactions and microbial catalyses, it is considered a complex biogeochemical process (NORDSTROM, 1982; XIN et al., 2021), and is characterized by promoting low pH values and high concentrations of sulphates and dissolved metals (DOULATI ARDEJANI et al., 2011; SARMIENTO et al., 2018; UNDERWOOD; KRUSE; BOWMAN, 2014).

AMD related issues are studied worldwide, in Asia (JUNG; THORNTON, 1997; LEE; CHON; JUNG, 2001; LIN et al., 2005; OUYANG et al., 2015; PARK et al., 2019; RAMBABU et al., 2020; TAO et al., 2012; WANG et al., 2021), Oceania (LOTTERMOSER; ASHLEY; LAWIE, 1999; WRIGHT; PACIUSZKIEWICZ; BELMER, 2018), Europe (HAIGH; KILMARTIN, 2015; OLÍAS et al., 2006; SÁINZ et al., 2002; SRACEK et al., 2010), Africa (OCHIENG; SEANEGO; NKWONTA, 2010; RÖSNER; VAN SCHALKWYK, 2000), North America (BURROWS; PETERS; CRAVOTTA, 2015; KIMBALL et al., 2002), and Latin America (PRIETO; DUITAMA, 2004). In Brazil, AMD affects multiple regions across the country, including the more southern states (Santa Catarina and Rio Grande do Sul), but also the Paraná and Minas Gerais states, respectively located in the south and southeast regions (CAMPANER; LUIZ-SILVA; MACHADO, 2014; CASAGRANDE; MOREIRA; TARGA, 2019).

Among the published studies related to AMD impacts in water resources, we believe it is important to highlight the work of Olías et al. (2006) which studied the amount of metals transported to the ocean due to AMD contamination in the Tinto and Odiel basins in Spain.

They reached transportation quantities of 7900 tons per year of iron, 5800 tons per year of aluminum and 3500 tons per year of zinc, all directly related to AMD. According to the authors, those values were considered to be 60% of zinc global gross flux and 17% of copper transported to the ocean by rivers. Wang et al. (2021) reviewed AMD-related publications about abandoned coal mines in Shanxi, China, the authors showed that the mines have aggravated the situation of water shortages, causing an ecological and environmental problem and a drinking water safety crisis. In another study, Haigh and Kilmartin (2015) analyzed four reclaimed opencast coal-lands in Southeast Wales, Great Britain, in order to verify if these sites continue to impact the quality of the region's water resources. The authors concluded that compacted surface layers contribute to flood peaks and the main impact on water quality was due to diffuse pollution caused by AMD reactions in the aeration zone above the water table within the spoils banks.

In the state of Santa Catarina, southern Brazil, coal mining began in the late nineteenth century. However, the escalation of the exploration and the aggravation of environmental contamination happened in the 1970s, with the mechanization of the mines (ALEXANDRE, 1999). Neglect and lack of environmental supervision during this period caused serious repercussions to the local environment. This culminated in 1980, when the Federal government signed a decree recognizing the coal region of Santa Catarina as a critical pollution zone in the country, consequence of coal mining.

The first scientific studies on environmental pollution in the region date back to the 90s, some featuring the participation of government agencies (ALEXANDRE; KREBS, 1995; ALEXANDRE, 1999; GOTHE, 1993). Since then, some other AMD related works in the region have been published: modeling of contamination sources (GOMES; MENDES; COSTA, 2011), water resource toxicity (LATTUADA et al., 2009), sediment assessment and treatment (FREITAS et al., 2017; VOLPATO; MENEZES; SILVA, 2017), tailings desulfurization method (DO AMARAL FILHO et al., 2017), adsorption of heavy metals from coal AMD (NÚÑEZ-GÓMEZ et al., 2019) and background analysis of the water in the coal area (SIMÃO et al., 2019). These studies have made significant contributions to the scope of knowledge concerning degraded areas and their impact on the regions' environment. However, none of these works has fully investigated the reclamation of these degraded areas' local water resources.

By the force of the law, environmental reclamation actions in these abandoned areas have been carried out by different agents, including private companies and even Federal agencies. After the reclaiming process of the areas, the monitoring and assessment of water resources are carried out by those responsible, the results are then forwarded to the State Environmental

Agency. However, the real effectiveness, impacts and critical analyses of these reclaiming strategies has not been scientifically assessed and discussed in the literature.

Given this scenario, the objective of this research is to work towards filling this gap, while presenting and discussing, for the first time, the environmental reclamation strategy of a former degraded coal mining area, reclaimed by the Federal Government, located in Southern Brazil, and its impacts on local water resources.

2.2 Materials and methods

2.2.1 Location of the study area

The study area, known as “Area IV”, has 42.23 ha and is located in the municipality of Siderópolis, southern state of Santa Catarina, Brazil (Fig. 2.1). The area is situated in the sub-basin of the Fiorita River, which belongs to the Araranguá river basin, one of the most affected basins by Acid Mine Drainage (AMD) in the state of Santa Catarina.

In accordance with the Köppen classification, the climate of Siderópolis is characterized as a Humid subtropical climate (Cfa). The average annual temperature ranges from 16 to 20ºC, with an increase observable from December to February. Additionally, it is noteworthy that during the winter, the mean of the minimum temperatures remains below 10 degrees, contributing to a cooler winter climate. Conversely, the summer season witnesses the mean of the maximum temperatures rising above 27 degrees, signifying a warm summer period. The local average annual rainfall is 1,630 mm, its distribution varies according to the seasons, in autumn and winter the accumulated average is around 350 mm in each season, in spring the accumulated average is 430 mm and 500 mm in summer (BACK, 2020; GOTARDO et al., 2018).

The area is located in the vicinity of the urban center of the Siderópolis city. At the north-northeast limit is located an industrial sector, which includes industries within the polygonal area. At the southern limit is the Albina hill, where springs of a few streams originate. These streams flow into the ponds formed by the old open pit mines.

The surface water flows from the southern boundary, enters the area through pond 4 and moves into pond 3, then pond 1. The water flows through the outflow from pond 1 towards the northwest of the area until it meets the Fiorita River. Pond 2 has no significant surface inlets or outlets.

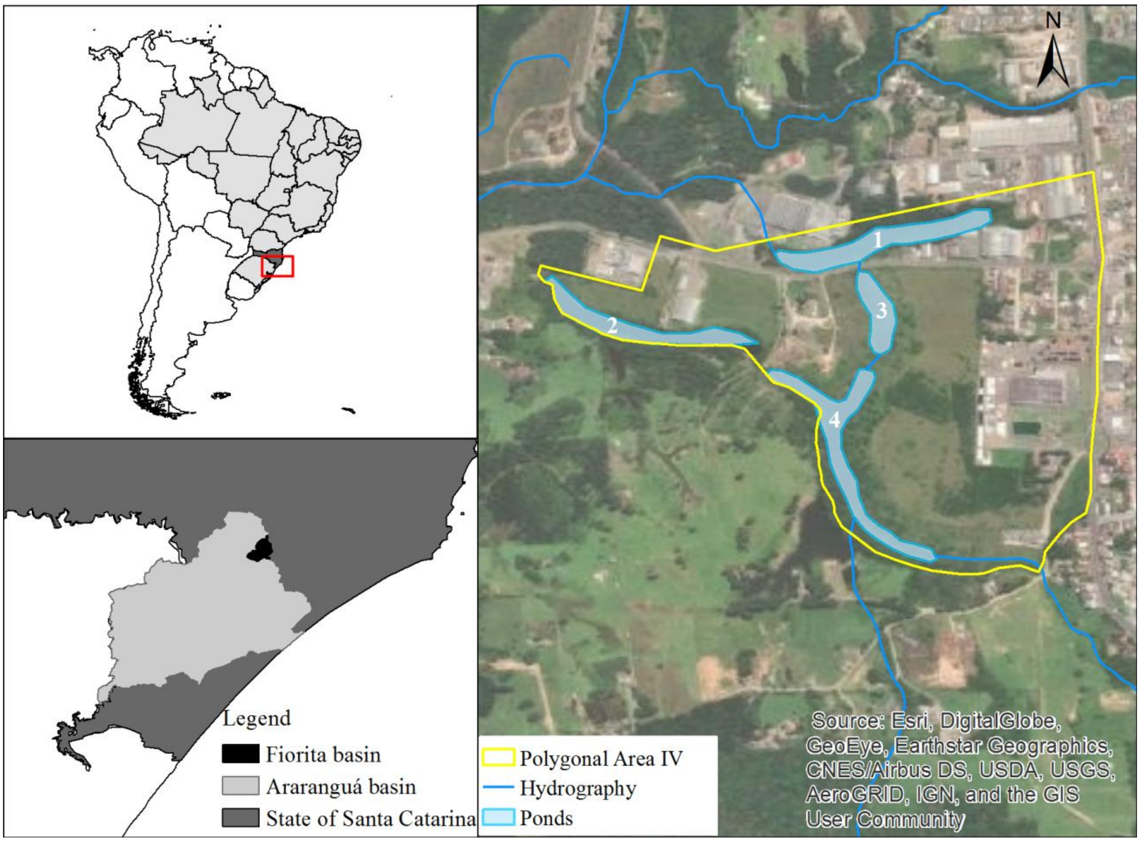

Fig. 2.1. Study area location.

2.2.2 Area History

Area IV is part of a region called "Vila Funil", one of the first areas mined using heavy equipment in the southern region of the Santa Catarina state. Research carried out in documents from the National Mining Agency of Brazil showed that the request for mining in the area dates back to 1936, but it was not possible to determine the date of the mine's closure. Based on information from local residents, we estimated that mining took place between the 1940s and 1950s.

Due to the proximity between the coal layer and the land surface, Area IV was mined using the technique called open cast mining. This technique consists of completely removing the upper lithological layers in order to access the coal layer. At the time this area was being mined, there was no environmental care in the removal of these layers and the reclaiming of the area. The removal of the rock layers above the coal was performed using explosives. After detonation, the mixed rock layers, including soil, were disposed of by huge machines, called dragline excavators, in piles from 10 to 20 meters tall. This material, characterized by the mixture between lithological layers and soil, is referred to in this work by “waste rock”.

2.2.3 Reclamation techniques

The reclamation technique which has been applied in this surface mined area includes: (i) the constitution of a new stable topography conformation made from the waste rock; (ii) implementation of a drainage system in order to guarantee stability and minimize erosion processes; (iii) construction of a clay cover over the waste rock. The primary objective of this clay cover is to isolate the waste rock from water infiltration, ensuring that rainfall does not come into contact with the sulfides present in it. Notably, this isolation is critical throughout the entire reclaimed area. However, in specific parts of the area, known as the permanent preservation area, the clay cover also serves an additional function. Here, it acts as a supporting medium for Atlantic rainforest plant species, thus facilitating ecological restoration alongside waste isolation.

Despite that clay cover was not introduced at the bottom of the pond, it was decided even so to carry out the treatment of the pond water. This treatment was applied to the acidity stored in the water ponds, and calcium carbonate ($CaCO_3$) was used to neutralize them.

It was not possible to perform interventions on pond 1's banks due to its margins already being occupied by industrial structures, as shown in Figure 2.2.

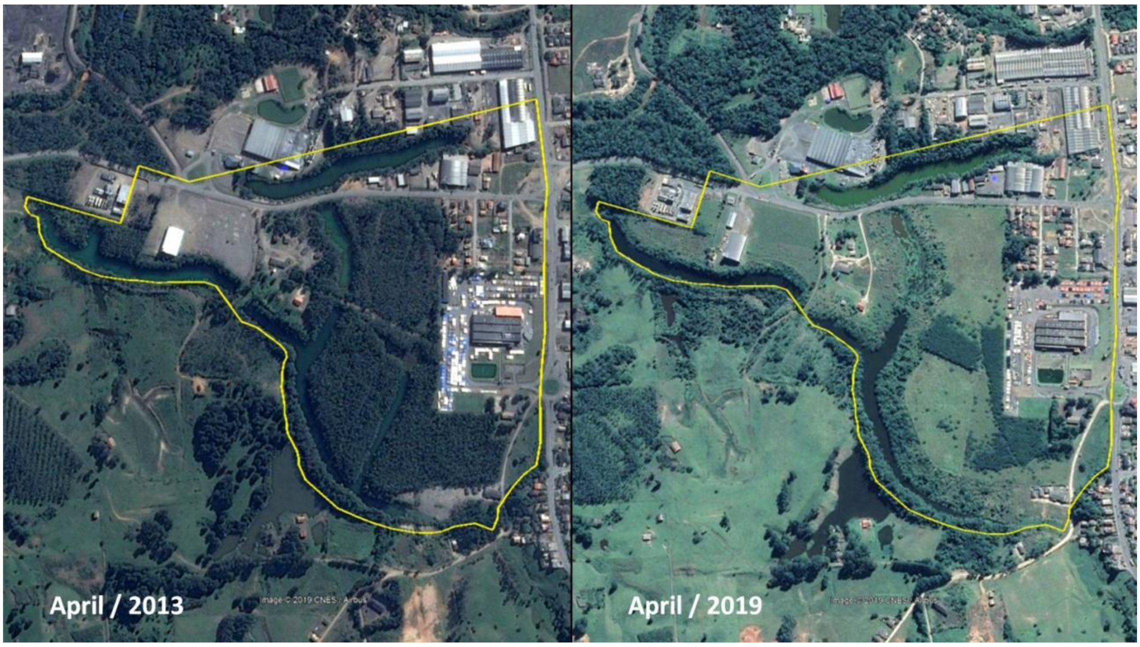

Fig. 2.2. Area IV before, april 2013, and after reclaiming process, april 2019 (Google Earth 2019).

2.2.4 Monitoring strategy (data and periods)

The water monitoring plan in Area IV's surface is carried out in lentic (ponds) and lotic (rivers) environments (Fig. 2.3). The lotic sampling sites are situated in a stream both before

(HIDS07) and after (HIDS10) Area IV. This stream is a tributary of the Fiorita River. Additionally, the Fiorita River has two more sampling sites: one upstream (HIDS11) and not affected by the Area IV and one downstream (HIDS12) of the confluence. There are four ponds in Area IV, in each pond two samples are collected, one at the water surface level and the other at half of water column. The samples of the intermediate portion of the water column are collected using the Van Dorn sampler (BOITEN, 2008).

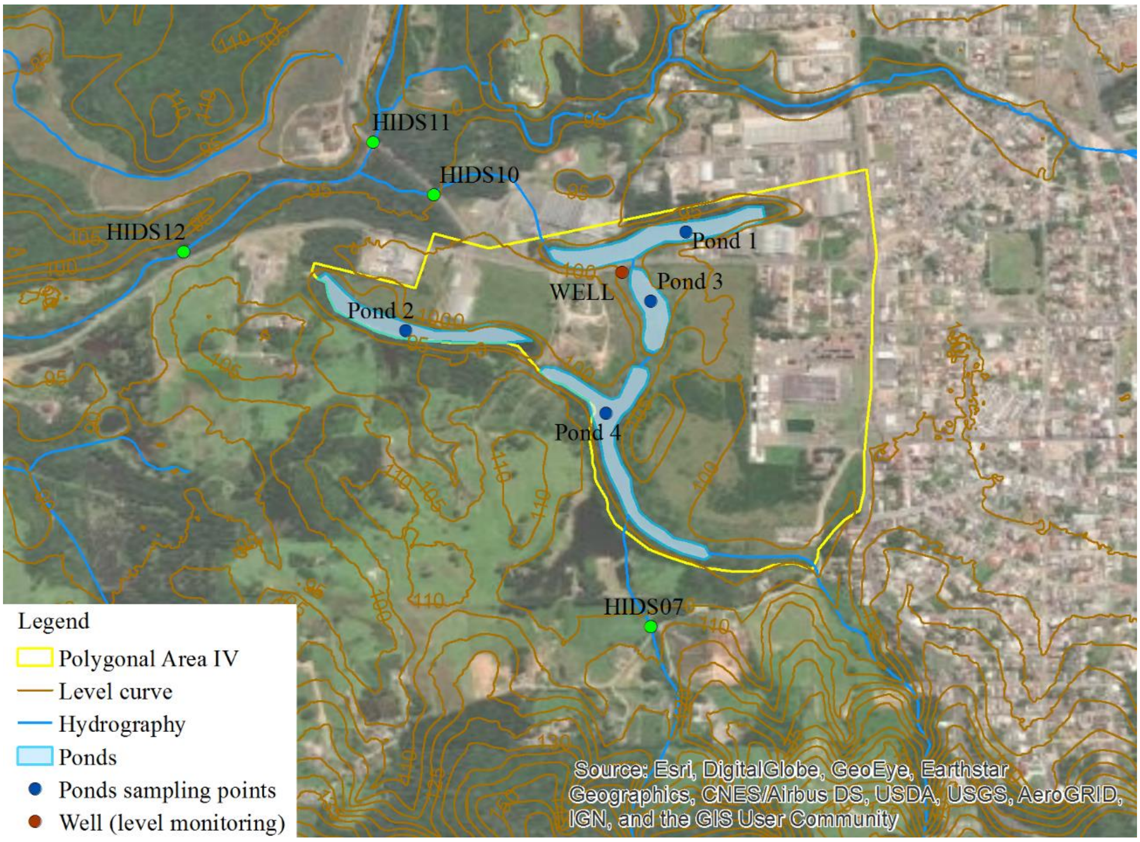

Fig. 2.3. Surface water sampling points

Surveys are also performed at one point of groundwater and four points located in upstream and downstream area rivers (Fig. 2.3). Table 2.1 presents the label of the points, mean sea levels and pond depths, the number of campaigns performed and their coordinates.

Fourteen monitoring campaigns were conducted. Campaign 0 was carried out prior to the start of the area reclamation, during the environmental diagnosis of the area, which took place in 2010. Throughout this research, the company hired by the Federal government to carry out the diagnosis used only a few points to characterize surface water. For a better understanding of the qualitative and quantitative hydrological processes in the area, the Geological Survey of Brazil team decided to insert additional monitoring points from the start of the reclaiming operation.

Campaign 1 was carried out after the beginning of the area's environmental reclamation, but before the ponds' neutralization.

For improved readability, following in the text the Pond's samples collected at surface level are in capital letter and the acronyms of the ponds with B at their end means that these are the points that were sampled at half water depth.

Tab. 2.1 Sampling points, depths, sea levels, monitored period and coordinates (SIRGAS 2000).

	Point	Depth (m)*	Sea level (m)*	Sampling campaigns	E	N	Intervention
Rivers	HIDS07	-	-	0** to 13	0653011	6835074	-
	HIDS10	-	-	0** to 13	0652625	6835951	-
	HIDS11	-	-	1 to 13	0652530	6836062	-
	HIDS12	-	-	1 to 13	0652475	6835907	-
Ponds	POND01	7.89	95.14	0** to 13	0653042	6835866	Neutralized
	POND01B			0** to 13	0653042	6835866	Neutralized
	POND02	9.01	93.97	0** to 13	0652577	6835685	Neutralized
	POND02B			0** to 13	0652577	6835685	Neutralized
	POND03	1.71	95.74	1 to 13	0653008	6835719	Neutralized
	POND03B			1 to 13	0653008	6835719	Neutralized
	POND04	8.27	96.25	0** to 13	0652932	6835516	Neutralized
	POND04B			0** to 13	0652932	6835516	Neutralized
Groundwater	WELL***	-	93.73	9 to 13	0652956	6835791	-

*The sea level and pond reference depth were established based on the average of the measurements taken across all campaigns; **Campaign 0 refers to the samples taken during the environmental diagnosis of the area, prior to the beginning of the reclaiming process. This campaign was carried out in just a few sampling points. ***Groundwater monitoring started in campaign 9, after the construction of the well.

2.2.5 Analytical data

In the field, the pH, dissolved oxygen ($mg.L^{-1}$), electrical conductivity ($\mu S.cm^{-1}$) and temperature (°C) parameters were measured with a multiparameter *Aquaread AP-800* probe. From the seventh campaign onwards, the oxidation/reduction potential (mV) parameter was also monitored. In rivers, streamflow is also measured using a Sontek acoustic current meter, *FlowTracker* equipment (SONTEK 2019). Groundwater sampling was conducted through low flow method (PULS; BARCELONA, 1996).

In the ponds, the water level was recorded with staff gauges and the estimation of water turbidity was assessed with a Secchi Disk. Once collected, the samples were sent to the Mining Pollution Control Center laboratory (*Centro de Controle de Poluição Mineral* - CECOPOMIN) of the Geological Survey of Brazil for analysis of the parameters listed in Table 2.2.

To check the laboratory data consistency technical QA/QC procedures were performed following the Brazilian Geological Survey standards based on duplicates and comparative tests with data from similar areas, trend analysis, mass fluxes calculation, frequency distribution, and regression analysis.

Tab. 2.2 Parameters analyzed in the last campaign

Parameter	Minimum value detectable	Analysis method
pH (23ºC)	0.1	Potentiometric
EC - Electrical conductivity (µS.cm^{-1} 23ºC)	0.001	Conductivity
Acidity (mg $CaCO_3L^{-1}$)	1	Potentiometric
SO_4^{-2} - Sulfate (mg.L^{-1})	0.1	Gravimetric Analysis
Fe - Total Iron (mg.L^{-1})	0.01	Atomic Emission Spectrometry
Al - Total Aluminum (mg.L^{-1})	0.01	Atomic Emission Spectrometry
Mn - Total Manganese (mg.L^{-1})	0.002	Atomic Emission Spectrometry
Cu – Total Copper (mg.L^{-1})	0.002	Atomic Emission Spectrometry
Pb – Total Lead (mg.L^{-1})	0.005	Atomic Emission Spectrometry
As - Total Arsenic (mg.L^{-1})	0.002	Atomic Emission Spectrometry
Hg - Total Mercury (mg.L^{-1})	0.0003	Atomic Emission Spectrometry
Cd - Total Cadmium (mg.L^{-1})	0.002	Atomic Emission Spectrometry
Zn - Total Zinc (mg.L^{-1})	0.005	Atomic Emission Spectrometry

2.2.6 Data analysis

The characterization of water resources was made through graphical and basic descriptive statistical analysis (mean, standard deviation, max and minimum) of the monitoring data. Initial analysis was performed with data from these descriptive statistics, which presents the data of the entire series in a simplified and summarized manner (MULHOLLAND; BOAVENTURA; ARAÚJO, 2013). Time discretization of the most relevant parameters was also performed, at this point the purpose was to track the evolution of the parameters motivated by the interferences conducted in the study area.

One hundred and sixty-nine (169) synoptic water samples were analyzed for this study, sampled between the years of 2010 and 2019. In total, 54 were collected in rivers (Tab. 2.3), 110 in ponds (Tab. 2.4) and 5 in the well (Tab. 2.5).

The pH and conductivity parameters were analyzed in duplicate, both in the field and in the laboratory. Due to the difficult sampling conditions and the unreliability of the field equipment calibration in the first campaigns, only values of both parameters obtained in laboratory were considered in this work. However, in a comparison between these two databases one can see that there are no major differences, as showed in the Supplemental Material.

Regarding the parameters analyzed in the laboratory for this study's analysis, only those with mean concentrations equal or superior to 0.1 mg.L^{-1} were used. Thus, the elements Cd, Pb, As and Hg were excluded since they had an average concentration below 0.01 mg.L^{-1}, as well as the elements Cu and Zn, which had average concentrations of 0.02 $mg.L^{-1}$ and 0.08 $mg.L^{-1}$, respectively. With these eliminations, the only parameters that remained in the analysis were the ones that, according to Younger et al. (2004), are more likely to be found in contamination by open pit mining: Fe, Mn, Al and Sulfate.

2.3 Results

The results from the river quality monitoring points (Tab. 2.3) showed that the upstream area sampling point, HIDS07, has quite different characteristics from those monitored downstream. At this point, the mean pH was in the neutral range, 7.1, the mean conductivity was around 74.15 $\mu S.cm^{-1}$ and the other parameter values were below the other rivers' points. In the downstream area point (HIDS10) and in the points located in the Fiorita river (HIDS11 and HIDS12), the water quality was worse and the values of pH, conductivity and sulfate showed little variation between them. At these three points, mean pH values ranged from 3.3 to 3.6, conductivity ranged from 397.95 to 467.14 $\mu S.cm^{-1}$, and sulfate from 136.9 to 151.5 $mg.L^{-1}$.

Although the areas in the most downstream point and the Fiorita river points have similar mean values of some parameters, the mean of manganese and iron concentration is respectively around 40.7% and 56.4% less in the HIDS10.

Tab. 2.3 Summary of descriptive statistics for stream sampling sites including number of observations (n), mean, standard deviation (s), and range (minimum and maximum values)

	Point	HIDS07	HIDS10	HIDS11	HIDS12
	n	14	14	13	13
pH	Mean	7.1	3.3	3.6	3.5
	s	0.4	0.2	0.3	0.3
	Min	6.6	3.0	3.1	3.2
	Max	7.7	3.6	4.1	4.1
EC	Mean	74.15	467.14	397.95	421.68
	s	10.22	150.35	127.40	139.68
	Min	56.00	178.10	210.40	231.50
	Max	89.50	782.50	631.00	700.80
Acidity	Mean	7	95	77	76
	s	6	35	20	22
	Min	1	25	51	35
	Max	24	166	111	111
SO_4^{2-}	Mean	9.4	136.9	143.4	151.5
	s	6.1	43.6	52.4	48.7
	Min	0.4	65.9	67.4	75.4
	Max	23.9	246.1	267.5	258.5
Fe	Mean	0.50	3.89	8.96	8.87
	s	0.34	2.51	4.00	3.25
	Min	0.00	1.40	3.10	3.67
	Max	1.25	11.10	17.70	15.20

Mn	Mean	0.08	0.99	1.63	1.71
	s	0.10	0.44	0.65	0.61
	Min	0.01	0.40	0.75	0.78
	Max	0.31	2.27	2.93	2.82
Al	Mean	0.10	5.24	4.79	4.62
	s	0.11	2.00	1.52	1.49
	Min	0.00	1.73	2.75	2.74
	Max	0.37	10.60	7.39	7.09

Figure 2.4 displays the rivers' temporal evolution of pH throughout the campaigns. These points are located outside the reclaimed area polygon and, for this reason, have not undergone any type of reclaiming intervention. These checkpoints are used to compare the water quality before and after passing through the area. Figure 2.4 shows that there was no change in the pH parameter trends over time for all points. It is also verified that the HIDS07 point presents pH values on average 3.7 units above the others.

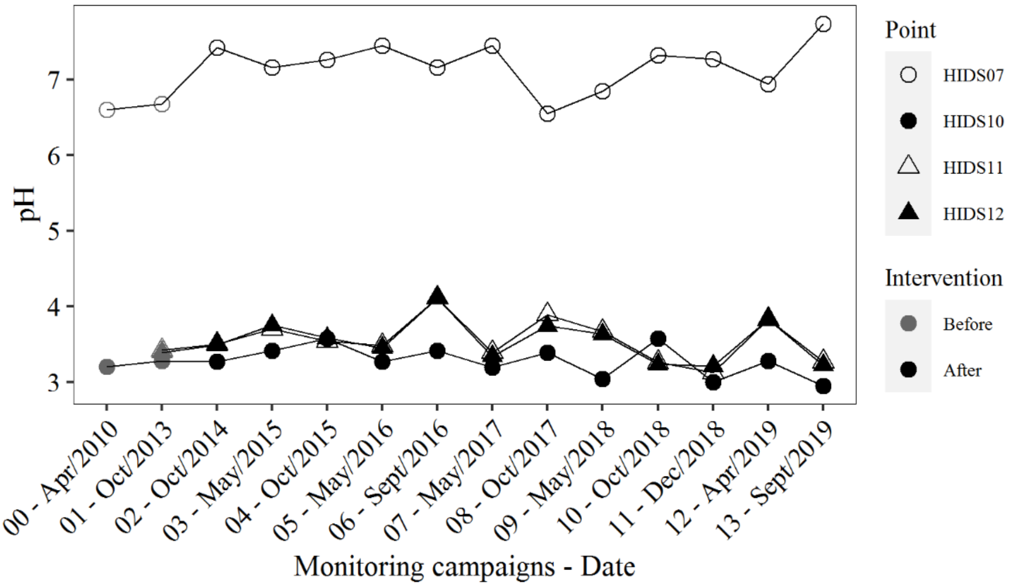

Fig. 2.4. Temporal evolution of pH at river sampling points

The descriptive statistical results of the points located in the ponds are shown in Table 2.4.

Thirteen campaigns were carried out in pond 3, while fourteen in the others.

In ponds 1, 2 and 4, the samples collected at half depth exhibited poorer quality than the surface ones. In pond 3, however, these values are close, which is probably related to its low depth (Tab. 2.1).

When comparing ponds it is perceptible that pond 1, downstream of the area, presents worse quality in its water samples, with low pH and high values of other parameters. Pond 2 has intermediate quality, while 3 and 4 stand out as having the highest quality.

Tab. 2.4. Summary of descriptive statistics for ponds sampling sites including number of observations (n), mean, standard deviation (s), and range (minimum and maximum values)

	Point	POND01	POND01B	POND02	POND02B	POND03	POND03B	POND04	POND04B
	n	14	14	14	14	13	13	14	14
pH	Mean	3.3	3.1	5.0	5.1	6.2	6.2	6.6	6.2
	s	0.2	0.2	0.9	0.9	0.8	0.8	0.6	0.7
	Min	3.0	2.7	3.7	3.6	3.5	3.6	4.7	4.2
	Max	3.6	3.6	6.4	6.2	6.7	6.9	7.2	6.8
EC	Mean	425.97	668.86	207.44	235.95	123.41	125.21	97.51	105.85
	s	114.27	300.33	98.38	107.13	92.29	90.68	34.72	50.48
	Min	257.70	292.40	91.20	91.50	72.10	72.10	70.00	74.30
	Max	645.30	1282.80	389.50	437.00	426.30	420.80	204.80	265.30
Acidity	Mean	89	155	23	29	18	18	10	17
	s	33	95	19	22	18	18	7	8
	Min	58	78	1	5	4	5	2	8
	Max	175	409	70	77	70	73	32	29
SO_4^{2-}	Mean	121.3	198.8	83.4	87.7	31.8	36.5	24.8	26.4
	s	33.9	108.2	37.4	33.4	26.0	25.7	16.7	22.0
	Min	75.3	93.8	23.1	29.2	8.6	14.0	4.8	9.1
	Max	200.9	449.1	160.9	150.0	110.1	111.3	66.5	82.1
Fe	Mean	3.62	25.79	0.47	1.49	1.84	1.74	0.53	1.39
	s	2.26	41.82	0.26	2.92	1.84	0.94	0.41	1.79
	Min	0.92	2.17	0.00	0.00	0.00	0.35	0.00	0.00
	Max	8.60	159.00	1.11	11.06	6.97	3.88	1.50	6.72
Mn	Mean	1.01	1.20	1.16	1.64	0.45	0.48	0.33	1.29
	s	0.47	0.40	0.92	1.15	0.66	0.65	0.42	1.35
	Min	0.55	0.71	0.18	0.19	0.05	0.06	0.06	0.00
	Max	2.47	2.27	3.14	3.38	2.53	2.50	1.59	4.38
Al	Mean	4.68	7.46	0.48	0.42	0.39	0.39	0.25	0.32
	s	1.48	3.47	0.63	0.67	0.72	0.75	0.32	0.47
	Min	2.55	3.23	0.00	0.00	0.00	0.00	0.00	0.00
	Max	8.66	15.00	1.92	2.01	2.59	2.69	0.95	1.37

Pond 1 is highlighted by its low mean pH values, 3.3 and 3.1, and by the greater values of the other parameters.

Pond 2 has the highest concentration of manganese, however it is only slightly higher than the others.

Considering the ponds' pH values, it is noticeable that the standard deviation of pond 1 is considerably smaller than the one observed in the other ponds, 0.2, for the surface and subsurface samples. In regard to other ponds the standard deviation varied from 0.6 to 0.9, gradually increasing from pond 4 to pond 3, then 2. In Figure 2.5 it is possible to observe the ponds' average pH values (bar graph) and the dispersion of the values around the average (points), as well as the sampling values of campaigns 0 and 1 (black filled circles), carried out before the ponds' neutralization.

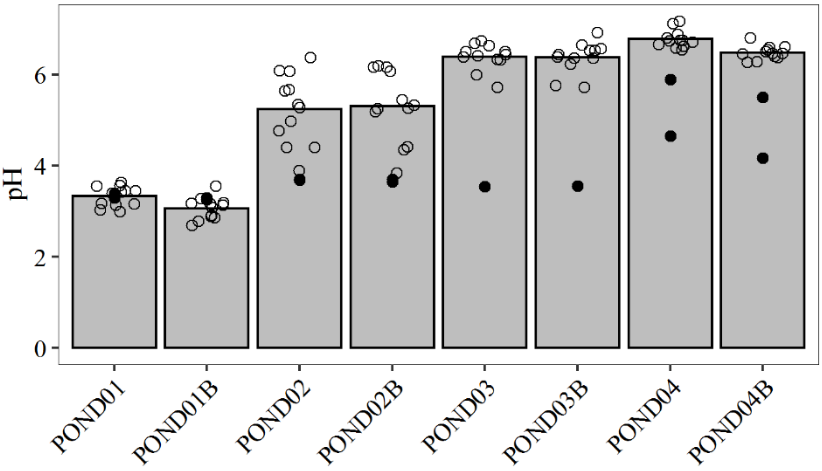

Fig. 2.5. Mean (gray rectangle) and dispersion (circles) of pH between ponds. The black filled circles refer to campaigns 0 and 1, which respectively occurred prior to the ponds' intervention and prior to neutralization

Analyzing the temporal evolution of pH values in the ponds across the campaigns (Fig. 2.6), it is noted that even after the neutralization, which occurred between the first and the second campaigns, pond 1 did not present changes in this parameter. This stagnation has not happened in the other ponds, which had high pH values after the application of the neutralizer. Figure 2.6 shows that ponds 3 and 4 had their pH elevated in the campaign following the usage of the neutralizer, while pond 2 had its pH gradually increased in the campaigns that followed the intervention.

Pond 1's pH stagnation behavior over time was also observed in the other tracked parameters, indicating that the environmental intervention in the area did not influence the water quality of this pond.

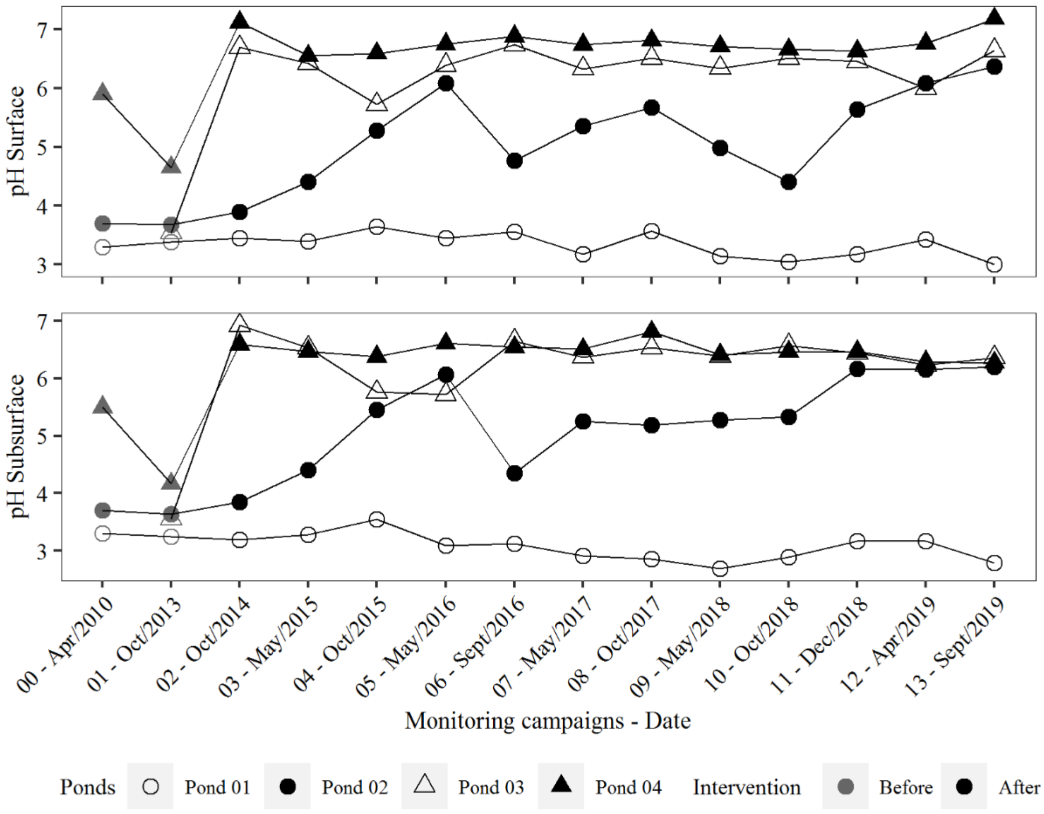

Fig. 2.6. Temporal evolution of pH in the ponds

The results of groundwater monitoring are shown in Table 2.5. As the well monitoring began at campaign 9 it was not possible to compare the effect of pond's neutralization in the groundwater. Along the five groundwater campaigns carried out, quality parameters did not show substantial changes or trends in their results. The standard deviations of pH, EC, acidity, sulfate, and Mn were around 18% of the mean, while all Al values were lower than the detection limit of the analytical method. Fe values showed the greatest oscillation, the standard deviation for this parameter was close to 60% of the mean value, with Fe values ranging between 77 and 222 mg.L^{-1}.

Tab. 2.5. Summary of descriptive statistics of the well including number of observations (n), mean, standard deviation (s), and range (minimum and maximum values)

	n	mean	S	min	max
pH	5	5.6	0.3	5.1	6.0
EC		454.40	35.77	430.00	516.00
Acidity		169	30	142	219
SO_4^{2-}		127.0	8.8	115.7	137.5
Fe		109.32	63.25	77.00	222.00
Mn		0.534	0.088	0.390	0.618
Al		<LD	<LD	<LD	<LD

<LD: Lower than detection limit.

2.4 Discussion

The environmental monitoring and assessment revealed that the area's upstream and downstream river sampling points did not display any trend after the reclamation efforts. However, despite being subjected to the same reclaiming procedures, the surveyed ponds showed different results, particularly ponds 2, 3 and 4 whose water quality improved significantly after the reclaiming process.

Figure 2.7 shows the evolution of pH and acidity in the area combined with flow of surface runoff, ponds and rivers (only the surface pond data was used for this analysis). An improvement of these parameters is noted in the graph after the neutralization in the three first ponds: 4, 3 and 2, while pond 1 and the downstream point, HIDS10, remained with the same characteristics that were identified in the diagnosis period.

It is possible to deduce that the employed environmental reclaiming method was efficient in neutralizing the water acidity in three out of four ponds. However, the method was not effective for neutralizing the downstream water course, as the stream that receives the contribution from the area persists with its water quality compromised in terms of pH and acidity.

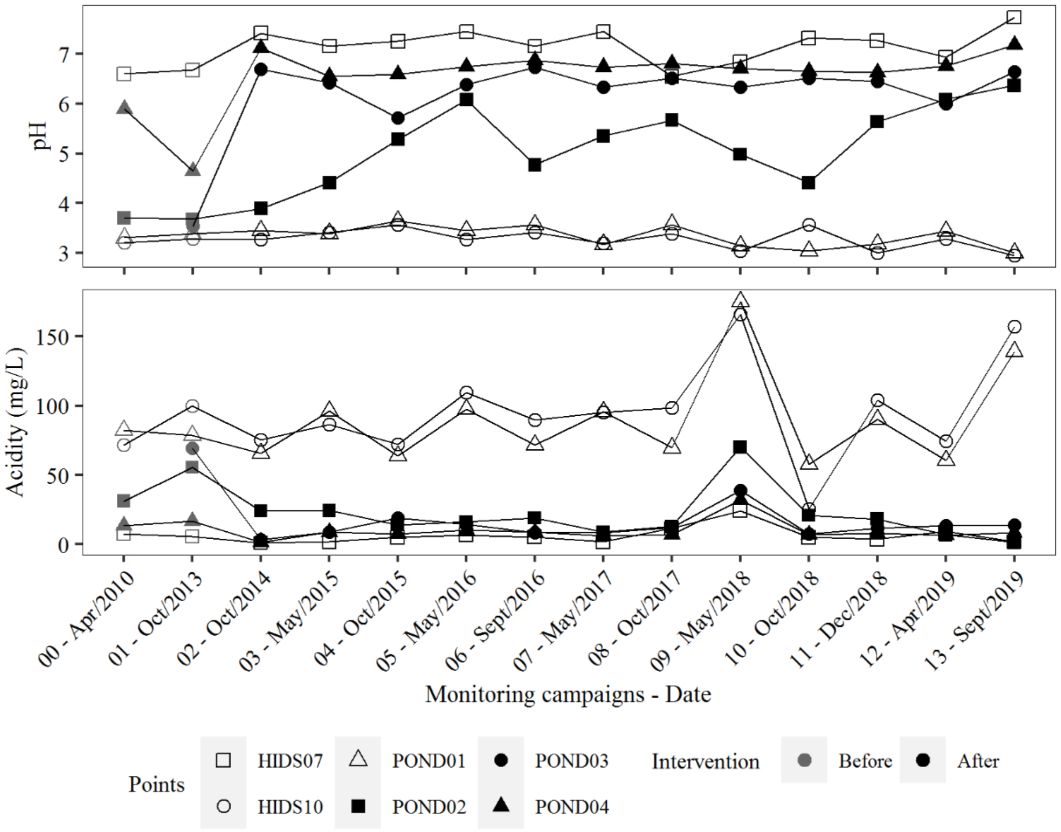

Fig. 2.7. Temporal evolution of pH and acidity in the combined runoff points of the area

Based on the presented data, it is possible to assess that the reclaiming problem occurs before the water arrives in pond 1. Through studies, we can make the following assumptions from this outcome:

The first hypothesis, Hypothesis 1, concerns the leaching of surface water around the pond. As the area around pond 1 was occupied by industries before the reclamation, there was no intervention in these places. The runoff from these banks would be leaching the material into the pond. Even though the presence of tailings was not found in the area, the diagnosis report (IPAT/UNESC, 2010) points out that the waste rock found there have a high acid generating potential, the results showed negative neutralization potential ($\bar{x}$= -5.9 kg $CaCO_3$/tonne), positive acid-producing potential ($\bar{x}$= 7.3 kg $CaCO_3$/tonne) and high levels of sulphur content ($\bar{x}$= 23.3%). In this situation, as the reaction takes place in the presence of atmospheric air, the pyrite is oxidized by oxygen, as detailed by Nordstrom (1982).

Another hypothesis, called Hypothesis 2, is related to contamination by groundwater. The groundwater in the area flows in the southeast-northwest direction and pond 1 receives this outflow. For this reason, the pond is affected by this subsurface flow after it passes through the entire area. Based on the data, a conceptual groundwater flow model of the area, shown in Figure 2.8, was established. Mean and standard deviation of the parameters most related to AMD (pH, sulfate and iron) were calculated considering the monitoring values obtained after the ponds intervention. According to Haigh and Kilmartin (2017), the pollutants mobilized by the water inside the submerged mine spoils, especially in the regions of water level movement, are one of the biggest impacts of past open cast mining. This fact becomes even more relevant when considering the high hydraulic conductivity found in this type of material, Younger et al. (2004) showed that slug and bail testing performed on this material found hydraulic conductivities ranging from 1 m/d up to 10 m/d, three to four orders of magnitude above values typical for natural materials. With further aggravating factors such as lentic environments and little acid neutralization capacity, as is the case here, the impact of acidic groundwater intake is significant (HAYASHI, MASAKI; ROSENBERRY, 2002). We believe that the quality parameters presented supports the contaminant transport model proposed (hypothesis 2), as a low concentration of sulfate and iron is observed in ponds 3 and 4, while in groundwater (WELL) and in pond 1 concentrations increase by a considerable amount, mainly for the samples collected at a half of water column (POND01B).

Considering hypothesis 2 it is possible that the other ponds have improved their water quality for the following reasons: (i) Ponds 2 and 4, being located at the upstream limit of the area, do not receive inflow of contaminated water; (ii) Pond 3, which is less than 2 meters deep, does not receive a contribution from the groundwater flow, but, as observed through monitoring wells, contributes water inflow to this aquifer (Fig. 2.8).

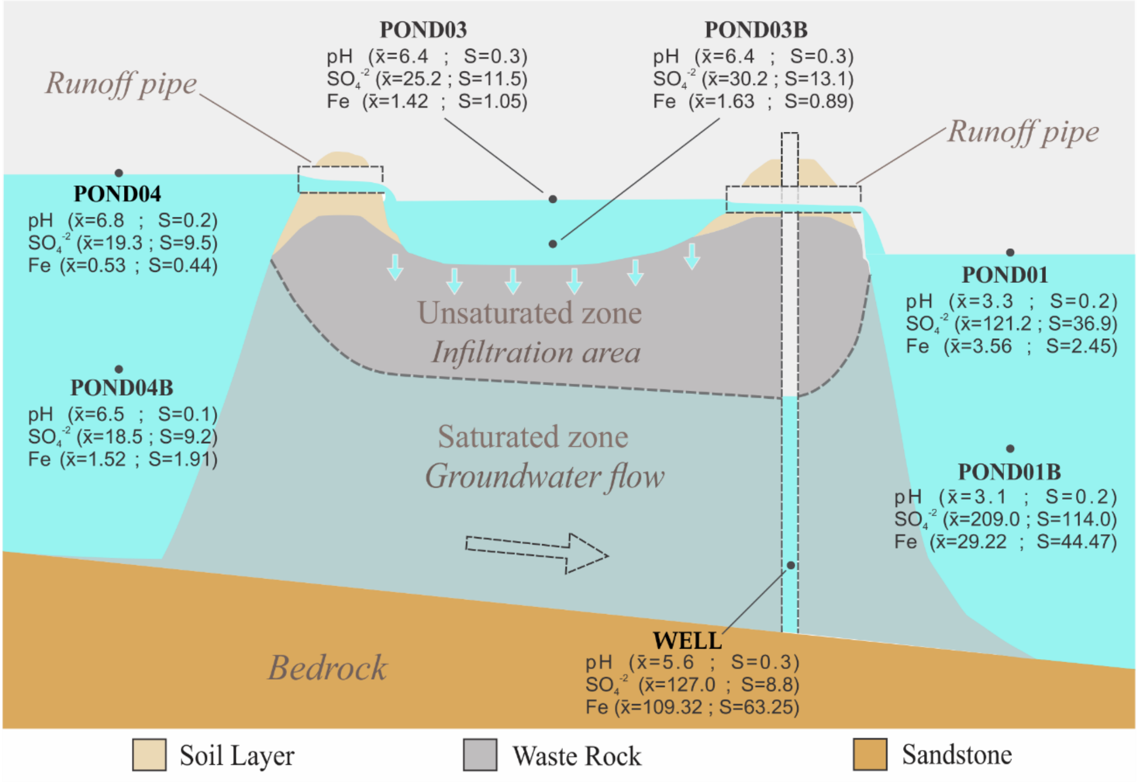

Fig. 2.8. Hypothesis 2, conceptual contaminant transport model

At the moment it is not consistently possible to prove which hypothesis is correct, as it is also possible that both hypotheses work in conjunction.

The presented limitations in surface water quality improvements are directly related to the method used in the environmental reclaiming. As the main purpose of this method is based on surface isolation with the insertion of a clay cover and groundwater is still allowed to enter laterally in the subsurface regions and to run through the sulfide waste rock material. The urbanized sites are also a problem for the reclaiming strategy because if they are inside the area polygon it is not possible to intervene in these places, as in the case of pond 1.

2.5 Conclusions

The study aimed to evaluate changes in water resource quality after an environmental reclamation process in a former open cast coal mining area. Fourteen monitoring campaigns were carried out, one before and thirteen after the reclaiming operation, taking place in the adjacent affected streams and in artificial ponds formed by open cast mining located within its area.

Descriptive statistics showed that upstream and downstream river points have different water qualities, with the downstream points having poorer water quality, still affected by past mining activities even after the reclamation. The temporal analysis also showed that the streams remained with similar concentrations and parameters and were not affected by the reclaiming effort.

Analysis of pond 1, located downstream of the area surface flow, showed that this pond presents the worst water quality of all. The data showed that pond 01 was the only one that did not react to the neutralization process executed during the reclamation endeavors.

Considering the surface flow in the area, it was found that the contamination problem probably occurs before the water enters pond 1. From this analysis, two hypotheses were proposed, operating separately or simultaneously. The first hypothesis is the contamination happens due to leaching of the material that still remains on the on the pond's bank. The other hypothesis is that the contamination comes from the upstream water table inflow into the pond, which runs through the entire area before reaching the pond. It is important that further research analyse these hypotheses, so they can be confirmed or refuted, promoting the new recovery projects that are being developed.

From the surface water perspective, the reclaiming method adopted was effective in 3 of the 4 ponds, presenting problems only in the downstream one. The surveyed upstream pond exhibited good quality and steady parameters persisted across all campaigns, serving as a reference point for the evolution of the other monitoring sites. As the downstream stream in the area is pond 1’s outlet, its quality is similar to this one.

Finally, from the perspective of our data analysis, we believe that the reclamation strategies employed in the studied areas must be improved if they are to fully live up to the idea of eliminating environmental issues related to the consequences of past mining activities.

CHAPTER 3

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

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This chapter presents a research previously published in Brazilian Journal of Water Resources: CARDOSO, A. T.; FAN, F. M.; FRANZEN, M.; SIMÃO, G.; TROIAN, G. C. Surface water resources of Santa Catarina state's southern region – geochemical background of the coal mining territory. **Revista Brasileira de Recursos Hidricos**, v. 27, 2022. Available at: https://doi.org/10.1590/2318-0331.272220220084

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.

3.1 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; OTTENSTEIN; REIMANN, 2000) that is, knowing what is the natural concentration of the elements present in the location being investigated. According to Mast et al. (2008), 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 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 monitoring, 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; MENEZES; SILVA, 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 reclaiming 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 (GTA, 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.

3.2 Materials 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.

3.2.1 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 3.1): Araranguá River Basin (BHRA), 3025 km², Tubarão River Basin (BHRT), 5960 km², and Urussanga River Basin (BHRU), 709 km². 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 3.1.

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

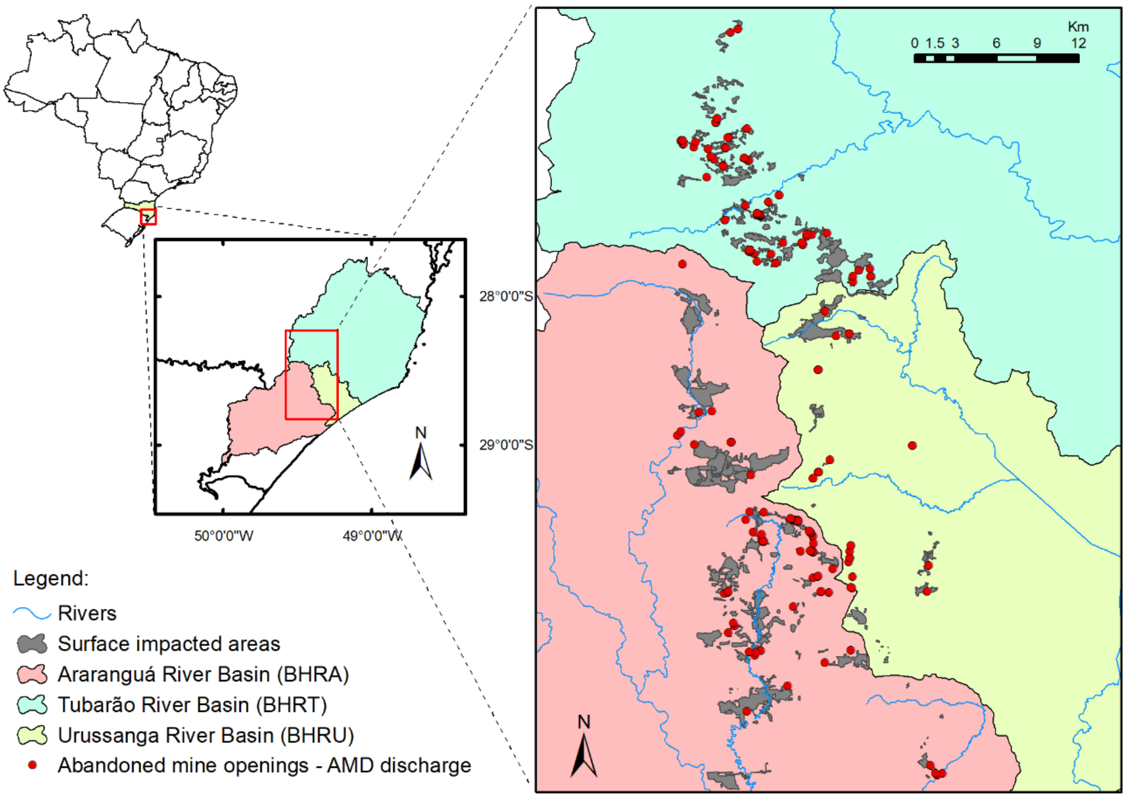

Fig. 3.1. Study area location.

Expanding on this classification, according to the local classification suggested by Braga & Ghellre (1999), which is rooted in the Köppen classification, the region can be further subdivided into two distinct climate domains and types. The eastern and northeastern parts of the region fall under the subwarm domain and are characterized by subtropical climate type 1. Conversely, the remaining area is classified under the mild mesothermal domain and is characterized by temperate climate type 2. This localized subdivision provides a more detailed and nuanced understanding of the climatic variation across the study region.

3.2.2 Geology

According to Silva and 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 3.2).

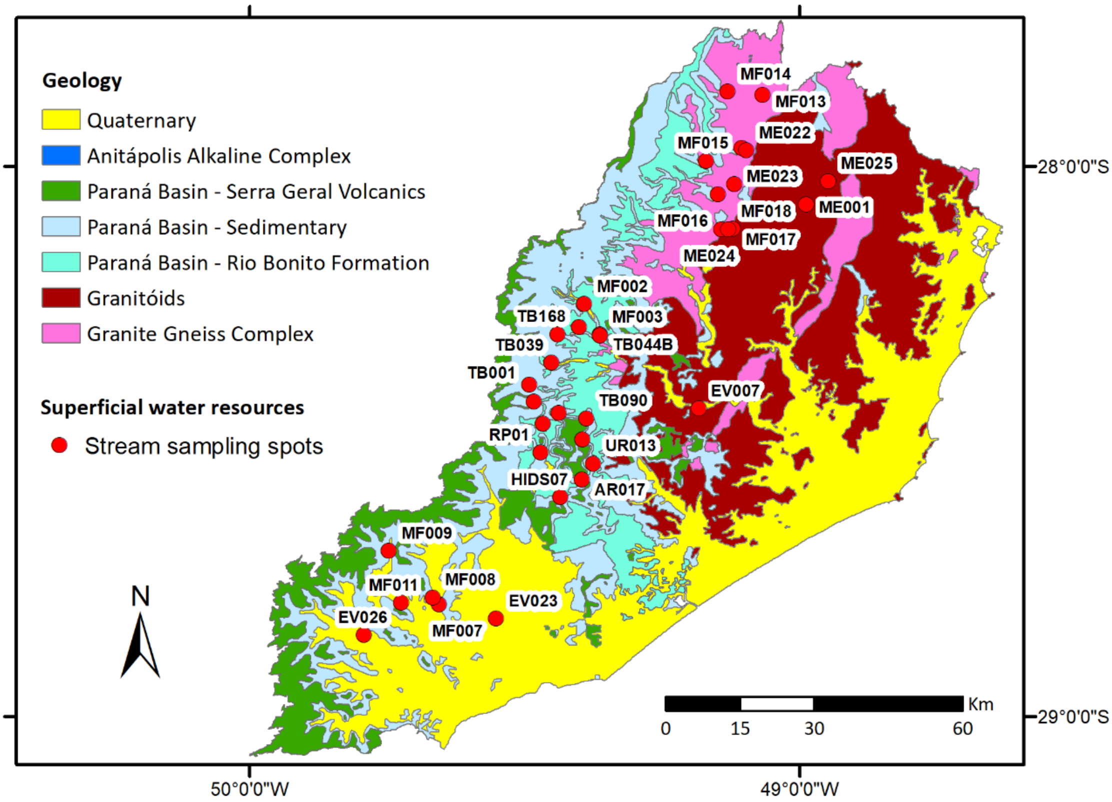

Fig. 3.2. Geology of the study area and location of the stream sampling spots.

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 6km² 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 3.2 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 Geral formation; and (iv) unconfined aquifers related to Cenozoic coastal aquifer systems.

3.2.3 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 basins, 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 (GTA, 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 3.2).

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 (E_H), 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 3.1 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).

Tab. 3.1. 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)	µS.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*
Total Sodium (Na)	(mg.L^{-1})	Laboratory	0.07	ICP OES*
Total Magnesium (Mg)	(mg.L^{-1})	Laboratory	0.01	ICP OES*
Total Calcium (Ca)	(mg.L^{-1})	Laboratory	0.025	ICP OES*
Total Potassium (K)	(mg.L^{-1})	Laboratory	0.07	ICP OES*
Total Copper (Cu)	(mg.L^{-1})	Laboratory	0.002	ICP OES*
Total Cadmium (Cd)	(mg.L^{-1})	Laboratory	0.002	ICP OES*
Total Lead (Pb)	(mg.L^{-1})	Laboratory	0.005	ICP OES*
Total Zinc (Zn)	(mg.L^{-1})	Laboratory	0.005	ICP OES*
Total Arsenic (As)	(mg.L^{-1})	Laboratory	0.002	HVG ICP OES**
Total Mercury (Hg)	(mg.L^{-1})	Laboratory	0.0003	ICP OES*

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

3.2.4 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, 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 while the analyzes carried out in this study refer to the total portion of these 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).

3.2.5 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.

The grouping analyzes of the samples were performed using a hierarchical and non-hierarchical method. 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. (2008), 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.

3.2.6 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) and whiskers plot.

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:

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

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.

3.3 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.

3.3.1 Descriptive statistics and correlations

The result of descriptive statistics of the field and laboratory data for all samples is featured on Table 3.2. 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^{-1} OD, most samples were also charted, at 93%.

Tab. 3.2. Statistic summary with results of the parameters (Highlighted values are beyond the established legislation).

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 to 9	6 to 9.5
E_H	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

* Dissolved fraction; **SD: Standard Deviation; ***CV: Coefficient of variation

The electrical conductivity (EC) rested between 39 and 220 µS/cm², with the median and the mean placing respectively at 88.4 µS/cm² and 83.0 µS/cm². The larger EC values were observed in samples that also possessed elevated magnesium, calcium and sodium values; the correlations between these parameters and EC were all strong: Na: 0.54, Mg: 0.75 and Ca: 0.73 (Table 3.3).

Table 3.3 presents the results of spearman's nonparametric correlation in the lower triangle and significance (p-values) for the correlations in the upper triangle. Values of Spearmann's above 0.5 or below -0.5 are highlighted as an indication of relatively strong and reliable monotonic relationships.

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 3.3.

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 strong across all analyzed parameters, with r = 0.76.

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

Tab. 3.3. Spearman's nonparametric correlation matrix (lower triangle) and p-values (upper triangle).

	pH	E_H	DO	EC	Acid	SO_4^{2-}	Fe	Mn	Al	Na	Mg	Ca	K	Cu	Zn
pH		0.00	0.27	0.67	0.01	0.34	0.45	0.07	0.76	0.65	0.05	0.71	0.59	0.04	0.35
E_H	-0.55		0.12	0.57	0.60	0.32	0.58	0.23	0.23	0.07	0.29	0.83	0.20	0.02	0.91
OD	0.19	-0.26		0.00	0.13	0.02	0.60	0.00	0.00	0.12	0.00	0.03	0.08	0.07	0.48
EC	-0.08	-0.10	-0.47		0.04	0.06	0.96	0.06	0.05	0.00	0.00	0.00	0.37	0.52	0.49
Acid	-0.43	0.09	-0.26	0.34		0.03	0.14	0.00	0.69	0.28	0.00	0.02	0.93	0.12	0.01
SO_4^{2-}	-0.16	0.17	-0.40	0.32	0.36		0.72	0.00	0.12	0.56	0.00	0.07	0.01	0.16	0.95
Fe	-0.13	-0.10	0.09	-0.01	0.25	-0.06		0.05	0.00	0.08	0.90	0.18	0.00	0.20	0.27
Mn	-0.31	0.21	-0.59	0.32	0.46	0.61	0.34		0.64	0.01	0.00	0.27	0.78	0.09	0.13
Al	0.05	-0.21	0.49	-0.33	0.07	-0.27	0.76	-0.08		0.92	0.03	0.01	0.00	0.10	0.29
Na	-0.08	-0.31	-0.27	0.54	0.19	0.10	0.30	0.42	0.02		0.02	0.21	0.03	0.09	0.71
Mg	-0.34	0.18	-0.65	0.75	0.61	0.57	0.02	0.64	-0.36	0.39		0.00	0.18	0.01	0.08
Ca	-0.07	0.04	-0.37	0.73	0.38	0.31	-0.23	0.19	-0.46	0.22	0.80		0.05	0.06	0.08
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		0.03	0.52
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		0.09
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	

* r values below -0,5 and above 0,5 are highlighted.

3.3.2 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.

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 3.3 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 3.3). 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 3.3 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 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.

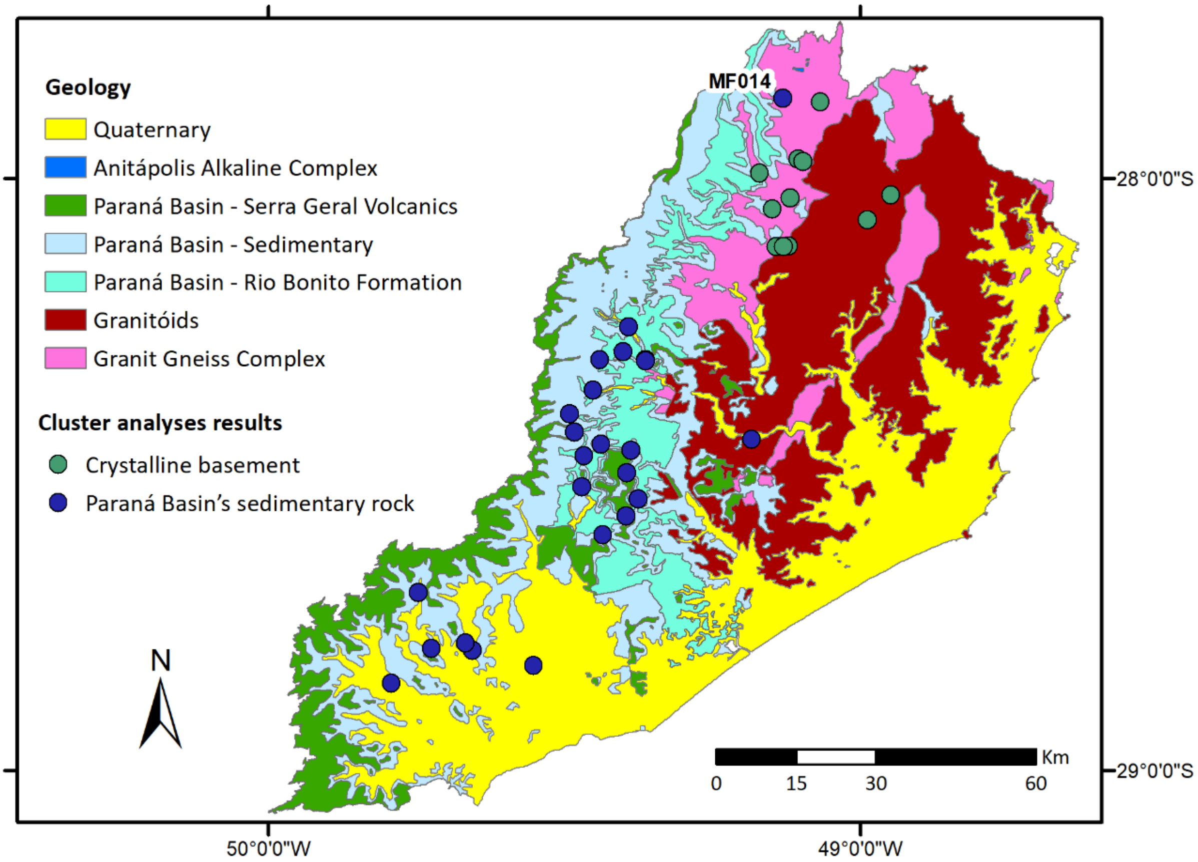

Fig. 3.3. Results of the samples' cluster analyses sorted into two clusters.

The result of the interrelations between the variables, which were analyzed through PCA, is featured on Figure 3.4. Figure 3.4 a) 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 3.4 b) shows the significance of each variable within the principal components. Considering the results displayed on Figure 4 a) and b), one verifies that the sedimentary basin samples are positively correlated to the variables: E_H, SO_4^{2-}, Ca, Mg, EC, Mn, acidity, Zn and 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, I. F., 2010; LEPSCH, I. F., 2016).

Sample MF014, which during cluster analysis was ascribed to the sedimentary basin set, also presented indefinite results in PCA. As shown in Figure 3.4 a), this sample is located in the intermediate area between the two sets composed by the analysis (green dot).

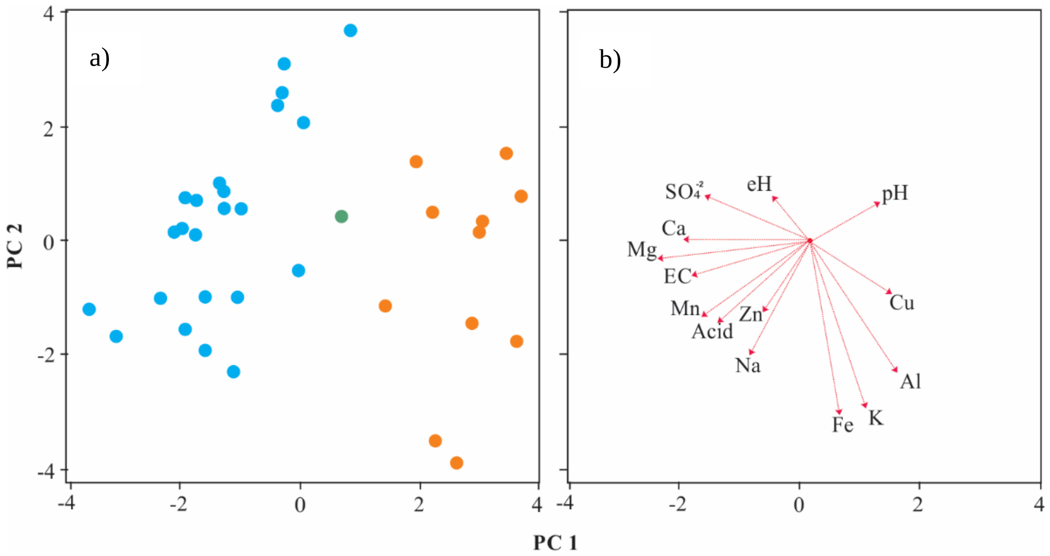

Fig. 3.4. Results of Principal Component Analysis (PCA), a) graph with the first two principal components (PC) sorted by the resulting clusters of the cluster analysis (blue: sedimentary

basin, red: crystalline basement); b) significance of each variable within the principal components 1 (PC1) and 2 (PC2).

3.3.3 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 3.4 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 3.4) were defined 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 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 value 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. However, it is necessary to consider, as already mentioned in the methodology section, that the limit established for iron in the CONAMA resolution refers to the dissolved fraction of this element, while in this work its total fraction was analyzed. The analysis of the total fraction is always equal to or greater than the dissolved fraction of the element, as it encompasses both its soluble and insoluble form.

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. For aluminum, it should also be considered that the value established by CONAMA refers to the dissolved portion, while in this study the defined value should be used for the total portion of the element.

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 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 (IPAT/UNESC, 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; WHITLEY; ROACH, 2009; MAST et al., 2008; NORDSTROM, 2015; RUNNELLS; SHEPHERD; ANGINO, 1992; VERPLANCK et al., 2009). According to Eppinger and 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). The present study is the precursor in pointing out the need for such a future analysis.

Tab. 3.4. 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							
						Boxplot		Median ± 2 MAD		Defined Limits		CONAMA 357 Resolution	MS Portaria 888/21
		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	($\mu S.cm^{-1}$)	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
Total 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
Total 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
Total 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
Total 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
Total Mg	($mg.L^{-1}$)	2.38	2.23	1.4	4.49	0.66	3.89	1.29	3.85	**0.66**	**3.85**	-	-
Total Ca	($mg.L^{-1}$)	5.9	5.54	2.94	10.7	1.16	10.39	2.97	10.35	**1.16**	**10.35**	-	-
Total K	($mg.L^{-1}$)	0.97	0.87	0.38	2.41	0.04	1.83	0.45	1.69	**0.04**	**1.69**	-	-
Total 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
Total 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
Total 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
Total 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
Total 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
Total 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

* Dissolved fraction

3.4 Conclusions

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, for iron and aluminum, it should be considered that the CONAMA resolution establishes reference values for the dissolved fraction of these elements, while this work indicates values for the total fraction. In addition, 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.

CHAPTER 4

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

This chapter presents a research study that was submitted to the Geochimica Brasiliensis Journal in June 2023: CARDOSO, A. T.; FAN, F. M. Mining's legacy: Unraveling the impacts of acid mine drainage on the rivers and streams of the Santa Catarina coal region, Brazil.

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 basin, 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 E_H, 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 basin.

Keywords: Acid Mine Drainage, Santa Catarina carboniferous basin, surface water resources contamination.

4.1 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 basin; 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.

4.2 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. 4.1). 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 4.1.

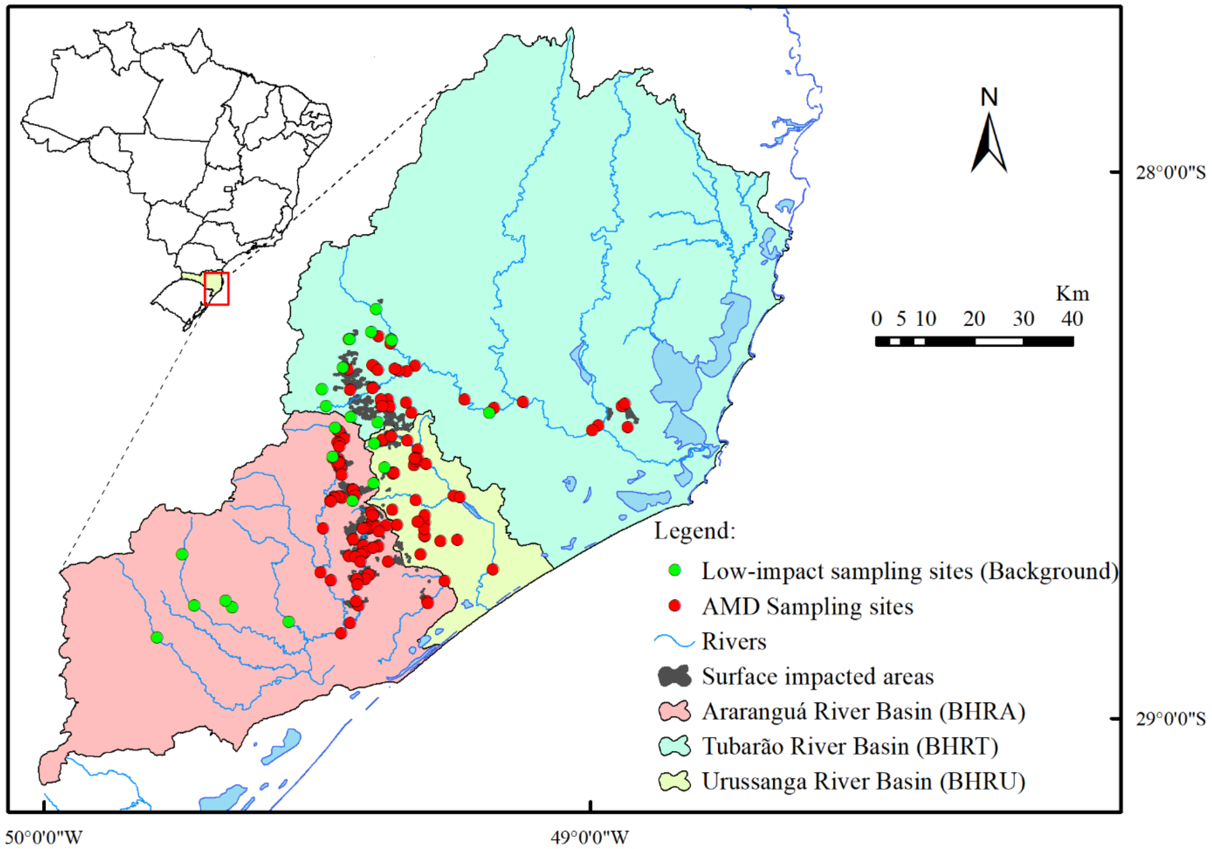

Fig. 4.1. Study area and sampling sites locations.

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).

4.2.1 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 1,241.3 km of streams are still affected by AMD in three watersheds: Araranguá, Tubarão, and Urussanga (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 (Reaction 4.1), 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+}), Reaction 4.2, and this to ferric hydroxide ($Fe(OH)_3$), Reaction 4.3 (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.

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (4.1)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \quad (4.2)$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \quad (4.3)$$

In very acidic pH values (close to or below 2.3), hydrolysis (Reaction 4.3) practically does not occur. This causes an increase in the concentration of Fe^{3+} in the environment, which oxidizes the pyrite, according to Reaction (4.4) (DE MELLO; DUARTE; LADEIRA, 2014).

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad (4.4)$$

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).

4.3 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 AM

4.3.1 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. Most of samples are result of a continuous monitoring project, thus, the 652 samples are divided in 162 sampled sites. (Fig. 4.1). In contrast to the study conducted by Cardoso et al. (2022) (Chapter 3), the present research exclusively employed the samples collected from the sedimentary geology region. 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 4.1 presents the parameters and their corresponding units, as well as the analysis site, quantification limits, and analysis method used for each parameter.

Tab. 4.1. 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)	$\mu S.cm^{-1}$	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*
Total Sodium (Na)	(mg.L^{-1})	Laboratory	0.07	ICP OES*
Total Magnesium (Mg)	(mg.L^{-1})	Laboratory	0.01	ICP OES*
Total Calcium (Ca)	(mg.L^{-1})	Laboratory	0.025	ICP OES*
Total Potassium (K)	(mg.L^{-1})	Laboratory	0.07	ICP OES*
Total Copper (Cu)	(mg.L^{-1})	Laboratory	0.002	ICP OES*
Total Cadmium (Cd)	(mg.L^{-1})	Laboratory	0.002	ICP OES*
Total Lead (Pb)	(mg.L^{-1})	Laboratory	0.005	ICP OES*
Total Zinc (Zn)	(mg.L^{-1})	Laboratory	0.005	ICP OES*
Total Arsenic (As)	(mg.L^{-1})	Laboratory	0.002	HVG ICP OES**
Total Mercury (Hg)	(mg.L^{-1})	Laboratory	0.0003	ICP OES*

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

4.3.2 Classification of sampling sites affected by AMD

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. 4.1).

4.3.3 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.

4.4 Results and discussion

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

4.4.1 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 4.2 presents the statistical summary of the physicochemical variables, while Figure 4.2 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.

Tab. 4.2. Statistical summary with parameter results for mining-affected samples.

Vars	**mean**	**SD***	**median**	**min**	**max**	**CV** (%)**	**Geochemical Background*****	**CONAMA 357**	**MS 888/21**
pH	4.4	1.5	3.8	2.0	8.1	34.6	5.4 - 8.1	6 - 9	6 - 9.5
E_H	0.50	0.20	0.59	0.07	0.78	40.3	0.01 - 0.53	-	-
DO	6.5	2.4	6.9	0.0	13.9	37.4	-	5.0	-
EC	823	724	593	56	4287	87.9	153.7	-	-
Acid	203.1	351.9	73.6	<0.5	3022.0	173.3	13.6	-	-
SO_4^{2-}	346.3	504.4	174.5	<0.5	3678.1	145.6	29.4	250	250
Fe	30.90	82.43	6.14	<0.01	840.20	266.9	1.01	0.3	0.3
Mn	2.17	3.94	0.93	<0.002	37.90	181.4	0.06	0.1	0.1
Al	15.20	31.86	3.84	<0.01	316.00	209.7	0.01	0.1	0.2
Na	17.62	24.78	11.90	2.43	268.00	140.6	6.99	-	200
Mg	11.31	12.59	8.04	1.42	105.00	111.3	3.85	-	-
Ca	42.73	52.05	26.40	1.41	370.00	121.8	10.35	-	-
K	4.48	3.22	3.52	<0.07	23.20	72.0	1.69	-	-
Cu	0.014	0.083	<0.002	<0.002	1.180	585.9	<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	199.0	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; **Coefficient of Variation; *** Cardoso et al. (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. 4.2). 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 environment 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 4.2.

Electrical Conductivity is typically high in AMD waters due to the elevated concentration of dissolved metals and minerals. The average EC was 823 µS/cm² with an SD of 724 µS/cm². 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.

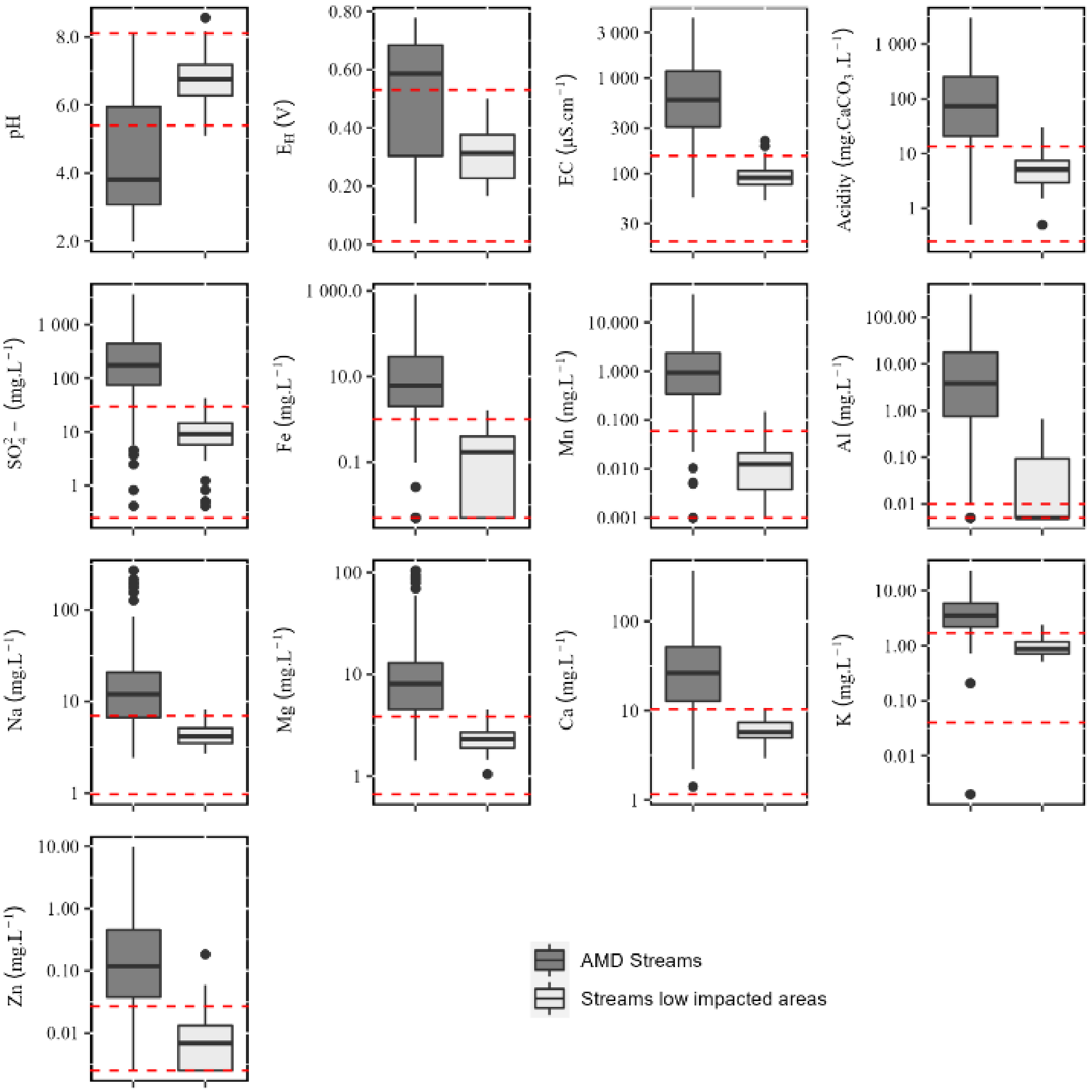

Fig. 4.2. Comparative boxplots presenting the distribution between groups samples from AMD Streams and Streams from low impacted areas. Dashed red lines indicate the limit values of the geochemical background of the region.

According to Bartos & 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). However, most of the samples collected in the Santa Catarina coal basin 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).

4.4.2 Correlations

To further understand the relationships between the various physicochemical parameters in the Santa Catarina coal basin, we conducted a Spearman correlation analysis. The results of this analysis are presented in the correlation matrix below (Table 4.3). In Table 4.3, results from Spearman's nonparametric correlation are presented in the lower triangle, while the correlation's significance levels (p-values) are in the upper triangle. Values of Spearman's correlation that are above 0.5 or below -0.5 are highlighted to indicate relatively strong and reliable monotonic relationships.

Several strong and significant correlations can be observed between the physicochemical parameters (Table 4.3). 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.

Tab. 4.3. Spearman's nonparametric correlation matrix (lower triangle) and p-values (upper triangle). 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	Zn
pH		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.01	0.00
E_H	**-0.88**		0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00	0.00	0.00
DO	0.19	-0.06		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.43	0.00
EC	**-0.7**	**0.62**	-0.23		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.24	0.00
Acid	**-0.85**	**0.77**	-0.3	**0.85**		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
SO_4^{2-}	**-0.68**	**0.6**	-0.21	**0.94**	**0.85**		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.00
Fe	**-0.68**	**0.55**	-0.3	**0.81**	**0.85**	**0.8**		0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00
Mn	**-0.79**	**0.72**	-0.22	**0.87**	**0.87**	**0.89**	**0.79**		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	**-0.85**	**0.78**	-0.2	**0.82**	**0.93**	**0.83**	**0.83**	**0.86**		0.00	0.00	0.00	0.00	0.09	0.00
Na	-0.1	-0.05	-0.4	**0.54**	0.3	0.48	0.42	0.32	0.22		0.00	0.00	0.00	0.02	0.00
Mg	**-0.62**	**0.54**	-0.22	**0.9**	**0.76**	**0.9**	**0.74**	**0.89**	**0.74**	**0.53**		0.00	0.00	0.07	0.00
Ca	**-0.55**	0.45	-0.17	**0.9**	**0.71**	**0.91**	**0.73**	**0.83**	**0.71**	**0.59**	**0.94**		0.00	0.39	0.00
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**		0.23	0.00
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		0.04
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	0.1	

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.

4.5 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 basin. 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 physicochemical 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 (DO) 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 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 deeper understanding of the extent and severity of AMD in the Santa Catarina coal basin.

CHAPTER 5

A decade-long journey shed light on chemical composition and field determination of acid mine drainage in Santa Catarina, southern Brazil

This chapter presents a research study that was submitted to the Environmental Monitoring and Assessment Journal in February 2023. Following the peer review process, the paper was revised and resubmitted to the journal in May 2023: CARDOSO, A. T.; FAN, F. M. VIERO, A. P. A decade-long journey shed light on chemical composition and field determination of acid mine drainage in Brazil

Abstract - Regular monitoring of Acid Mine Drainage (AMD) is essential for understanding its extent and impact on water resources. Traditional manual sampling methods have limitations, such as limited representativeness and delayed lab analysis. High-frequency monitoring offers an alternative, enabling real-time analysis of AMD fluctuations and determination of constituents in the field. This study assessed a decade-long environmental monitoring database from watersheds impacted by coal mining in Brazil to analyze the relationships between physical properties and constituents from different water sources affected by AMD. Samples were grouped into four categories based on location and contamination levels. Results revealed that water samples from the two groups not affected by AMD exhibited near-neutral pH, low metal and sulfate concentrations, and a large portion of samples below the quantification limit for Mn and Al. In contrast, samples from groups affected by AMD displayed high metal and sulfate concentrations and acidic pH, with the highest contamination observed in the underground mine discharges group (AMD UMD). Spearman correlation analyses between field (pH and electrical conductivity (EC)) and lab (SO_4^{2-}, Fe, Mn, and Al) parameters showed no significant correlations in non-AMD-affected groups, but significant correlations in AMD-affected groups, particularly the Streams group. A regression model between sulfate and EC was identified as the best predictor for AMD, enabling continuous, low-cost monitoring of contaminated streams and providing insight into previously unobserved AMD processes, such as variations in contamination during storm events and river flushing.

Keywords: Pyrite oxidation, Water resources monitoring and assessment, Southern Brazil.

5.1 Introduction

Acid mine drainage (AMD) is a major environmental problem, responsible for the contamination of surface and groundwaters, and affecting aquatic life and posing a risk to human health. It is the result of sulfide oxidation in the presence of water and oxygen. AMD is characterized by low pH, elevated concentrations of sulfate and iron, and, depending on the host rock geology, high concentrations of a wide variety of metals. (FYTAS; HADJIGEORGIOU, 1995; GRAY, 1996; BLOWES et al., 2003; DOULATI ARDEJANI, 2011; GALVÁN, et al., 2012; AKCIL; KOLDAS, 2006; SRACEK et al., 2010; CAMPANER et al., 2014).

Coal mining produces a large volume of waste, and in strip mines, overburden material. Waste and overburden material, the latter with lower potential, in contact with water and atmospheric oxygen are AMD generators from the oxidation of pyrite, which occurs in two stages. The first stage is associated with the exposure of pyrite to oxygen in an aqueous environment, and the second involves ferric iron (Fe^{3+}) dissolved in water, even in the absence of O_2, according to Reactions 5.1, 5.2, 5.3, and 5.4.

$$FeS_{2(s)} + \frac{7}{2} O_{2(g)} + H_2O_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2\ SO^{2-}_{4\,(aq)} + 2\ H^{+}_{(aq)} \tag{5.1}$$

$$Fe^{2+}_{(aq)} + \frac{1}{4}\ O_{2(g)} + H^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + \frac{1}{2}\ H_2O_{(aq)} \tag{5.2}$$

$$Fe^{3+}_{(aq)} + 3\ H_2O_{(aq)} \rightarrow Fe(OH)_{3(s)} + 3\ H^{+}_{(aq)} \tag{5.3}$$

$$FeS_{2(s)} + 14\ Fe^{3+}_{(aq)} + 8\ H_2O_{(aq)} \rightarrow 15\ Fe^{2+}_{(aq)} + 2\ SO^{2-}_{4(aq)} + 16\ H^{+}_{(aq)} \tag{5.4}$$

Reactions 5.1 and 5.2 occur on the surface, mainly in coal beneficiation waste. They also occur on the subsurface during underground mining while the galleries are dry. Reactions 5.3 and 5.4, on the other hand, produce AMD in all mining environments, including decommissioned and flooded underground mines where oxygen is not present.

Regular monitoring of AMD is essential to assess its magnitude and impact on affected water resources. According to Acharya and Kharel (2020), regular monitoring of AMD and water quality is crucial to determine emerging problems, reclaim degraded mining sites, and choose and adjust treatment designs.

Typically, fixed-frequency manual sampling is used for AMD monitoring, with some parameters measured in the field and others collected for subsequent analysis in laboratories. However, despite being fundamental, this approach can have some disadvantages, as such samples are not necessarily representative of the full time period, and the delay related to lab analysis does not allow immediate identification of AMD constituent concentrations (RYBERG, 2003). One solution to this problem is the implementation of high-frequency monitoring, which offers a viable alternative that can better follow seasonal and event fluctuations, helping to understand AMD processes, and making it easier to determine AMD constituents in the field (FYTAS; HADJIGEORGIOU, 1995).

The field determination and high-frequency monitoring of water resources affected by AMD can be useful in situations such as i) rapid compliance tests; ii) during extreme events, to facilitate a faster response time and expedite remedial action; iii) to estimate loads of transported contaminants; iv) to better design monitoring programs and rationalize sampling (GRAY, 1996; GALVÁN et al., 2012; SMITH et al., 2022).

The application of high-frequency monitoring and field determination in future studies could be grounded on the establishment of relationships between constituents of manually collected water-quality samples and physical properties of water that serve as surrogates for constituents of interest. These relationships, which this study investigates, might be essential for developing efficient high-frequency monitoring strategies. As these physical parameters can be measured more easily and cost-effectively in the field using simple quality analysis probes, they are ideal for high-frequency monitoring. An example of such a parameter is electrical conductivity (EC). EC can be measured easily and cost-effectively in the field because it requires relatively simple and portable equipment. The measurement of EC is a direct method that does not require any chemical reagents, making it both time-efficient and environmentally friendly. Furthermore, the data from EC measurements can be obtained and processed immediately.

In general, some prior research carried out in waters affected by AMD found relationships between the concentration of dissolved metals and sulfates and electrical conductivity. Gray (1996) studied AMD waters in the Avoca mines, Ireland, exploring alternative parameters to identify a rapid field assessment of AMD. Through regression analysis, the author found a significant predictive capacity between electrical conductivity and sulfate in raw AMD (R^2: 0.966) and AMD-affected surface waters (R^2: 0.993). To estimate daily constituent loads in the Red River (North Dakota), Ryberg (2003) also used regression analysis from a two-year dataset. Among the physical properties monitored by the author, electrical conductivity was found to be a significant explanatory variable for alkalinity, chloride, dissolved solids, and sulfate. On the other hand, pH was not a statistically significant explanatory variable for any of the study constituents. The purpose of Galván et al. (2012), as well as Ryberg (2003), was to estimate constituent (metal) loads by using the relationships between these dissolved elements and specific conductivity measured in the field. The authors found relatively high correlations between conductivity and the concentration of dissolved metals ($R^2 > 0.90$). Additionally, Smith et al. (2022) used regression equations to understand the chemical composition of acid mine drainage to improve AMD water treatment processes. The authors concluded that electrical conductivity could be a useful surrogate for predicting total acidity, dissolved iron, and sulfur concentrations in AMD-affected waters.

As shown by the existing literature, variables that can be monitored using physical-chemical parameter probes can help to better understand AMD contamination in water resources. These variables are also useful for developing high-frequency monitoring strategies through the use of correlation curves (GRAY, 1996; KIMBALL et al., 2002; RYBERG, 2003; GALVÁN et al., 2012; SMITH et al, 2022). These results are essentially connected to local data and environmental circumstances. However, the available number of studies is limited and does not provide information from all places known globally for the impact of coal mining. Some studies used relatively short time series, and not all processes that allow for good or poor correlations are well explained in the research findings.

This work has the following objectives: 1) to analyze physical properties and water quality constituents from different water sources affected by AMD in a large mass of data (> 10 years) from the Santa Catarina coal mining area in Brazil, South America; 2) to evaluate and understand the behavior of these water resources affected by AMD; and 3) to propose relationships for estimating AMD constituents, which can be used for real-time field analysis and high-frequency monitoring. By addressing these objectives, we aim to contribute to a better understanding of AMD impacts and monitoring strategies in the context of the Santa Catarina coal mining area, providing insights that may be applicable to other locations affected by AMD.

5.2 Methodology

5.2.1 Case study

The study area is located in the southern region of the State of Santa Catarina, Brazil (Fig.5.1). The region impacted by AMD encompasses three watersheds Araranguá River (3,025 km²), Tubarão River (5,960 km²), and Urussanga River (709 km²).

According to the Köppen classification, the climate of the area is characterized as a humid subtropical climate (Cfa). The average annual temperature ranges from 16 to 20 °C, with an increase from December to February. The local average annual rainfall varies between 350 mm and 500 mm per season (Gotardo et al.,2018). These values are representative of the state southern region, where the study area is located. The rainfall amounts tend to increase towards the northwest due to the mountains presence, and decrease towards the east and southeast due to the coast influence. The low seasonal variation in rainfall does not significantly interfere with the water regimes, which helps maintain relatively stable conditions throughout the year.

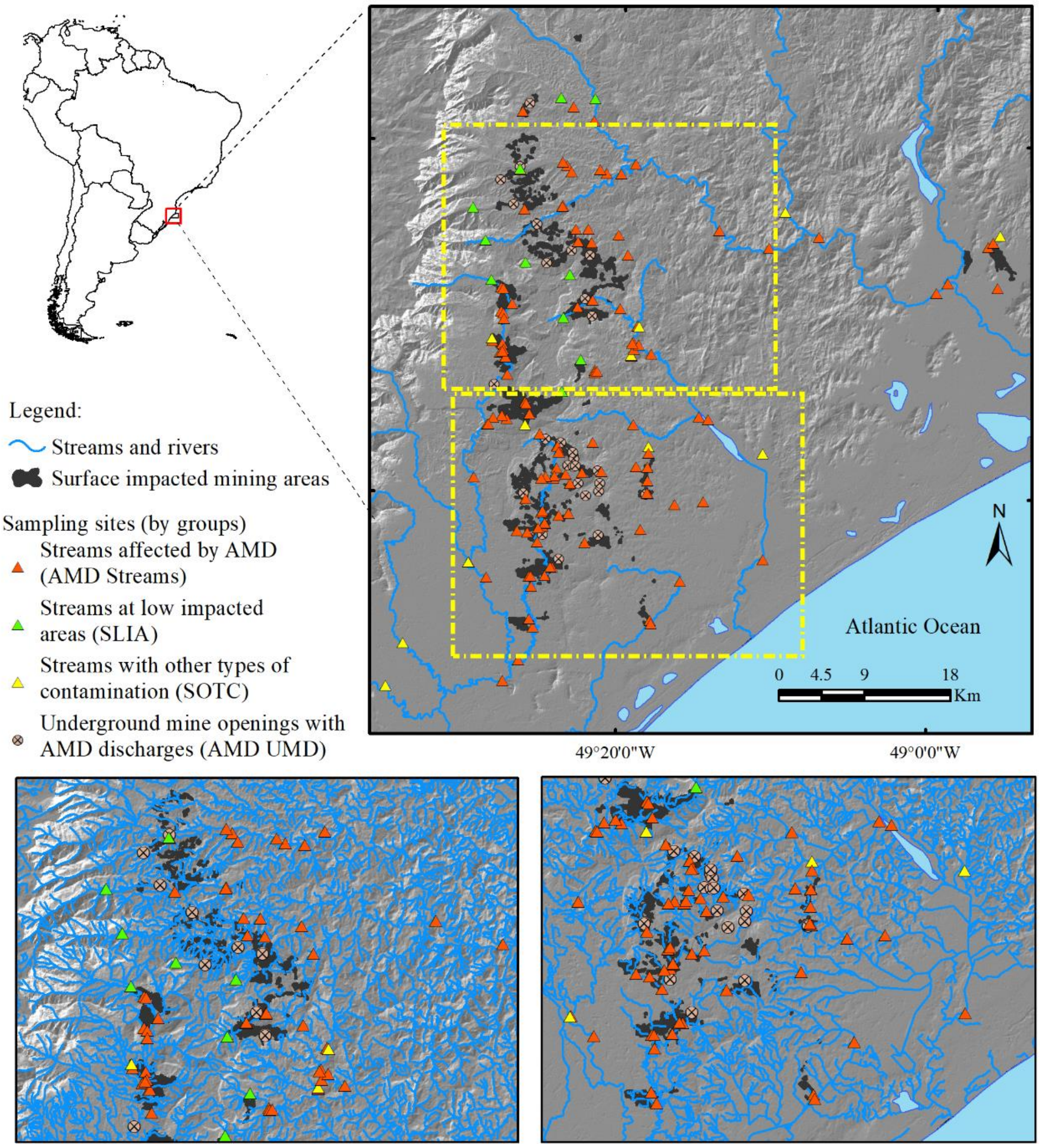

Fig. 5.1. Study area location and sampling sites. The dashed yellow rectangles indicate two areas of special interest, enlarged for better visualization in the subsequent figures. The upper rectangle corresponds to the figure shown below and to the left, while the lower rectangle corresponds to the figure below and to the right.

Sedimentary rocks of the Paraná Basin can be found at the basement's western and southern edges, as well as predominantly in the central-east portion (Fig. 5.1). These rocks consist of continental deposits and shallow shelf formations that were established during the Paleozoic-Mesozoic period (MILANI et al., 2007). The exposed rock formations in the study area belong to the Gondwana I Supersequence, which is predominantly Paleozoic and contains

South Santa Catarina's coal deposits. Additionally, there are arenite exposures from the Botucatu Formation and magmatites from the Serra Geral Formation, consisting mainly of basic volcanics located at the highest elevations of the terrain, at the northwest (CARDOSO et al., 2022).

To the south and southeast (Fig. 5.1) lies the Coastal Plain, which is characterized by Cenozoic sedimentation that developed during the Quaternary. This region encompasses various sedimentary deposits, including continental (alluvial fans), transitional (fluvial-lagoon and coastal, associated with the evolution of two sandy barriers—one Pleistocene and the other Holocene), and marine (fluvio-deltaic-marine) types (CARDOSO et al., 2022).

Depending on the depth of the coal layer, mining in the region was carried out using two main techniques: strip or underground. Strip mining was conducted when the ore layer was at depths of up to 30 meters, while underground mining, which adopted the room and pillar method, was used when the ore was deeper than 30 meters. Given that numerous mining companies in the region went bankrupt, detailed records of the extraction process, along with technical documents specifying the precise locations of the mines, as well as the volume and location of the extracted materials, have been lost.

The inadequate environmental practices of the time are responsible for the environmental impacts that still persist in the region. Strip mining occurred without proper environmental reclamation of the areas, resulting in extensive surface areas of waste rock with infertile and contaminated soils (Fig. 5.1). In underground mining, many mine entrances, after flooding, began to release acidic water to the surface. Until the mid-1980s, waste from the beneficiation process was deposited near rivers, affecting water and soil quality. Furthermore, waste materials were used as the base for roads, exacerbating environmental damage.

This region is extensively studied due to its environmental sensitivity within the country. This sensitivity stems from historical neglect and lack of supervision, which led to severe environmental impacts. Consequently, the Federal government designated the coal region of Santa Catarina as a critical pollution zone in 1980. Scientific studies in this area are diverse and comprehensive. They include analysis of the effectiveness of environmental reclamation methods (Cardoso and Fan, 2021) and tailings desulfurization methods (do Amaral Filho et al., 2017). Researchers have also examined water resource toxicity (Lattuada et al., 2009) and the concentrations of major and trace elements in coal mine drainage (Silva et al., 2011). Other important work involves modeling of contamination sources (Gomes et al., 2011) and the background of water resources (Simão et al., 2019; Cardoso et al., 2022). More specialized studies have explored the adsorption of heavy metals from coal AMD (Núñez-Gómez et al.,

2019) and the mineralogical characterization of sediments in streams impacted by AMD (Silva et al., 2013).

5.2.2 Water sample collection, categorization, and lab analysis

This study involved collecting, categorizing, compiling, systematizing, and analyzing data from ten years of fieldwork (2011-2020) conducted by the Geological Survey of Brazil (SGB/CPRM) for a monitoring project in the coal mining region of Santa Catarina state, southern Brazil. During this period, 3,234 water samples were analyzed, consisting of 2,676 samples from surface waters and 558 samples from underground mine openings with AMD discharges. Since monitoring activities were performed every six months, the total number of samples is spread across 180 sampling sites (Fig. 5.1). All sampling points are georeferenced, ensuring that sampling can be precisely repeated at the same location.

For analysis purposes, the samples were grouped by their location and contamination perspective into four categories: i) located in streams in low-impact areas (SLIA); ii) located in streams affected by other types of contamination besides AMD (SOTC); iii) located in streams affected by AMD (AMD Streams); and iv) from underground mine openings with AMD discharges (AMD UMD). The samples were grouped using GIS software based on impacted/explored area polygons, abandoned mine opening data, and the Geological Survey of Brazil's regional knowledge (local existing surveys and studies). Mine opening samples (AMD UMD) were considered contaminated due to their connection to abandoned underground mines. River samples upstream of contamination sources were considered SLIA, while downstream samples were considered affected (AMD Streams). Many uncontaminated samples were found downstream of urban centers and agricultural areas, potentially affecting quality parameters; these samples were classified as SOTC.

Physical properties of water (field parameters), pH, and electrical conductivity (EC) were measured on-site using an AP-800 Aquaread probe (AQUAREAD, 2017). pH was measured with a glass electrode sensor sensitive to hydrogen ion activity, having a resolution of 0.01 pH and an accuracy of ± 0.1 pH. EC was determined by a four-electrode cell, with a resolution of 0 - 9999 μS/cm and an accuracy of ± 1% of reading or ± 1μS/cm if greater, with conductivity calculations referencing a temperature of 25°C.

At each site, samples were collected manually using pre-cleaned high-density polyethylene bottles. Prior to sampling, the bottles were rinsed with the stream water to minimize any potential contamination. The bottles were then inserted directly into the streams, always attempting to collect samples near the area with the highest flow, just below the water surface, and aligned with the flow direction, ensuring a representative sample of the water body. Two bottles of samples were collected at each site: one for physico-chemical analysis and the other for metals analysis, preserved with 2% HCl. The collected samples were sent to the SGB/CPRM laboratory, where they were filtered with a Millipore® filter, 0.45 μm pore size. The sulfate parameter (SO_4^{2-}) was analyzed by gravimetric analysis, and Fe, Mn, and Al were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Quantification limits of the analytical methods were 0.5 for SO_4^2- (mg.L^{-1}), 0.01 for Fe (mg.L^{-1}) and Al (mg.L^{-1}), and 0.002 for Mn (mg.L^{-1}). Analytical methods were defined by the Standard Methods for the Examination of Water and Wastewater (EATON et al., 1998). Details of the analytical procedure are provided in the supplementary material.

To ensure the consistency of laboratory data, technical QA/QC procedures were carried out in accordance with the Brazilian Geological Survey standards. These procedures included duplicate analyses, comparisons with data from similar areas, trend analysis, frequency distribution analysis, and regression analysis (CARDOSO; FAN, 2021).

5.2.3 Data compilation and analysis

The database analysis aimed to determine the distribution and relevance of certain AMD parameters in the study area, as well as to understand and justify their correlations and the possibility of predicting AMD contamination from field analyses.

Based on the knowledge generated by previous studies conducted on the water resources of the impacted area (SILVA et al., 2011; SIMÃO et al., 2019; CARDOSO; FAN, 2021), this study chose to analyze only the most relevant constituents of AMD in the region (SO_4^{2-}, Fe, Mn, and Al).

Analysis of parameters distributions was carried out through descriptive statistics and boxplot graphics (TUKEY, 1977). To evaluate the correlation of the parameters it was used Spearman’s nonparametric correlation matrix (GLASSER and WINTER, 1961). Spearman's correlation evaluates the relationship between two continuous variables, capturing not only linear relationships but also monotonic functions.

For the data analysis we utilized the R software (R CORE TEAM, 2022), a free software environment that offers tools for statistical computing and graphics.

Values below the quantification limits were replaced by half the limit's value, following the practice proposed in previous studies (KEITH et al., 1983).

Parameters EC, sulfate, Fe, Mn, and Al did not display a Gaussian distribution; therefore, a logarithmic transformation was used for these data in the regression analysis.

The following results were obtained from the statistical analysis and graphical representation of data:

Chemical composition – Distribution and relevance of main AMD parameters

I. Descriptive statistics: Key statistical values that describe all the parameters of the monitored groups;
II. Boxplot: Distribution and representativeness of chemical and physicochemical parameters in AMD contamination.

Field determination – Correlation and regression analysis

III. Spearman correlations: The strength of relationships between field and lab parameters;
IV. Regression analysis graph and statistical summary: Results of regression adjustments between predictors and predicted variables for all the groups.

From the statistics, we determined the distribution and relevance of field (pH and EC) and lab (SO_4^{2-}, Fe, Mn, and Al) parameters. Correlation analysis was used to determine the relationship between the parameters, and regression statistical models demonstrated the possibility of using field parameters in a cost-effective and high-frequency manner to predict AMD.

5.3 Results and discussion

5.3.1 Chemical composition – Distribution and relevance of main AMD parameters

Descriptive statistics (n, mean, standard deviation, coefficient of variation and median) of the four groups for the fields (pH, EC) and lab (SO_4^{2-}, Fe, Mn and Al) parameters, as well as the background limits of surface water, are presented in Table 5.1.

As shown in Table 5.1, the standard deviation values in many cases closely approximate the mean and median. This variability is also reflected in the results of the coefficient of variation. This observation is significant for the research, as understanding this variability may help in interpreting the data and be beneficial for developing correlations. The high variability in the data presented in Table 5.1 can be attributed to several factors. Firstly, the study adheres to the established monitoring protocol for water resources in the coal mining-impacted watersheds in Santa Catarina (Brazil). This protocol seeks to encompass the broad spectrum of water quality conditions across the region by distributing sampling sites throughout the entire affected area, including sites upstream of contaminated zones, downstream, and near the watershed's outlet. Secondly, the samples, derived from natural environments, are inherently subject to influences from a variety of factors, such as geological, geochemical, biological, and anthropogenic interactions, which result in considerable variability in the data (STUMM; MORGAN, 1996). Lastly, the decision was made to incorporate the entire available database without excluding any outliers, thereby preventing the potential omission of genuine values and leading to data points spanning a wide range. Taken together, these factors account for the high variability observed in Table 5.1, which reflects the heterogeneous and dynamic nature of water quality conditions in the affected watersheds.

Tab. 5.1. Summary of descriptive statistics for the groups including number of observations (n), mean, standard deviation (s), coefficient of variation (CV) and median along with the regional background values of each parameter defined by Cardoso et al. (2022).

		AMD Unaffected		AMD Affected		Background limits (Cardoso et al., 2022)	
		SLIA*	SOTC**	AMD Streams ***	AMD UMD****		
	n	230	163	2283	558	Lower	Upper
pH	mean	6.4	6.2	4.4	4.1	5.4	8.1
	s	0.8	0.8	1.4	1.2		
	CV (%)	12.5	12.9	31.8	29.3		
	Median	6.3	6.2	4.0	3.8		
EC (µS.cm^{-1})	mean	72	99	733	1125	19.5	153.7
	s	34	76	704	880		
	CV (%)	47.2	76.8	96.0	78.2		
	median	61	75	513	879		
SO_4^{2-} (mg.L^{-1})	mean	9.6	13.8	403.1	659.6	<0.5	29.4
	s	9.0	12.3	603.1	715.1		
	CV (%)	93.8	89.1	149.6	108.4		
	median	7.4	11.5	184.3	458.4		
Fe (mg.L^{-1})	mean	0.30	1.11	40.50	62.03	<0.01	1.01
	s	0.68	1.22	99.99	136.90		
	CV (%)	226.7	109.9	246.9	220.7		
	median	0.18	0.92	7.73	25.43		
Mn (mg.L^{-1})	mean	0.021	0.093	2.683	4.247	<0.002	0.060
	s	0.055	0.127	5.004	10.318		
	CV (%)	261.9	136.6	186.6	242.9		
	median	0.009	0.061	1.210	2.180		
Al (mg.L^{-1})	mean	0.07	0.21	18.29	24.57	<0.01	0.01
	s	0.23	0.34	39.29	55.26		
	CV (%)	328.6	161.9	214.8	224.9		
	median	0.01	0.10	4.81	9.08		

*Streams at low impacted areas; **Streams affected by others types of contamination than AMD; ***Streams affected by AMD; ****Underground mine openings with AMD discharges.

The two groups unaffected by AMD presented similar values for the evaluated parameters, with pH near neutral and low metal concentrations. Compared to background values, the SLIA group had only the mean Al value exceeding the upper limit. On the other hand, the SOTC group had three parameters with means exceeding the limits: Fe, Mn, and Al, and for the latter two, the medians were also above background limits. Higher values for these parameters may be related to other types of contamination, such as agriculture and industries.

In the groups affected by AMD, all parameters (mean and median) widely exceeded the background limits. The mean values of Al were particularly notable, being 1,828 and 2,456 times greater than the established values for AMD Streams and AMD UMD, respectively. Compared to the AMD streams, the group of samples from underground mine discharges exhibited more concerning mean and median values, with higher levels of EC, SO42-, Fe, Mn, and Al, and lower pH levels. Part of this result can be explained by the fact that samples from the AMD Streams were collected throughout the watershed, with some sampling points located right after contamination spots and others farther away, where the stream had already received contributions from non-affected rivers. In contrast, sampling points for the underground mine group were always just after the discharge reached the surface, and thus were not affected by dilution.

The impact on water quality observed in groups affected by AMD results from the oxidation of pyrite (FeS_2), which is abundant in Brazilian coals (KALKREUTH et al., 2006; SILVA et al., 2009). Concentration of metals in AMD will depend on two factors: i) the type of gangue minerals present in the host rock, and ii) the type and amount of sulfide mineral oxidized (AKCIL; KOLDAS, 2006). The acidic pH of AMD promotes the dissolution of minerals, predominantly carbonates, and encourages the desorption of metals from insoluble minerals. This, in turn, increases the salinity and electrical conductivity of the contaminated water.

After the descriptive statistics, boxplot graphics were carried out to verify if the lab parameters are significantly different between the groups (Fig. 5.2). To aid visualization the values were log transformed. Comparison of group means were performed by t-student test, the results are presented in the supplementary material.

Even after log transformation, samples from streams at low impacted areas presented an asymmetrical distribution (right-skewed) for Mn and Al. This behavior is justified because a considerable portion of the data is equal to or below the method's quantification limit, with 26% for Mn and 60% for Al (Figure 5.2).

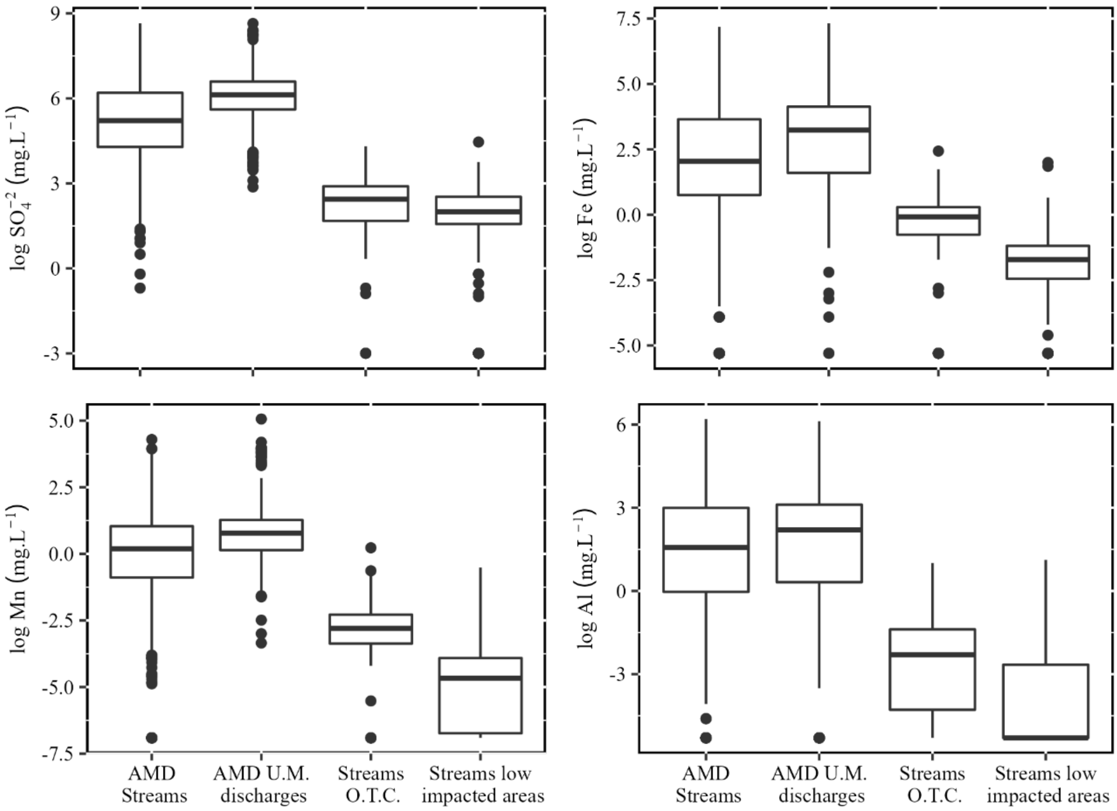

Fig. 5.2 Visualization of data groups distribution (box-plot) of SO_4^{2-}, Fe, Mn and Al

As showed in Figure 5.2 and corroborated by the t-test (Supplementary material), the groups are significantly different, except for the aluminum between the groups AMD streams and AMD Underground Mine discharges (t-student: 0.73). Visually, it is possible to notice that there are great differences between the groups affected by AMD and the groups not affected (Fig. 5.2). The differences in the distributions of these parameters between the AMD-affected and non-affected groups justify their use as reference variables for AMD characterization.

5.3.2 Field determination – Correlation and regression analysis

The difference in concentrations between the databases, identified through exploratory analysis, indicates that the studied parameters reflect the contamination of water resources caused by AMD. However, regular laboratory analysis to gain a better understanding of AMD-related contamination processes is both costly and labor-intensive. As pH and EC continuous monitoring has been successfully employed (FYTAS KHADJIGEORGIOU, 1995), it is necessary to verify the existence of significant correlations between these parameters and the parameters to be predicted.

Correlations between the field and lab variables non-log transformed were performed through Spearman's correlation (Table 5.2). Correlation coefficients with absolute values below -0.5 or above 0.5, which are indicated in bold in Table 5.2, also exhibit significant p-values, as presented in the supplementary material.

Tab. 5.2. Values of Spearman correlation between field and lab variables (r values below -0.5 or above 0.5 are bold)

	Correlation between pH and				
	EC	SO_4^{2-}	Fe	Mn	Al
AMD Streams	**-0,74**	**-0,73**	**-0,66**	**-0,77**	**-0,82**
AMD UMD	-0,26	-0,17	-0,04	-0,19	**-0,71**
Streams OTC	0,15	-0,02	0,09	-0,01	0,06
Streams low impacted areas	0,42	0,14	-0,23	-0,08	-0,08

	Correlation between EC and				
	pH	SO_4^{2-}	Fe	Mn	Al
AMD Streams	**-0,74**	**0,94**	**0,81**	**0,85**	**0,83**
AMD UMD	-0,26	**0,80**	**0,65**	**0,73**	0,32
Streams OTC	0,15	0,43	-0,05	0,12	-0,17
Streams low impacted areas	0,42	0,24	-0,12	0,11	-0,06

As observed in Table 5.2, in the two groups of samples not contaminated by AMD, there were no significant correlations between pH or EC and the other parameters, as indicated by the Spearman correlation coefficients. The AMD UMD group showed three relevant correlations between EC and SO_4^{2-}, Fe, and Mn, but only one relevant correlation for pH, with Al. pH and EC had a significant correlation for all parameters in the AMD Streams group, between them, the weakest was pH and Fe (r: 0.66) and the strongest was EC and SO_4^{2-} (r: 0.94).

Figure 5.3 presents scatterplots of the unaffected AMD groups, along with regression lines and the corresponding R-squared values, which provide a measure of model accuracy and goodness of fit. These measures were calculated to evaluate the correlations between field and lab parameters. Figure 5.3 show that all lab parameters presented samples under the method's quantification limit. The graphs also exhibit the dispersion of the correlations, which do not present any significant ones, as indicated by their low R-squared values. The parameter ranges for both groups are tighter than those for the AMD-affected groups, and the values are distributed randomly within this range.

It is important to clarify that while the EC generally correlates positively with the total ionic content in waters, the absence of significant correlation between EC and the constituents (SO_4^{2-}, Fe, Mn, and Al) in waters not impacted by AMD in our study does not contradict this well-established relationship. This apparent inconsistency can be explained by the fact that, in the non-AMD affected waters, the EC may be influenced more significantly by ions other than SO_4^{2-}, Fe, Mn, and Al. The presence of these other ions, potentially due to natural geological conditions or other anthropogenic sources, could overshadow the impact of the relatively lower concentrations of SO_4^{2-}, Fe, Mn, and Al on the EC. Consequently, despite changes in the concentrations of SO_4^{2-}, Fe, Mn, and Al, the impact on the overall EC may be relatively minor, leading to a weak correlation in the non-AMD affected waters.

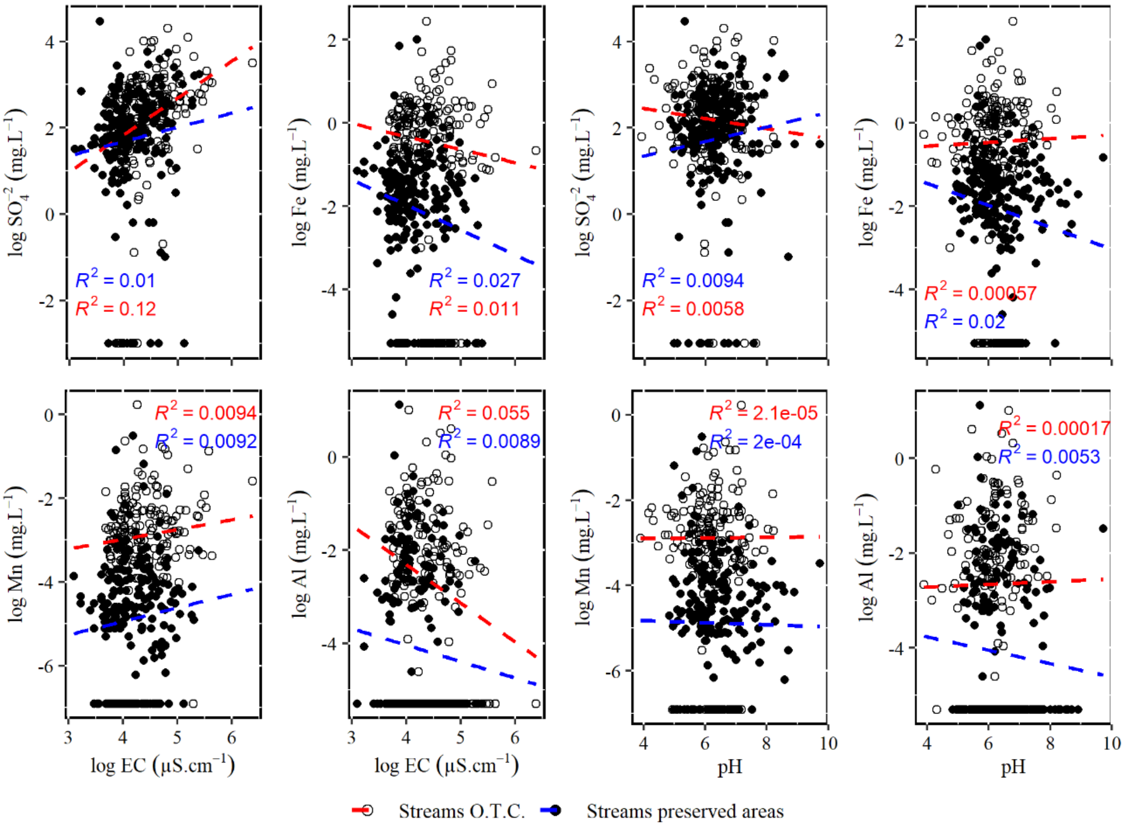

Fig. 5.3. Correlation between EC/pH and SO_4^{2-}, Fe, Mn and Al for two groups of samples: i) Streams with other types of contamination, and ii) Streams in low impacted areas (except for the pH, all parameters are log normalized)

In Figure 5.4, scatterplots of the two groups affected by AMD are shown, along with regression lines and the R-squared values calculated to evaluate the correlations between variables.

As illustrated in Figure 4, the number of samples from the two AMD-affected groups (n: 2841) significantly exceeds that of the two non-impacted groups (n: 393). This is primarily due to the majority of sampling sites being located downstream from contaminated areas (Fig. 5.1). Unlike rivers not impacted by AMD, Figure 4 shows that in both Streams and Underground Mine Discharges affected by AMD, there exists a clear correlation between field and lab parameters. Out of the sixteen correlations presented in Figure 5.4, only seven had R-squared values below 0.5; among these, two were with EC and five with pH. It is also possible to verify the best fit of the correlations with EC due to the smaller dispersion of the points around the regression line.

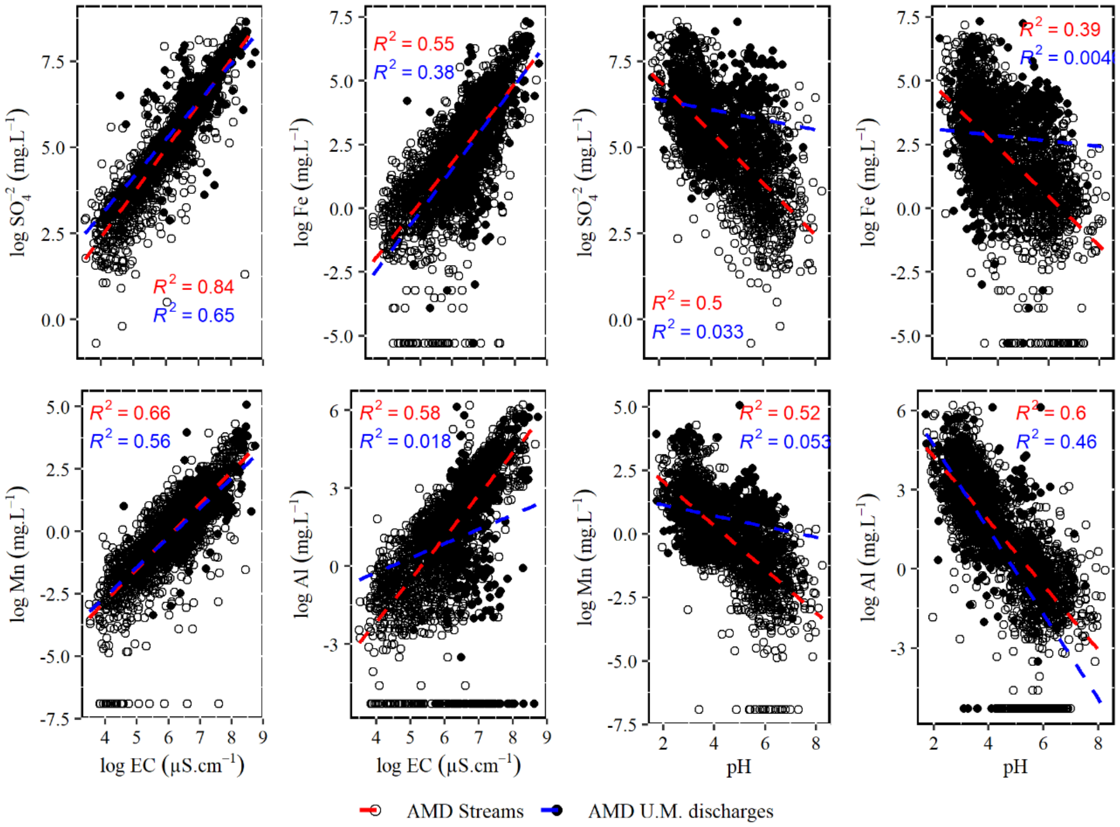

Fig. 5.4. Correlation between EC and pH with SO_4^{2-}, Fe, Mn and Al for two groups of samples impacted by AMD: i) Streams, and ii) Discharges of underground mine (except for the pH, all parameters are normalized)

Table 5.3 display the results of regression analysis between field and lab parameters for the two AMD affected groups. The results indicate that field parameters, primarily EC, can serve as a predictor for AMD. For pH, the highest coefficient of determination was 0.6, in relation to Al for AMD Streams; however, this result lacks the robustness required for usage as a predictive equation. Additionally, as presented in the supplementary material, pH has a bimodal distribution for both groups affected by AMD, which makes it even harder to fit an accurate correlation. Similarly, Cravotta et al. (1999) found a bimodal distribution of pH in AMD from Pennsylvania. According to them, near-neutral pH values result from carbonate buffering and indicate the presence of calcareous minerals; in this case, the acid produced by pyrite oxidation is neutralized. Acidic pH values, on the other hand, result from pyrite oxidation and indicate a deficiency of calcareous minerals and the absence of carbonate buffering.

Although the EC parameter demonstrated stronger correlations with laboratory parameters than pH (as shown in Table 5.3), only the EC/Sulfate relationship for AMD streams displayed a coefficient robust enough for predictive use. This happens because sulfate is directly related to the pyrite oxidation process and has the characteristic to be extremely sensitive to AMD even after dilutions. This sensitivity may be attributed to sulfate's ability to remain in the water, without precipitation, even at lower concentrations, thereby maintaining a consistent correlation with EC. Additionally, according to Gray (1996), the reduction of this anion is unlikely to occur in surface waters, which are predominantly oxidizing environments, further contributing to its sensitivity.

Tab. 5.3. Equations, R-squares and probability values (p-value) of linear regression from the two groups impacted by AMD.

Parameters		AMD Stream			AMD UMD		
Predictor	Predicted	Equation	R²	p-value	Equation	R²	p-value
EC	SO_4^{-2}	$\log(SO_4^{-2}) = -2.74 + 1.28 \log(EC)$	0.84	2.20E-16	$\log(SO_4^{-2}) = -1.33 + 1.09 \log(EC)$	0.65	2.20E-16
	Fe	log(Fe) = -7.55 + 1.56 log(EC)	0.55	2.20E-16	log(Fe) = -8.43 + 1.66 log(EC)	0.38	2.20E-16
	Mn	log(Mn) = -8.01 + 1.30 log(EC)	0.66	2.20E-16	log(Mn) = -7.37 + 1.19 log(EC)	0.56	2.20E-16
	Al	log(Al) = -8.64 + 1.63 log(EC)	0.58	2.20E-16	log(Al) = -2.46 + 0.56 log(EC)	0.02	1.31E-03
pH	SO_4^{-2}	$\log(SO_4^{-2}) = 8.42 - 0.74$ pH	0.50	2.20E-16	$\log(SO_4^{-2}) = 6.68 - 0.15$ pH	0.03	2.25E-05
	Fe	log(Fe) = 6.27 - 0.97 pH	0.39	2.20E-16	log(Fe) = 3.27 - 0.11 pH	0.00	1.12E-01
	Mn	log(Mn) = 3.77 - 0.86 pH	0.52	2.20E-16	log(Mn) = 1.56 - 0.21 pH	0.05	4.04E-05
	Al	log(Al) = 6.71 - 1.22 pH	0.60	2.20E-16	log(Al) = 7.89 - 1.60 pH	0.46	2.20E-16

The weaker correlations between field parameters and metals in the two AMD-affected groups, compared to sulfate, can be attributed to the influence of sorption processes and metal precipitation, which can attenuate their concentrations and result in weaker correlations with field parameters (CAMPANER et al., 2014; RUNKEL et al., 1999; SILVA et al., 2013).

The general equation to predict sulfate concentration in AMD affected surface water of the Santa Catarina coal mining area is:

$$\text{Log } SO_4^{-2}(\text{mg.L}^{-1}) = -2.74 + 1.28 \log \text{EC } (\mu\text{S.cm}^{-1}) \qquad (5.1)$$

Figure 5.5 illustrates the scatterplot of EC/Sulfate correlation for AMD Streams along with the prediction interval of the regression line. On the right side, the residuals plot is displayed. The residuals are demonstrated to be normally distributed and random—characteristics that validate the model. This suggests that the model adequately captures the underlying relationships between the variables and can provide accurate predictions.

The prediction of sulfate concentration (as per Equation 5.1) in water bodies affected by AMD can be improved by taking into account the baseline values for electrical conductivity in the area, as highlighted in the study by Cardoso et al. (2022). As presented in Figure 5.5, the lower portion of the graph displays a higher degree of dispersion, which can be attributed to the increased influence of other elements present in the water on the composition of electrical conductivity when sulfate concentrations are low. Therefore, the accuracy of the equation for predicting AMD in the study area, through the assessment of sulfate concentrations in water resources, can be enhanced when applied to electrical conductivity values that exceed the region's background level of 153.7 µS.cm^{-1} (Cardoso et al., 2022).

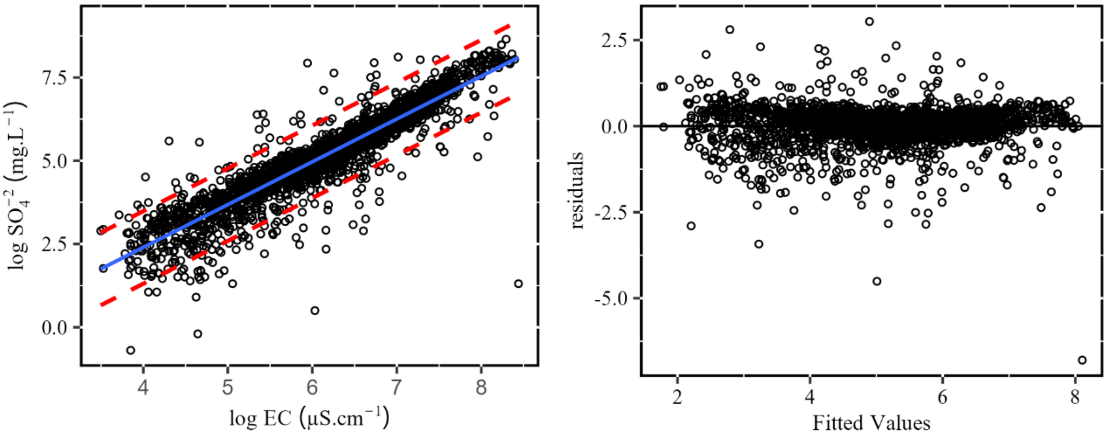

Fig. 5.5. Scatterplot showing the correlation, regression line and prediction interval (95%) between EC and SO_4^{2-} for the group of AMD Streams (left side), along with a residuals plot (right side).

5.4 Conclusions

The examination of a decade-long environmental monitoring database from the Santa Catarina coal mining territory disclosed that certain parameters have a stronger association to AMD contamination, and they could potentially serve as field indicators for this phenomenon.

Exploratory analysis of data revealed that parameters of the two groups not affected by AMD had values close to each other, characterized by low concentrations of metals and sulfate and near neutral pH. Streams in preserved areas even had a large portion of their samples below the method's quantification limit for Mn and Al.

In the two groups affected by AMD, the sample values were similar in terms of magnitude, featuring high concentrations of metals and sulfates, as well as acidic pH values. Of these, the data samples from underground mine discharges (AMD UMD) showed more contamination compared to the AMD Streams. The parameters' responses in the AMD-affected groups occur due to their relation to the pyrite oxidation process.

For the groups AMD Streams and AMD UMD, the Spearman test showed that the field and lab parameters have significant correlations. This correlation indicates that for AMD-affected groups, the field parameters vary in accordance with the corresponding laboratory parameters.

The regression models for the AMD-affected groups demonstrated that EC had the most optimal R-squared values, notably in relation to sulfate. On the other hand, field parameters and metals in the two AMD-affected groups had less robust correlations, which might be a result of sorption processes and metal precipitation, which can lower their concentrations in the water.

Of all the regression models generated, the relationship between EC and sulfate displayed the most favorable conditions for AMD prediction (R^2: 0.84). The relationship between these parameters is justified because, in addition to being a direct byproduct of pyrite oxidation, sulfate remains in the water resource because it is not sensitive to precipitation or reduction processes. Predicting sulfate levels in the region's impacted waters can be improved by considering the regional background of the EC. Given that the model shows more significant dispersion at low EC values, using values that exceed those found in the region's background will yield more accurate results from the proposed model.

The calibration of the model linking sulfate and EC facilitates continuous, cost-effective monitoring of contaminated streams for future studies. This permits the evaluation of previously unobserved AMD processes in these environments, such as variations in contamination levels during storm events and river flushing. This research is pivotal as it elucidates correlations between AMD contamination and field parameters, enabling low-cost, real-time monitoring. The enhanced understanding and prediction models offer immediate value to current research projects. Ultimately, these insights bolster our accuracy in diagnosing the impacts on water resources, therefore helping to mitigate the environmental impacts of mining activities.

CHAPTER 6

Final Chapter

6.1 Conclusion

The main objective of this research was to investigate and comprehend the processes of water resource contamination by Acid Mine Drainage in the coal mining regions of Santa Catarina, Brazil. This has been an attempt to widen the scientific discourse and understanding surrounding this critical environmental issue. This objective was approached through a series of interconnected studies, each analyzing a distinct facet of the problem and together forming a comprehensive picture.

The initial study, presented in chapter 2, focused on assessing the effectiveness of current environmental reclamation strategies. It was essential to establish a starting point to understand the current state of affairs before digging deeper into the mechanisms underlying the contamination. The assessment was undertaken by monitoring the water quality in the region and gauging the impact of past mining activities on local water resources. The evaluation of the environmental reclamation efforts revealed a mixed picture. The environmental reclaiming method was efficient in neutralizing water acidity in most of the surface water resources of the area. However, it was not effective in neutralizing the downstream watercourse. It is crucial to consider that neighboring areas which have not undergone reclamation might also be contributing to the downstream contamination, influencing the results observed. Water-monitoring data highlighted the persistence of heavy metal contamination in some surface waters, with elements such as iron, manganese, and aluminum lingering at levels above acceptable standards. This heavy metal contamination is a reminder of the region's coal mining past. A legacy not easily erased, these contaminants present a substantial risk to aquatic ecosystems, human health, and agriculture in the region. The findings from the first study suggest that despite the initiation of environmental reclamation strategies, there remains a significant challenge in fully mitigating the impacts of past mining activities. This finding served as the motivation for our subsequent investigations, which aimed to dig into the underlying processes of contamination and reclamation in the region.

In response to the need identified in the first study for more representative information on the hydrogeochemical backgrounds of the region's waters, the second study (Chapter 3) aimed to establish the natural geochemical baseline of the affected region. This was a pivotal step in distinguishing between naturally occurring element concentrations and those resulting from anthropogenic activities. Establishing this baseline allowed for a more accurate evaluation of the reclamation methods and the extent of contamination. Our study revealed that the natural geochemical background values in the region were not consistent with the expected values established by the Brazilian legislation. It became apparent that the region's unique geological formation and hydrological dynamics resulted in naturally higher concentrations of certain chemical elements in the waters.

The third study, presented in chapter 4, delved into the impacts of AMD on water quality. Analyzing the physicochemical parameters of water samples collected from rivers and streams affected by mining, we assessed the extent and severity of AMD impact. This study revealed statistical differences between the geochemical parameters of contaminated areas and background values, indicating a significant impact of AMD on water quality. These findings serve as a reminder of the long-lasting impacts of coal mining on water resources and the need for continuous monitoring and assessment of water quality.

The fourth and last study, presented in chapter 5, aimed to explore the significant correlations between typical monitoring parameters of AMD in the coal region of Santa Catarina. This study was critical in understanding the hydrochemical motivations behind these correlations and determining how these correlations could be utilized for effective monitoring strategies. The exploration of typical AMD monitoring parameters, such as pH, redox potential, and concentrations of iron, manganese, and aluminum, revealed several strong correlations. These correlations can be attributed to the geochemical behavior of these elements in the presence of AMD. For instance, the pH of the water plays a significant role in controlling the solubility of heavy metals. Similarly, the redox potential can influence the speciation and mobility of these metals. By understanding these correlations, we were able to develop a regression model that will be able to carried out effective and continuous monitoring of AMD in the region’s surface water. This model can provide real-time data on the water quality, allowing accurate recording of changes in AMD dynamics. Moreover, it can contribute to a cost-effective monitoring strategy, which is crucial for sustainable water resource management in the region. This is a contribution to the regional scene, as it provides a viable tool for assessing the effectiveness of reclamation efforts, analysis of AMD behavior with higher temporal frequency, and guidance for future actions.

In conclusion, this Thesis aimed to made contributions to the scientific understanding of the environmental impacts of coal mining activities in the Santa Catarina region, Brazil. It has furthered our knowledge of the mechanisms of AMD contamination and the effectiveness of reclamation strategies in mitigating these impacts. Moreover, it has underscored the importance of regular and comprehensive monitoring of water resources in areas affected by coal mining.

Our research has shown that while environmental reclamation efforts have led to improvements in the quality of surface water resources in the Santa Catarina coal mining region, more work needs to be done to mitigate the impacts of AMD on water resources. Additionally, our research has highlighted the need for a more in-depth understanding of the local geochemical background to accurately assess the extent and severity of AMD impacts.

The insights gained from this research can hold relevance not only for the Santa Catarina region but also for other areas with the environmental aftermath of coal mining activities. Therefore, it is our hope that the findings of this research will inspire further scientific inquiry into this critical area and inform more effective approaches to environmental reclamation.

In closing, it is crucial to note that the journey to a sustainable future for the Santa Catarina coal mining region is a long one. While this Thesis may represent a step in the right direction, much work remains to be done. The road ahead is undoubtedly challenging, but with continued research and a steadfast commitment to environmental stewardship, we are confident that it is a journey that we can successfully navigate.

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ANNEX A

Supplementary material of Chapter 2

Comparative analysis between field and laboratory datasets for pH and electrical conductivity.

Table A1 Comparative descriptive statistics for the streams datasets (Data presented in table 2.3)

	Point	HIDS07	HIDS10	HIDS11	HIDS12
	n	14	14	13	13
pH	Mean lab	7.1	3.3	3.6	3.5
	Mean field	6.0	3.3	4.0	4.0
	SD lab	0.4	0.2	0.3	0.3
	SD field	0.6	0.4	0.6	0.7
	Min lab	6.5	3.0	3.1	3.2
	Min field	5.0	2.6	2.9	3.0
	Max lab	7.7	3.6	4.1	4.1
	Max field	7.0	3.9	5.3	5.7
EC	Mean lab	74.2	467.1	397.9	421.7
	Mean field	99.9	497.5	386.6	420.0
	SD lab	10.2	150.3	127.4	139.7
	SD field	40.4	187.3	174.4	163.6
	Min lab	56.0	178.1	210.4	231.5
	Min field	56.0	255.0	189.0	219.0
	Max lab	89.5	782.5	631.0	700.8
	Max field	195.0	936.0	766.0	793.0

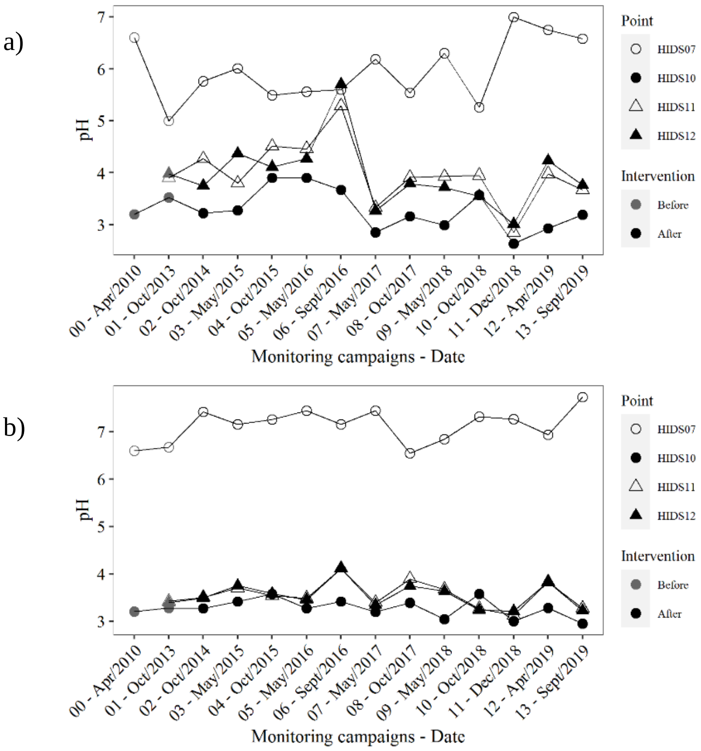

Fig. A1 Comparative pH analysis for river sampling points; a) field values, b) laboratory values (Figure presented as Fig. 2.4 in the paper)

Table A2 Comparative descriptive statistics for the ponds datasets (Data presented in table 2.4r)

Point	POND01	POND01B	POND02	POND02B	POND03	POND03B	POND04	POND04B
n	14	14	14	14	13	13	14	14
pH								
Mean lab	3.3	3.1	5.0	5.1	6.2	6.2	6.6	6.3
Mean field	3.3	3.2	5.2	5.1	6.2	6.1	6.6	6.4
SD lab	0.2	0.2	1.0	0.9	0.8	0.9	0.6	0.7
SD field	0.7	0.3	1.0	0.9	0.9	0.9	0.7	0.6
Min lab	3.0	2.7	3.7	3.6	3.5	3.6	4.7	4.2
Min field	2.4	2.7	3.7	3.7	3.9	4.0	4.9	4.8
Max lab	3.6	3.6	6.4	6.2	6.7	6.9	7.2	6.8
Max field	3.8	3.6	6.9	6.4	7.1	7.1	7.7	7.3
EC								
Mean lab	426.0	668.9	207.4	236.0	123.4	125.2	97.5	105.9
Mean field	462.6	588.9	232.9	264.6	140.1	140.8	116.5	127.7
SD lab	114.3	300.3	98.4	107.1	92.3	90.7	34.7	50.5
SD field	136.5	198.9	83.7	96.0	65.2	62.4	26.6	38.0
Min lab	257.7	292.4	91.2	91.5	72.1	72.1	70.0	74.3
Min field	258.0	345.0	114.0	140.0	83.0	84.0	81.0	80.0
Max lab	645.3	1282.8	389.5	437.0	426.3	420.8	204.8	265.3
Max field	767.0	1015.0	356.0	437.0	343.0	335.0	177.0	210.0

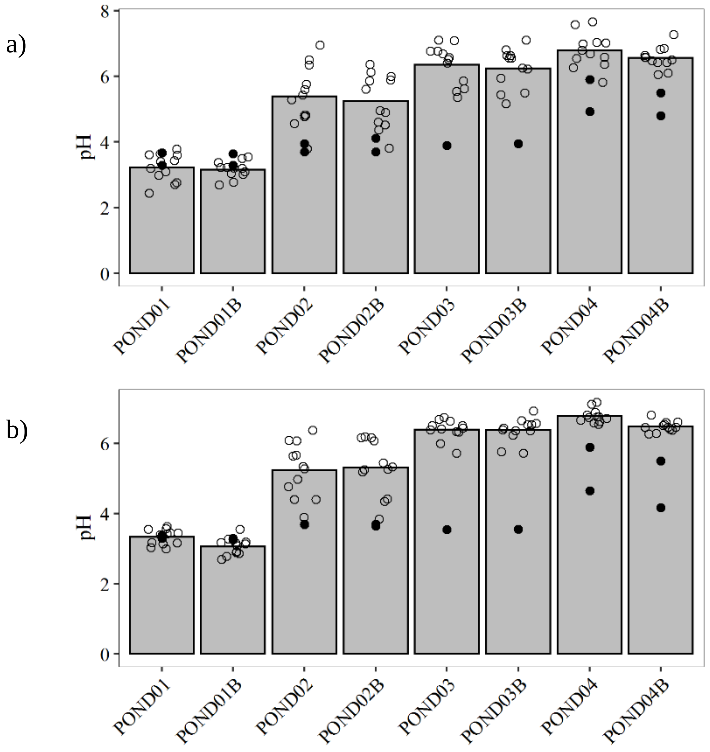

Fig. A2 Comparative pH analysis for pond sampling points; a) field values, b) laboratory values (Figure presented as Fig. 2.5 in the paper)

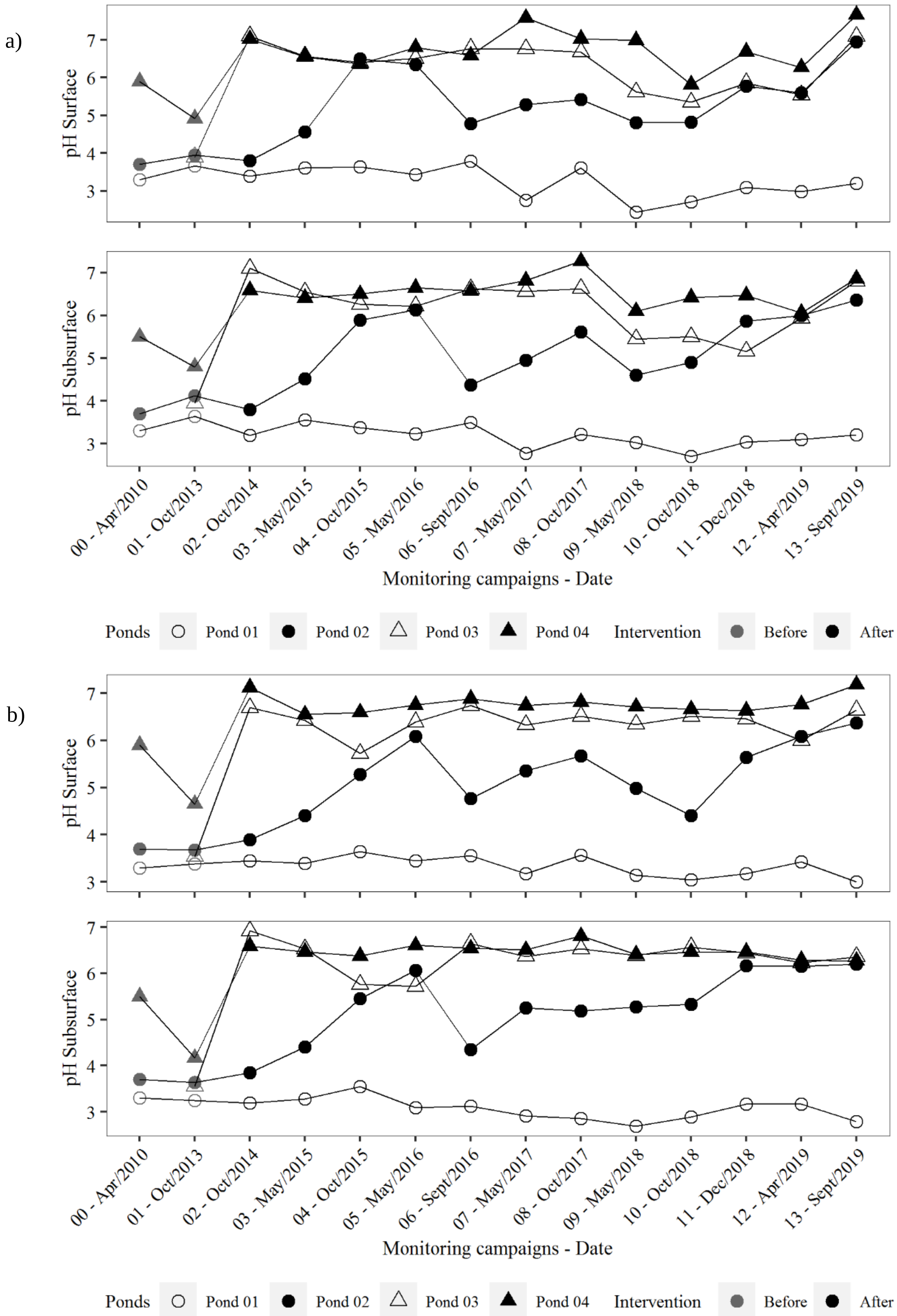

Fig. A3 Comparative temporal evolution analysis for pond sampling points; a) field values, b) laboratory values (Figure presented as Fig. 2.6 in the paper)

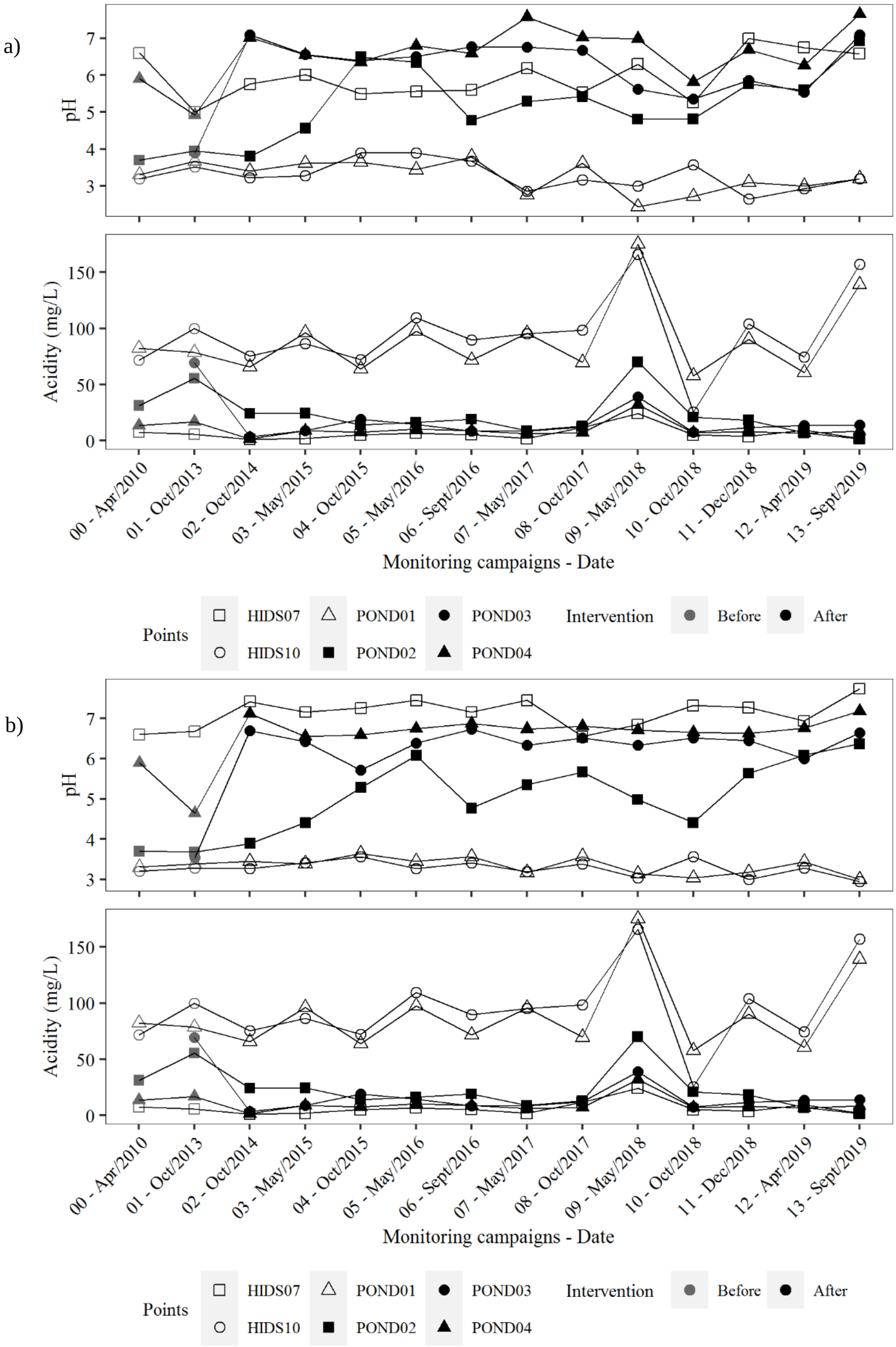

Fig. A4 Comparative temporal evolution analysis for the combined runoff points of the area; a) field values, b) laboratory values (Figure presented as Fig. 2.7)

ANNEX B

Supplementary material of Chapter 5

Table B1 T-test comparing water resources groups for their sulfate, iron, manganese, and aluminum concentration (95% confidence interval).

		AMD streams	AMD U.M. discharges	Streams O.T.C
SO_4^{-2}	AMD UMD	2,20E-16		
	Streams OTC	2,20E-16	2,20E-16	
	Streams preserved areas	2,20E-16	2,20E-16	7,45E-04
Fe	AMD UMD	2,20E-16		
	Streams OTC	2,20E-16	2,20E-16	
	Streams preserved areas	2,20E-16	2,20E-16	2,20E-16
Mn	AMD UMD	2,20E-16		
	Streams OTC	2,20E-16	2,20E-16	
	Streams preserved areas	2,20E-16	2,20E-16	2,20E-16
Al	AMD UMD	**0,7434**		
	Streams OTC	2,20E-16	2,20E-16	
	Streams preserved areas	2,20E-16	2,20E-16	9,06E-13

Table B2 Matrix of P-values for Spearman Correlations shown in Table 5.2.

	Correlation between pH and				
	EC	SO	Fe	Mn	Al
AMD Streams	0.00E+00	0.00E+00	7.37E-288	0.00E+00	0.00E+00
AMD U.M.D	9.84E-10	3.26E-04	3.87E-01	1.36E-05	3.99E-85
Streams O.T.C.	2.67E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Streams preserved areas	1.04E-11	2.83E-01	5.68E-02	8.81E-01	8.81E-01

	Correlation between EC and				
	pH	SO	Fe	Mn	Al
AMD Streams	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
AMD U.M.D	1.97E-10	5.96E-121	2.32E-67	2.18E-92	1.07E-13
Streams O.T.C.	3.34E-02	1.10E-07	1.00E+00	1.00E+00	1.77E-01
Streams preserved areas	7.99E-13	2.86E-03	7.77E-01	7.26E-01	8.81E-01

Density plot with the visualization of data points of pH from two groups: i) Samples from underground mine discharges, and ii) Samples from streams, both affected by AMD (Figure B1).

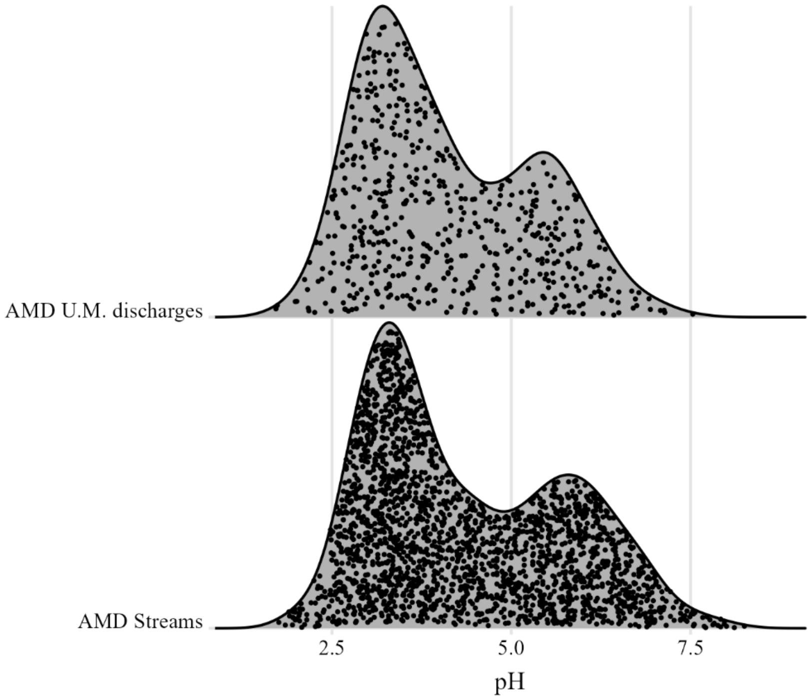

Fig. B1 Density plot with the visualization of data points of pH from two groups: i) Samples from underground mine discharges, and ii) Samples from streams, both affected by AMD.

Details of the procedure for metal and sulfate analysis.

ICP-OES metals analysis - The instrument was calibrated using multi-element standards in a matching sample matrix, and samples were introduced to generate an inductively coupled plasma. The intensity of emitted light at characteristic wavelengths was measured, and concentrations of metals in the samples were determined by comparing measured intensities to calibration standards. The calibration and accuracy of the analysis were verified using quality control samples and standard reference materials.

Gravimetric method for sulfate analysis - Sulfate precipitation was achieved by adding barium chloride to the sample aliquot, and the pH was adjusted as needed. The precipitated barium sulfate was filtered, washed, and dried before being weighed. The sulfate concentration in the original water sample was calculated using the weight of the barium sulfate precipitate, the volume of the sample aliquot, and the conversion factor between barium sulfate weight and sulfate concentration.