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GROUNDWATER QUALITY PARAMETERS IN CRYSTALLINE ROCKS IN THE SOUTH OF ESPÍRITO SANTO STATE, SOUTHEASTERN BRAZIL

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ABSTRACT

In hard rock terrains where gneisses and granitoids predominate, groundwater is generally considered to be of good quality due to the low solubility of the silicate minerals that form these rocks. However, in the long term, silicate minerals weathering can interfere in groundwater quality. In the case of fractured aquifers, these changes are less predictable due to the heterogeneous and anisotropic behavior of this aquifer type. The geological framework in the southern of the State of Espírito Santo is mainly formed by hard rocks, where the water quality parameters that serve to know the suitability for different types of use have not been studied. This work aimed to fill this gap by analyzing 62 groundwater samples collected in 38 wells that exploit the Crystalline Aquifer System in the Itapemirim River Catchment in the south of Espírito Santo. The hydrogen potential, electrical conductivity, total dissolved solids, turbidity, and concentrations of Ca, Mg, Na, Fe, Mn, Pb, Zn, Cd, and Co were analyzed. The concentrations of Cd, Co, Pb, and Zn were below the thresholds defined by the Brazilian standards for various uses of water. On the other hand, Fe, Mn, and Na, turbidity, and total dissolved solids were above the permitted limit for various types of water use. The dissolved solids and Na, as well as other groundwater main components, are controlled by geomorphological, lithological, and climatic factors, with increasing values to the central part of the basin. Differently, Fe, Mn, and turbidity show anomalous values randomly distributed in the area, probably due to pedogenetic enrichment of lateritic profiles and local structural control. It is possible that the lack of adequate maintenance of wells also contributes to such alterations.

Keywords: Fractured aquifers; Iron; Manganese; Hydrogeochemistry.

RESUMO

PARÂMETROS DE QUALIDADE DA ÁGUA SUBTERRÂNEA EM ROCHAS CRISTALINAS NO SUL DO ESTADO DO ESPÍRITO SANTO, SUDESTE DO BRASIL. Em terrenos de rochas cristalinas onde predominam gnaisses e granitoides, a água subterrânea é considerada geralmente de boa qualidade devido à baixa solubilidade dos minerais silicáticos que compõem essas rochas. Porém, em longo prazo, o intemperismo destes minerais silicáticos pode interferir na qualidade da água subterrânea. Quando se trata de aquíferos fraturados, essas alterações são menos previsíveis em função do caráter heterogêneo e anisotrópico intrínseco a tais aquíferos. A região sul do Estado do Espírito Santo tem seu arcabouço geológico constituído basicamente por terrenos cristalinos, onde os parâmetros de qualidade da água voltados à adequação para os diversos usos ainda não foram estudados. O objetivo desse trabalho foi voltado ao preenchimento dessa lacuna, por meio da análise de 62 amostras de água subterrânea coletadas em 38 poços tubulares profundos que explotam o Sistema Aquífero Cristalino na área de abrangência da Bacia Hidrográfica do Rio Itapemirim, no sul do Estado do Espírito Santo. Foram analisados: potencial hidrogeniônico, condutividade elétrica, sólidos totais dissolvidos, turbidez e as concentrações de Ca, Mg, Na, Fe, Mn, Pb, Zn, Cd e Co. Os teores de Cd, Co, Pb e Zn ficaram dentro da faixa permitida para os diversos tipos de uso previstos na normativa ambiental. Por outro lado, o Fe, Mn e Na, além da turbidez e sólidos totais dissolvidos estão acima do valor máximo permitido para muitos tipos de uso da água. O aumento dos sólidos dissolvidos e do Na, assim como outros constituintes essenciais das águas subterrâneas, obedece aos controles geomorfológico, litológico e climático, com enriquecimento na porção central da bacia hidrográfica. De forma diferente, o Fe, o Mn e a turbidez apresentam valores anômalos distribuídos de forma aleatória pela bacia, provavelmente devido ao enriquecimento pedogenético em perfis lateríticos e controle estrutural local. É possível que a falta de manutenção adequada dos poços também contribua com tais alterações.

Palavras-chave: Aquíferos fraturados; Ferro; Manganês; Hidrogeoquímica.

1 INTRODUCTION

In crystalline rock terrains formed by igneous and metamorphic rocks, groundwater flows through the Fractured Aquifer System, also called the Crystalline Aquifer System (CAS). In this aquifer type, water flows through discontinuities in fresh rock and the overlying saprolite (DEWANDEL et al. 2011), also called weathered mantle or regolith. Although low-solubility silicate minerals predominate in crystalline rocks, many researchers point out problems of high salinity and anomalous concentrations of metals and other components in those areas. Many of these works were conducted in arid and semi-arid regions (e.g., KHOZYEM et al. 2019, UDESHANI et al. 2022, NIYAZI et al. 2023). However, there are also cases of sites where other factors, such as the residence time of groundwater in CAS, contribute to increase the concentration of chemical elements (e.g., HARTE et al. 2012, ROQUES et al. 2014, ADEYEYE et al. 2020). The dissolution of minerals in silicate rocks can locally interfere with water quality. However, this can be difficult to predict in fractured aquifers due to this aquifer type´s heterogeneous and anisotropic character.

It is essential to highlight that most of the global population lives on crystalline rock terrains. So, in populous countries where water management policies are deficient or absent, the alterations from anthropic actions also interfere with groundwater quality (MACHIWAL & JHA 2015). Identifying the sources of chemical elements or substances that occur above the maximum permitted limits for different types of water use is crucial to guide water resources management policies.

The CAS is the primary groundwater source in the State of Espírito Santo, but its hydrogeological characteristics are still poorly known. Previous works carried out in the south of Espírito Santo showed that remarkable variations occur in the main composition of groundwater (NEVES et al. 2021, OLIVEIRA et al. 2022), but they did not evaluate the water quality parameters related to adequacy for consumption, as the presence of trace metals and others that appear in the environmental rules. Thus, this work aims to describe the groundwater quality parameters in crystalline terrains of the south of Espírito Santo State, involving the Itapemirim River Catchment (IRC) (Figure 1).

2 STUDY AREA

2.1 General settings

The IRC is located south of the State of Espírito Santo, covering a drainage area of nearly 5,927 km^2, with approximately 17 municipalities from this State and a small section of a municipality of Minas Gerais (the Lajinha County). According to the Espírito Santo State Water Resources Plan (ESPÍRITO SANTO 2018), there is a tendency for growth in industrial production in this region due to the petroleum exploration of pre-salt and the dimension stone production. The Cachoeiro de Itapemirim Municipality is a prominent Brazilian producer and exporter of dimension stones. The municipal headquarters, located in the central part of the IRC, is the principal city of the south, where most of the population, nearly 185,000 inhabitants,

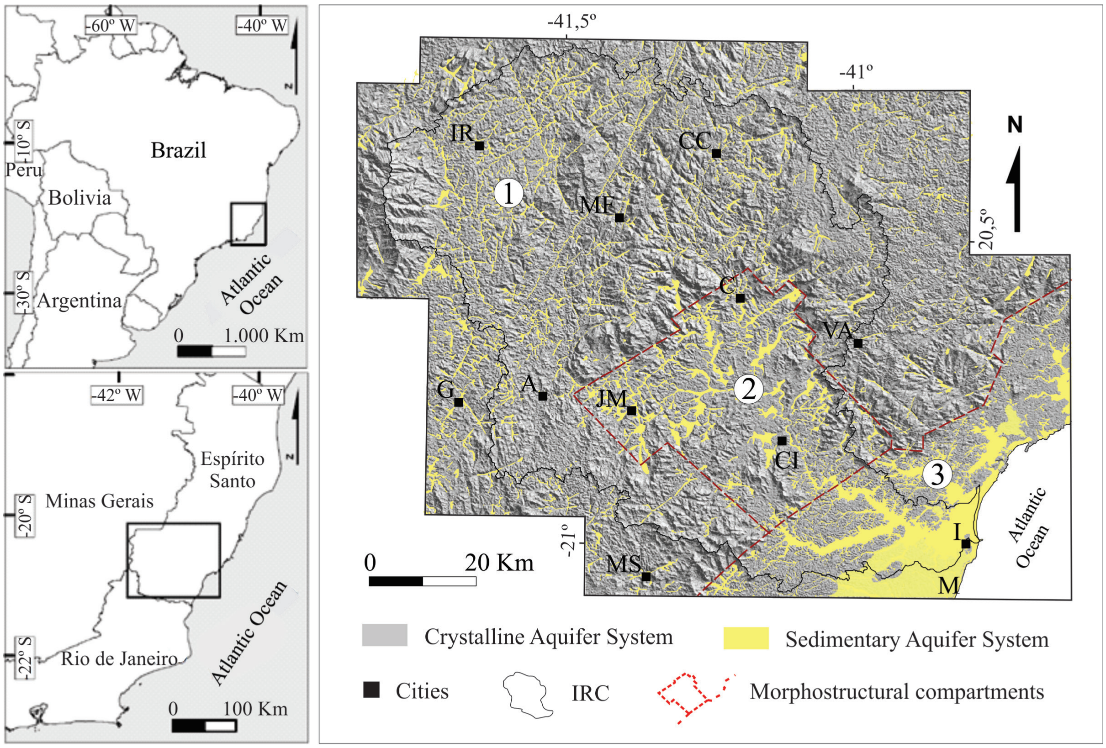


FIGURE 1 – Location of the Itapemirim River Catchment with the occurrence areas of the Crystalline and Sedimentary aquifer systems according to NEVES et al. (2021), and geomorphological sectors, according to PEIXOTO-OLIVEIRA et al. (2018) (Sectors - 1: Mantiqueira, 2: Cachoeiro, and 3: Litorâneo) (Cities - IR: Irupi, G: Guaçuí, A: Alegre, MF: Muniz Freire, JM: Jerônimo Monteiro, CI: Cachoeiro de Itapemirim, I: Itapemirim, M: Marataízes, MS: Mimoso do Sul, C: Castelo, CC: Conceição de Castelo, V: Venda Nova do Imigrante).

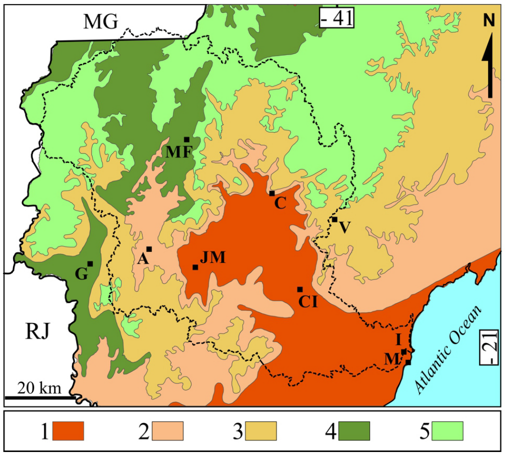
is concentrated (BRASIL 2022). Agriculture, livestock, and small cities predominate in the rest of the area.

According to the Köppen climate classification, the study area is under a dry winter tropical climate (Aw) and a high-altitude subtropical climate with mild summer (Cwb), and dry winter and hot summer (Cwa) (ALVARES et al. 2013). A fragment of the climate map of Espírito Santo (ESPÍRITO SANTO 1999) shows the distribution of climate zones in IRC, dividing the region into hot, mild, and cold lands, associated with dry, transitional, and rainy lands (Figure 2). An association between temperature distribution and rainfall and the region´s relief can be observed, i.e., the ridged land areas are cooler and rainier. In contrast, the central portion of the catchment, with less rough terrain, is hotter and drier.

2.2 Geological and hydrogeological settings

Most of the geological framework in ICR is composed of crystalline rocks, mainly metamorphic (gneisses) and intrusive igneous (granitoid) rocks (Figure 3). Locally, mylonites, marbles, granulites, and charnockites also occur (VIEIRA et al. 2018, SANTIAGO et al. 2020). The sedimentary covers comprise semi-consolidated sediments of the Barreiras Formation (WEST & MELO 2020, SANTIAGO et al. 2023) and unconsolidated colluvial, fluvial, and coastal deposits.

The relief in the region is generally rugged, with ridges and hills belonging far north of Mantiqueira Mountain Range (CALEGARI et al. 2021) that compounds the Mantiqueira Morphoestructural Sector (PEIXOTO-OLIVEIRA et al. 2018), where the upper part of the Itapemirim River Catchment is located – Upper IRC (Figure 1). In the middle part of IRC, referred to as Cachoeiro Sector (PEIXOTO-OLIVEIRA et al. 2018), the relief is smoother, and a *sea of hills* landscape predominates. Near the coastline, in the Coastal Sector (PEIXOTO-OLIVEIRA et al. 2018), the crystalline rocks are covered by the Barreiras Formation, where hills with flat tops of the Coastal Tables occur (GATTO et al. 1983). Fluvial



CHARACTERISTICS OF CLIMATE ZONES			
Zone	T min. (°C)	T max. (°C)	N° dry months
1	11.8 – 18.0	30.7 – 34.0	6.5
2	11.8 – 18.0	30.7 – 34.0	5.0
3	9.4 – 11.8	27.8 – 30.7	3.0
4	9.4 – 11.8	27.8 – 30.7	4.5
5	7.3 – 9.4	25.3 – 27.8	3.0

FIGURE 2 – Climatic zones in the south region of Espírito Santo State (adapted from ESPÍRITO SANTO 1999) (Zones - 1: dry and hot lands; 2: hot lands in wet-dry transition; 3: rainy lands with mild temperatures; 4: rainy and dry lands with mild temperatures; and 5: cold-wet lands) (Cities: capital bold letters inside the map - see legend figure 1).

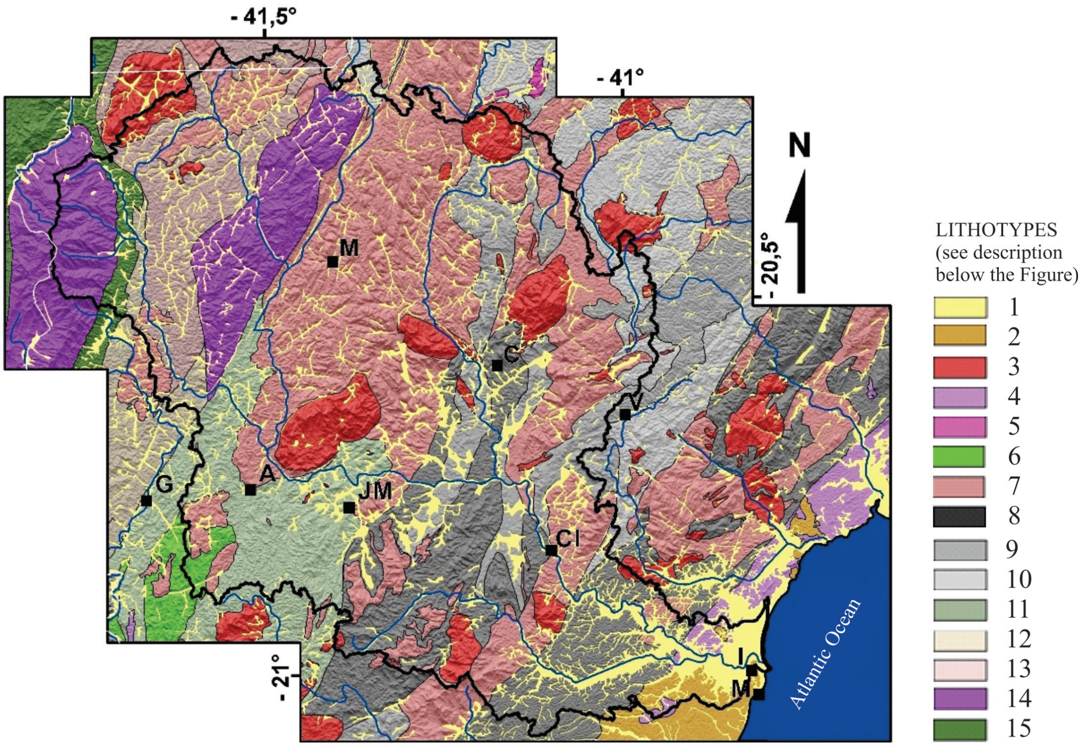


FIGURE 3 – Simplified geological map of the Itapemirim River Catchment, with lithological units of the crystalline basement (VIEIRA et al. 2018) and the sedimentary covers (PEIXOTO-OLIVEIRA et al. 2018) (1: alluvial deposits; 2: Barreiras Formation; 3: granitoids; 4: charnockites, 5: weakly foliated granitoids; 6: orthogranulites; 7: orthogneisses; 8: gneisses with quartzite, calciosilicates and amphibolites; 9: gneisses with amphibolites; 10: gneisses and quartzite; 11: gneisses and amphibolites; 12: gneiss and kinzingites; 13: biotite schist with metavolcanic rocks and quartzitic gneisses;14: mylonite gneisses; and 15: granulites) (Cities: capital bold letters inside the map - see legend figure 1).

sediments generally occur aligned along the main drainage channels and compound wider bodies close to the coast zone. The morphostructural sectors are delineated by structural lineaments, and this arrangement conditions the sedimentary deposition area. Therefore, the geomorphology also controls the distribution of the aquifer systems.

In the Crystalline Basement area, where CAS occurs, groundwater flows at the fresh rock´s discontinuities (joints, faults, and foliation plans) and in the weathered mantle above it. On the other hand, the Sedimentary Aquifer System (SAS) is a porous aquifer system that occurs in areas with sedimentary covers, where groundwater flows through intergranular spaces.

The distribution of the hydrochemical types in the region follows the geological and geomorphological sectors: in the Upper IRC, waters are calcic bicarbonate and calcic-magnesian bicarbonate, while in the Middle IRC, the sodium chlorinated and sodium bicarbonate types predominate (NEVES et al. 2021). In the Upper IRC, the composition of groundwater is controlled mainly by the weathering of silicate rocks. On the other hand, in the Middle IRC, the hydrochemical characteristics are also influenced by the presence of carbonate rocks, such as marbles and calcium-silicate rocks. The climatic conditions, with higher temperatures and lower air humidity in the Middle IRC, which is topographically lower, also cause mineral enrichment of groundwater due to evaporation of the water that infiltrates the soil.

Studies about isotopes in groundwater by OLIVEIRA et al. (2022) show that the Upper IRC is an important recharge area. Groundwater flows to the central part of the Middle IRC, where isotopic signatures similar to rain indicate a short renovation time. Still, waters with longer residence time also occur, suggesting a regional recharge. Indeed, the residence time of groundwater in crystalline terrains can vary considerably in nearby locations; there are waters 80 years old side by side with waters 2.5 years old about the infiltration time in the aquifer system (OLIVEIRA et al. 2022), highlighting that diverse recharge sources exist, with regional and local flows, besides mixtures from diverse sources. In crystalline terrains of Sri Lanka, PRIYADARSHANEE et al. (2022) describe a similar situation, where sedimentary aquifers are recharged by waters with residence time older than 50 years that infiltrated in higher lands of crystalline rocks and percolated along regional flow lines formed by fractured zones.

3 MATERIALS AND METHODS

Groundwater samples were collected in 38 wells that exploit the Crystalline Aquifer System (CAS) in the area of IRC (Figure 4). Well depth varies from 12 to 200 m, with an average of 72 m. This information was collected through interviews with owners during fieldwork, as these data are rarely in the official register.

Two or three samples were collected at the same sampling points at different moments, compounding repetitions. However, it was possible to get just one sample in some wells due to difficulties accessing some wells (generally in private properties). Thus, 62 groundwater samples were collected after analyzing the field parameters. In each sampling work, 1 liter of water was collected and sent to be stored in the laboratory. Sample collection and storage were carried out in accordance with the methods of NBR 9898/87 of the Brazilian Association of Technical Rules (ABNT 1987). Care was taken to avoid collecting stagnant water, always seeking collection in pumping wells and locations as close as possible to the well's outlet pipe. The bottles underwent a rigorous cleaning process with nitric acid solution and ultrapure water.

On the field, using multiparameter equipment Hanna Instruments (model HI9829-01042), it was measured the pH, electrical conductivity (EC) (in $\mu S\ cm^{-1}$) and content of total dissolved solids (TDS) (in $mg\ L^{-1}$); the turbidity (Turb) (in Formazine Turbidity Unit – FTU) was measured with portable turbidimeter Hanna Instruments (model HI93703). Samples were filtered with 0.45 µm membrane, acidified with ultrapure nitric acid (HNO_3) until reaching a pH lower than 2.0, and refrigerated until further analyses were conducted.

Optical emission spectrometry with inductively coupled plasma (ICP-OES) was used to measure the content of Ca, Mg, Na, Fe, and Mn (in $mg\ L^{-1}$), and inductively coupled plasma mass spectrometry (ICP-MS) was used to determine Pb, Zn, Cd, and Co (in $mg\ L^{-1}$). The data were compared with the maximum permitted limit (MPL) for different types of use, according to the Resolution 396/2008 of the National Environmental Council (Conselho Nacional de Meio Ambiente - CONAMA) (BRASIL 2008), while the Turbidity (turb.) has the maximum values determined by the Ordinance 888/2021 of Healthy Ministry (BRASIL 2021).

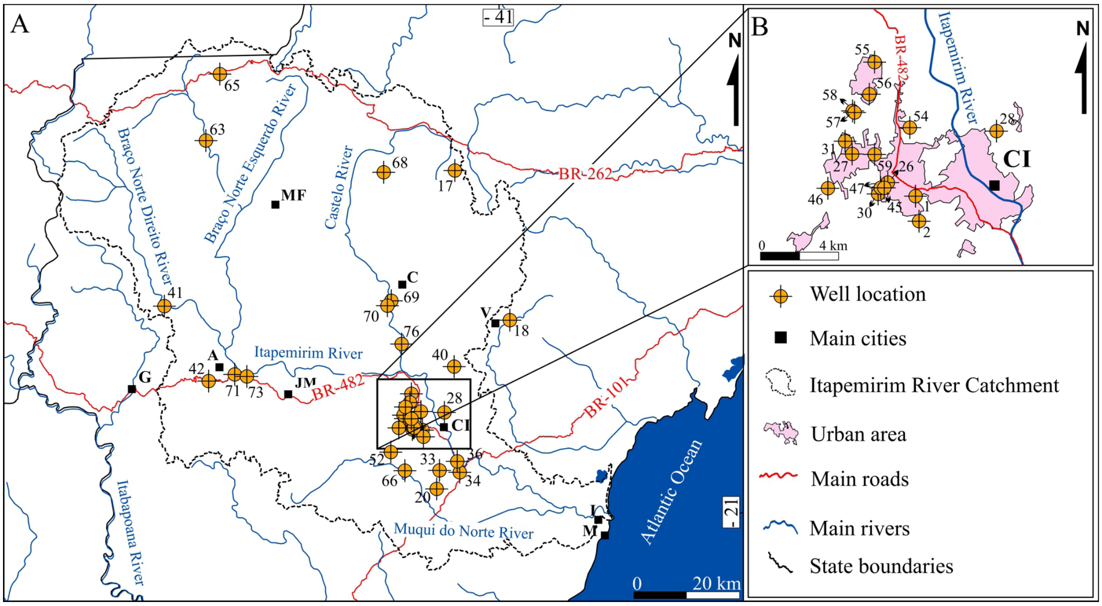


FIGURE 4 – Location of the wells that served as groundwater sampling points in the Itapemirim River Catchment (after NEVES et al. 2021). (Cities: capital bold letters inside the map - see legend figure 1).

4 RESULTS

Table 1 shows the descriptive statistics of the physical and chemical parameters of groundwater collected in tubular wells located in crystalline terrains of IRC (the raw data can be seen in the Supplementary Material). The values were compared with the maximum permitted limit (MPL) of Resolution 396/2008 of CONAMA (BRASIL 2008), which defines the classification of groundwater depending on the types of use. The Ca and Mg don't have MPL, as they constitute mineralizing elements of natural waters. On the other hand, the TDS, Na, Fe, and Mn are regulated and were above the MPL in at least one of the types of use previewed in the normative. The Cd, Co, Pb, and Zn contents are also regulated, but they were not registered in levels above the MPL for any of the types of use.

Table 2 presents the correlation coefficient between the analyzed parameters. The levels of Ca, Na, Mg, and Zn show a medium to high positive correlation, and these elements are responsible for the increase in TDS and EC. Turbidity and dissolved Fe, Mn, and Co contents form another group of parameters with a high positive correlation.

The parameters that were below the MPL according to CONAMA (BRASIL 2008), that is, Fe, Mn, TDS, and Na, in addition to turbidity, regulated by Ordinance 888/2021 of the Ministry of Healthy (BRASIL 2021), were plotted on a map (Figure 5), to verify the spatial distribution of variables that exceeded the limit of, at least, one type of water use. Notably, the group formed by Fe, Mn, and turbidity (which shows a high correlation according to table 2) does not follow a defined distribution pattern of values. In contrast, the high levels of TDS and Na are concentrated in the central portion of IRC.

5 DISCUSSION

The high concentrations of TDS in the central part of IRC (Figure 5) indicate salinized waters that have become unappropriated for human consumption at some points. This enrichment follows the increase of EC and the levels of Ca and Mg, which are natural groundwater components generally provided by the weathering of silicates and/or carbonates (HEM 1985). The Na also contributes to increasing the TDS in these waters, and both occur above the MPL of Resolution 396/2008 of CONAMA, mainly in the central portion of the IRC.

The most mineralized waters in this portion of the catchment (Middle IRC), contrasting to the higher portions where mineralization is low, have already been described by NEVES et al. (2021). According to these authors, in the Upper

TABLE 1 – Groundwater physical and chemical parameters in the crystalline terrains of the Itapemirim River Catchment (Turb: turbidity, EC: electrical conductivity, TDS: total dissolved solids, MPL: maximum permitted limit, CH: consumption by humans, CA: consumption by animals, IR: irrigation, RE: recreation).

Parameter	*unit*	*medium*	*median*	*stand dev.*	*min. v.*	*max. v.*	*MPLs Res. CONAMA 396/2008*			
							CH	*CA*	*IR*	*RE*
Turb	FTU	6.01	0.10	22.38	0.00	122.67	---	---	---	---
pH	---	6.80	6.63	0.66	4.96	8.09	---	---	---	---
EC	µS cm^{-1}	470.07	241.67	481.57	13.44	1,712.33	---	---	---	---
TDS	mg L^{-1}	285.23	130.49	321.87	5.81	1,254.33	1,000	---	---	---
Ca	mg L^{-1}	35.42	18.10	43.22	0.22	182.75	---	---	---	---
Mg	mg L^{-1}	4.83	1.03	9.14	0.00	38.44	---	---	---	---
Na	mg L^{-1}	47.30	16.08	62.67	0.96	231.98	200	---	---	300
Fe	mg L^{-1}	0.59	0.01	2.60	0.00	16.03	0.30	---	5.00	0.30
Mn	mg L^{-1}	0.41	0.01	1.47	0.00	7.01	0.10	0.05	0.20	0.10
Co	µg L^{-1}	0.32	0.00	1.20	0.00	8.37	---	1,000	50	---
Cd	µg L^{-1}	0.03	0.00	0.04	0.00	0.13	5.00	50	10	5
Pb	µg L^{-1}	0.52	0.41	0.53	0.00	2.34	10	100	5,000	50
Zn	µg L^{-1}	4.87	0.00	16.06	0.00	118.48	5,000	24,000	2,000	5,000

TABLE 2 – Correlation between groundwater quality parameters in crystalline rocks of the Itapemirim River Catchment (EC: electrical conductivity, Turb.: turbidity, TDS: total dissolved solids). Color legend: blue = low correlation, orange = intermediate correlation, red = high correlation

	pH	*EC*	*TDS*	*Turb*	*Ca*	*Mg*	*Na*	*Fe*	*Mn*	*Pb*	*Zn*	*Cd*	*Co*
pH	1.0	0.2	0.1	-0.1	0.1	0.0	0.2	-0.2	-0.1	-0.2	0.4	-0.4	-0.3
EC		1.0	0.7	0.0	0.5	0.2	0.8	-0.2	-0.1	0.1	0.8	-0.3	0.1
TDS			1.0	0.0	0.9	0.4	0.9	-0.2	-0.1	0.0	0.8	-0.1	0.1
Turb				1.0	0.0	0.0	-0.1	0.4	0.8	-0.1	-0.3	0.1	0.9
Ca					1.0	0.4	0.9	-0.2	-0.1	0.0	0.7	0.0	0.1
Mg						1.0	0.1	-0.1	-0.1	0.3	0.5	0.0	-0.1
Na							1.0	-0.2	-0.2	0.0	0.9	-0.2	0.1
Fe								1.0	0.8	-0.1	-0.1	-0.1	0.1
Mn									1.0	-0.1	-0.1	0.1	0.9
Pb										1.0	-0.1	-0.3	0.0
Zn											1.0	-0.1	-0.1
Cd												1.0	0.1
Co													1.0

IRC, calcic bicarbonate and calcic-magnesian bicarbonate waters occur, while in the Middle IRC, sodium-chlorinated and sodium-bicarbonate waters predominate. These variations are related to the region´s geomorphological, lithological, and climatic variations, besides the longer residence time of groundwater (OLIVEIRA et al. 2022). A similar pattern was observed in other regions of crystalline terrains (e.g., KUMAR & JAMES 2016) once the rock-water interaction commonly increases the concentration of Ca, Mg, Na, and K in the direction of groundwater flow, i.e., from the higher altitudes to the lower parts of the catchment. This fact is due to the change in the hydraulic gradient, which decreases as the relief becomes flatter. In crystalline terrains, the recharge can come from the meteoric water that infiltrates distant sites at higher altitudes and flows through discontinuities in the crystalline basement when they form regional flow zones.

The Fe and Mn contents, together with the turbidity values, follow a distribution pattern very

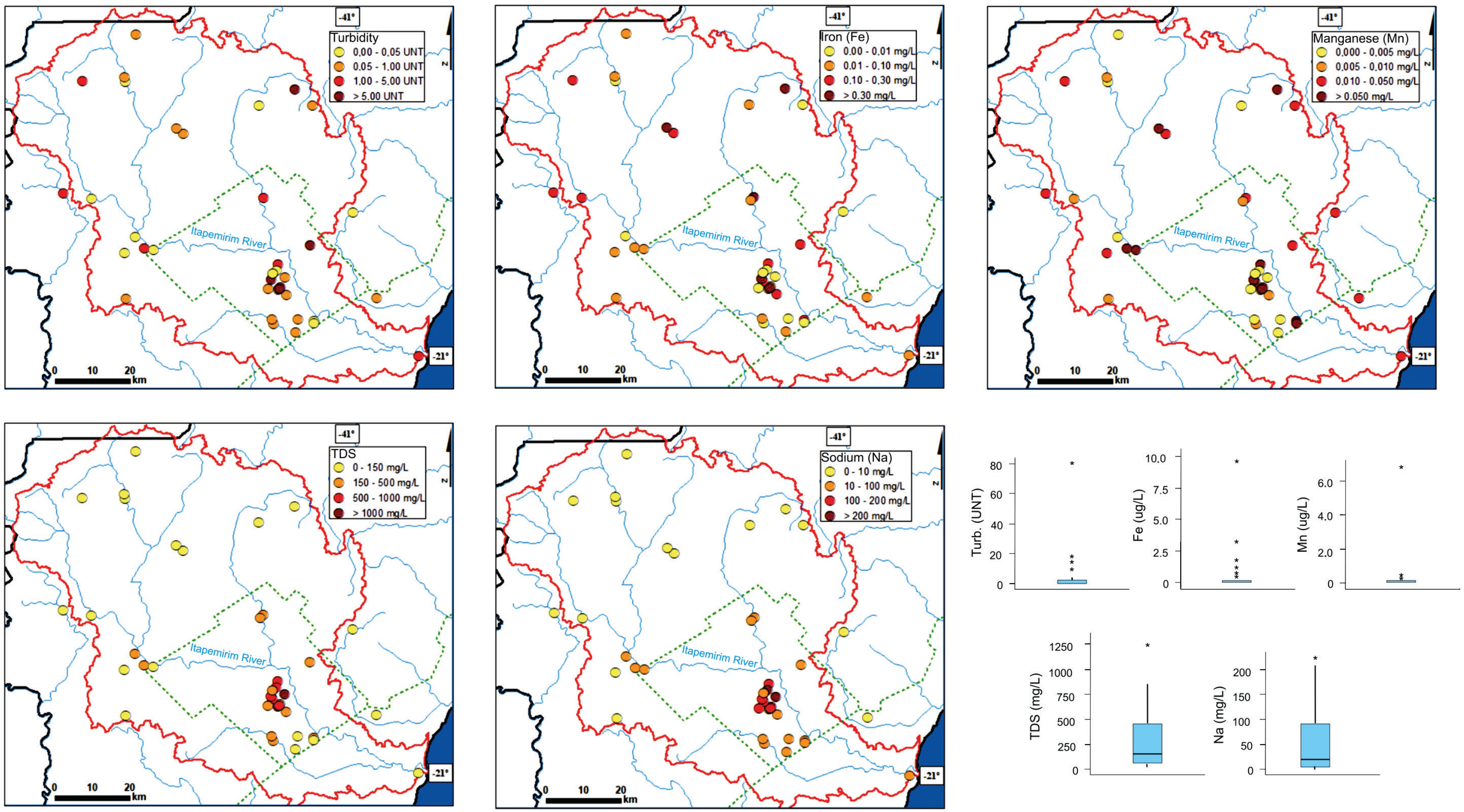


FIGURE 5 – Turbidity values and concentrations of Fe, Mn, total dissolved solids (TDS), and Na in the Itapemirim River Catchment, with boxplot graphs showing the statistical distribution patterns of the data (also see data correlation in table 2).

different from the parameters discussed (Ca, Mg, Na, and TDS) once higher values are disseminated in various sites of the catchment, including the Upper IRC and not only in the central portion (Figure 5). Co is another metal that shows similar behavior to Mn, with a high positive correlation. Although the Co content is below the MPL, its presence indicates restrictive points related to water use due to the local solubilization of potentially dangerous metals that accompany it, such as Pb, Zn, Cu, Ni, and Ba (HEM 1985).

The association between Mn and Fe in groundwater is widespread, as both participate in redox processes during mineral weathering (HEM, 1985). When the divalent Mn is released in an aqueous solution during weathering, it is more stable to oxidation than the ferrous Fe. However, if it comes into contact with the atmosphere, it will precipitate as an oxide crust, forming incrustation that usually contains a substantial amount of co-precipitated iron. HOMONCIK et al. (2010) report that the behavior of Fe can interfere with the solubility of Mn, as it dissolves when the Fe is reduced and, conversely, when the Fe oxides are formed, the Mn is sorbed into ferrous minerals.

Several works show that Fe and Mn in groundwater can be supplied by the rock or sediment that compounds the aquifer. Fe can be provided by mafic minerals in igneous and metamorphic rocks, such as pyroxene, amphibole, biotite, magnetite, and, mainly, olivine (HEM 1985). However, these elements are insoluble in oxidized form and will only be present in groundwater when environmental conditions are reducing (HAMER et al. 2020).

Therefore, the simple presence of these minerals in the rock is not a determinant factor for their solubilization, which depends on the redox conditions and environmental pH. Seasonal water level fluctuations in shallow sedimentary aquifers explain changes in redox conditions at the phreatic and vadose zone interface, promoting the cyclic dissolution of ferrous and ferric minerals (USMAN et al. 2021). CARRETERO & KRUSE (2015) studied the origin of Fe and Mn in a coastal sedimentary aquifer in Argentina and related them to the presence of pyroxene, amphibole, biotite, Fe oxy and hydroxides, and volcanic material. The authors did not observe relationships between the concentration of metals, nor between these and the pH or the Eh, attributing the fact to a redox balance.

The content of organic matter can cause environmental changes that promote the solubilization of Fe and Mn (STENVIK et al. 2022), in addition to ammonium and high turbidity associated with those metals (ADEYEYE et al. 2020). Anaerobic bacteria play an efficient role in reducing iron oxides (KHOZYEM et al. 2019), and the recharge from acid rainwater is also a factor to be considered as a contributor to the solubilization and enrichment of these metals in groundwater (USMAN et al. 2021).

Some authors point to residence time and water level fluctuations as factors that favor the dissolution of Fe and Mn in sedimentary aquifers (ZHANG et al. 2020) and in crystalline ones (ADEYEYE et al. 2020). However, in the studied area, the residence time influences the concentration of the primary ions, but not of Fe and Mn, that are considered trace metals in groundwater. The flux model of fractured aquifers presented by BOCHET et al. (2020) can explain the local occurrence and apparently random of waters rich in Fe and Mn in fractured aquifers, contrasting with the mineral enrichment of waters towards low topographically portion. The authors propose that the intersections between sets of fractures in the subsurface form points with fluctuating oxidizing and reducing conditions that, together with the action of microorganisms, can locally and sporadically favor the solubilization or precipitation of metals. Therefore, the wells that produce waters rich in Fe and Mn can be randomly distributed in an area, and a single well can find solutions with different redox potentials at various depths (HEM 1985).

It is believed that the Fe and Mn in groundwater (influencing turbidity) of several wells randomly distributed in the IRC are natural and originate from oxyhydroxides precipitated in discontinuities of crystalline rocks through which the recharged water flows. Occurrences of high-content Mn ore in the High IRC were studied by BELLON et al. (2019) and attributed to processes of supergene enrichment, while CALEGARI et al. (2020) show the occurrence of pellicles of Mn oxides (that are associated with Fe) filling discontinuities in the rocks, as faults and fractures in the south of Espírito Santo.

The Fe and Mn contents make the water unsuitable for different types of use at various points distributed randomly throughout the IRC. Although Fe is an essential element in animal and plant metabolism, in excess, it can form oxyhydroxide precipitates, which give color to the water, stain clothes, and form incrustation in pipes; therefore, it is undesirable in the domestic and industrial supply. Studies have shown that Mn can cause neurotoxic effects in children (BOUCHARD et al. 2007) and be associated with the presence of other dangerous metals in groundwater (BONDU et al. 2018). Some authors (e.g., ZHANG et al. 2020, USMAN et al. 2021) draw attention to the possibility of As dissolving in groundwater if it is adsorbed on Fe and Mn minerals, worsening water quality conditions. As was not analyzed in this work, and we do not expect to find this type of contaminant in the studied area; nevertheless, its investigation is recommended in locals with Fe and Mn anomalies, given the danger of this element. Another parameter that has yet to be evaluated is fluorine, as this anion has already been identified in high concentrations in groundwater from crystalline terrains (e.g., HALLET et al. 2015).

Although various components mentioned above may be of natural origin, coming from the rocks that form the aquifers, it is important to highlight that human interference needs to be considered. For example, corrosion of an old metal well casing can add Fe to the pumped water (HEM 1985). Even if a treatment is applied to reduce the dissolved Fe content, making the water more palatable, these wells are subject to the growth of ferrous bacteria, which are microorganisms that feed on Fe. These bacteria can coat the inside of the casing or any other submerged part of the plumbing. Furthermore, monitoring water quality to verify suitability for the different types of use provided for in environmental standards is a routine that needs to be followed by management institutions and water users.

6 CONCLUSIONS

Groundwater in crystalline terrains of the South of Espírito Santo State contains Cd, Co, Pb, and Zn within the limit allowed for the different types of use provided for in CONAMA Resolution 396/2008. On the other hand, according to the resolution above, the levels of Fe, Mn, and Na, in addition to turbidity and TDS, are above the maximum permitted limit for some uses.

The distribution pattern of the parameter values throughout the studied area varies in different ways. The increase in TDS and Na, as well as the other essential components of groundwater, obey the geomorphological, lithological, and climatic control, with enrichment in the central portion of the river catchment. Differently, Fe, Mn, and turbidity present anomalous values randomly distributed throughout the basin, probably due to the pedogenic enrichment of lateritic profiles and local structural control. The lack of adequate well-maintenance probably contributes to these changes.

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