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Hydrogeochemical modeling of fluoride contents in groundwater in outcrop area of Guarani Aquifer System, southern Brazil

Modelagem hidrogeoquímica de concentrações de fluoreto em águas subterrâneas em área de afloramento do Sistema Aquífero Guarani, sul do Brasil

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Abstract

Groundwater quality problems with high fluoride contents were studied in an outcrop area on a portion of Guarani Aquifer System (GAS), in the state of Rio Grande do Sul, southern Brazil. The methodology was based on the evaluation of tectonic structures lineaments and geochemical modeling of 13 groundwater physical-chemical data with anomalies of fluoride from tube wells. The lineaments trace and speciation code PHREEQC 3.3.5 used suggest the occurrence of distinct mineralogical contributions, in which the precipitation of carbonate minerals from the mineral structure of the GAS sandstone and cation exchange play a fundamental role in the hydrogeochemistry of fluoride. The results were analyzed by the main transects, which allowed the definition of characteristics of mineral dissolution and precipitation in the environment. The halite and sylvite showed dissolution tendencies along the traced transects, towards the mineral equilibrium. The fluorite mineral presented undersaturation with tendencies to mineral equilibrium and, possibly, precipitation in the most salinized waters. The applied methodology allowed the extraction of information for a better understanding of the hydrogeochemical dynamics of salinized waters and their water/rock interactions in outcrop area of the GAS, constituting a material to support the research of anomalous fluoride concentrations in groundwater and the practices of management of this important aquifer system.

Keywords: Groundwater; Geochemical modeling; Fluoride.

Resumo

Problemas de qualidade da água subterrânea com altos teores de fluoreto foram estudados em porção da área de afloramentos do Sistema Aquífero Guarani (SAG), no estado do Rio Grande do Sul, no sul do Brasil. A metodologia baseou-se na avaliação dos lineamentos das estruturas tectônicas e na modelagem geoquímica de 13 análises físico-químicas de águas subterrâneas de poços tubulares com informação de anomalias de fluoreto. O traçado dos lineamentos e a utilização do código de especiação PHREEQC 3.3.5 sugerem a ocorrência de contribuições mineralógicas distintas, em que a precipitação dos minerais carbonáticos oriundos da estrutura mineral do arenito do SAG e a troca catiônica exercem papel fundamental na hidrogeoquímica do fluoreto. Os resultados foram analisados pelos principais transectos, que permitiram determinar as características de dissolução e de precipitação no meio. A halita e a silvita apresentaram tendências de dissolução ao longo dos transectos traçados, em direção ao equilíbrio mineral. O mineral fluorita apresentou subsaturação com tendências ao equilíbrio mineral e, possivelmente, precipitação nas águas mais salinizadas. A metodologia aplicada permitiu extrair informações para melhor compreensão da dinâmica hidrogeoquímica das águas salinizadas e suas interações água/rocha em área de afloramento do SAG, constituindo um material para apoiar a pesquisa de concentrações anômalas de fluoreto na água subterrânea e para práticas de gestão desse importante sistema aquífero.

Palavras-chave: Águas subterrâneas; Modelagem geoquímica; Fluoreto.

INTRODUCTION

In some parts of Guarani Aquifer System (GAS), the occurrence of fluoride (F^-) in groundwater has attracted attention with fluoride concentration above 1.5 mg/L (0.079 milli-equivalent/liter), which is the maximum tolerance limit of fluoride on drinking water specified by the World Health Organization (WHO, 2011).

Fluoride concentrations are usually found in natural waters, and their high values are generally associated with underground sources. Concentrations are often found between 0.1 and 10.0 mg/L (Custodio and Llamas, 2001). According to Fawell et al. (2006), the most common minerals containing fluorine occur mainly in the form of fluorite (CaF_2), fluorapatite [$Ca_{10}(PO_4)_6F_2$] and cryolite (Na_3AlF_6).

The GAS is an important aquifer of the Paraná Basin and it is a part of a hydrogeological system responsible for the supply of fresh water for many activities. High fluoride concentration in the groundwater has been reported in many parts of GAS in Brazil, for example in the states of São Paulo, Paraná, Santa Catarina and Rio Grande do Sul, and it is a serious concern for the drinking water supply. The contents of fluoride in GAS have been extensively studied by Fraga (1992), Sracek and Hirata (2002), Marimon et al. (2013), Kern et al. (2008), Manzano and Guimaraens (2009), Silvério da Silva et al. (2014).

In Rio Grande do Sul, the occurrence of fluoride on GAS has been reported mainly in the central region (Santa Maria Formation and Sanga do Cabral Formation), where the concentration up to 11 mg/L was found. In this area, dental fluorosis is an endemic disease (Marimon et al., 2013).

In recent past, different statistical analysis and stable isotopes procedures have been used to identify the interrelationships between the chemical constituents of the water in the underground environment of GAS and to verify the main dynamics of the aquifer. However, the source of F^- is not a consensus among researchers in the area, as the arenitic rocks that compose the GAS are poor in this element.

Studies across the entire range of GAS have shown that the origin of the most saline waters are related to the dynamics of water movement in the aquifer, mainly due to upward flows from aquifers below the GAS that cause water mixing processes (Sracek and Hirata, 2002; Kern et al., 2008; Manzano and Guimaraens, 2009; Marimon et al., 2013). Kern et al. (2008) attributed the high concentrations of F^- in GAS due to the occurrence of pre-GAS water mixtures through fault zones and fractures that would be functioning as hydraulic connectors between these sediment packets.

This study aimed at contributing for the understanding of the complex relationships in the interaction between water and the underground environment, using for this purpose a knowledge on the integration of tectonic structures and geochemical modeling of groundwater with anomalies of fluoride to determine the speciation of dissolved chemical elements and its relationship with the system characteristics. Hence, the study analyzed the saline contributions from the aquifers adjacent to the GAS in their south portion, in the cities of Restinga Seca, Agudo, Paraíso do Sul and Novo Cabrais, in the state of Rio Grande do Sul.

MATERIALS AND METHODS

Description of the study area

Located in the eastern center of South America, in the Paraná and Chaco-Paraná sedimentary basins, the GAS is currently considered one of the largest groundwater sources in the world. It is estimated that the area covers approximately 1.2 km², occupying parts of Paraguay, Uruguay and Argentina territories and of eight Brazilian states (OAS, 2009).

The sedimentary constitution was formed during Jurassic and Triassic periods, in intercalations of layers of sandstones, having a lot of variable thicknesses. The OAS (2009) studies led to the identification of large areas with similar characteristics for the management of groundwater resources. This zoning was done mainly based on hydraulic characteristics, according to the type of aquifer, its natural quality, among others. The outcrop zone, located in the borders of the GAS, is a sandstone layer and generally an unconfined type, and may have characteristics of semi-confinement in some situations, which imply characteristics of recharge or groundwater discharge.

The confined zone was defined as the areas where the sandstone was confined by the Serra Geral basalt layer (Cretaceous), having the characteristic of fractured rock aquifer. The region chosen for this hydrogeochemical work involves the cities of Restinga Seca, Agudo, Paraíso do Sul and Novo Cabrais, in an area of 2,034 km², located in central region of the state of Rio Grande do Sul (Figure 1). The cities encompass two large hydrographic watersheds: the Vacacaí-Vacacaí-Mirim watershed and the Baixo Jacuí watershed.

Generally, in the recharge areas, the groundwater of the outcrop zone has a type with low mineralization and with low residence time, having mainly a low chemical evolution. These waters begin their mineralization of predominantly HCO_3-Mg and HCO_3-Ca types, proceeding to an intermediate confinement in which it evolves to HCO_3-Na waters (Machado and Freitas, 2005; Manzano and Guimaraens, 2009; Luiz and Silvério da Silva, 2017). When submitted to a high confinement or to mixture patterns, they have HCO_3-SO_4-Cl-Na, Cl-Na or SO_4-Na types, with high chemical evolution and residence time.

For Manzano and Guimaraens (2009), the origin of sulfate and chloride in saline groundwaters of GAS is mainly due to the dissolution of minerals associated with evaporite rocks rich in sulfates and chlorides, coming from deeper areas of the aquifer. Studies by Kern et al. (2008) in black shales in the Paraná Basin associate mineralogically materials with

quartz, illite, muscovite, kaolinite, smectite and significant amounts of organic matter. The authors suggest the dissolution of fluorite from the interaction of groundwater of the GAS with Permian and Devonian layers to explain the high concentrations of F⁻. These layers mainly of black shale belong to the Irati and Ponta Grossa Hydrostratigraphic Units in the Paraná Basin, which would be locally associated with the salinization of GAS groundwater.

The pre-GAS is a set of layers that form the basement of the GAS whose ages are comprised between the Medium to the Upper of Permian. Some units have a predominance of sandy strata like aquifers, while others, with a pelitic composition, correspond to aquitards (Freitas, 2016). In these layers, there is predominance of fine lithologies that may comprise siltstones, claystones, shales, pyro-bituminous shales and marls, interspersed with very thin, quartzous and quartzous carbonate cementous sandstone levels.

Structural geologic conditioning and database

In outcrop study region, the geologic conditioning is composed by the São Bento Group (Botucatu Formation) and Rosário do Sul Group (Caturrita, Santa Maria and Sanga do Cabral Formations). Overlying these formations there are the basalts of the Serra Geral Formation that compose the Serra Geral Aquifer System (SGAS). These basalt layers exert pressure on the sandstone layers of the GAS, forming areas where the Guarani aquifer is confined. In Table 1, a summary of the stratigraphic profile in the study area is shown.

The Santa Maria Formation has a Passo das Tropas Member (sandy fluvial facies) and an Alemoa Member (solid red claystone or silty claystone are practically impermeable, forming an aquiclude) in which regional fault systems influence the hydrological features in the GAS (Machado, 2005). In the Sanga do Cabral Formation, the lithologies are
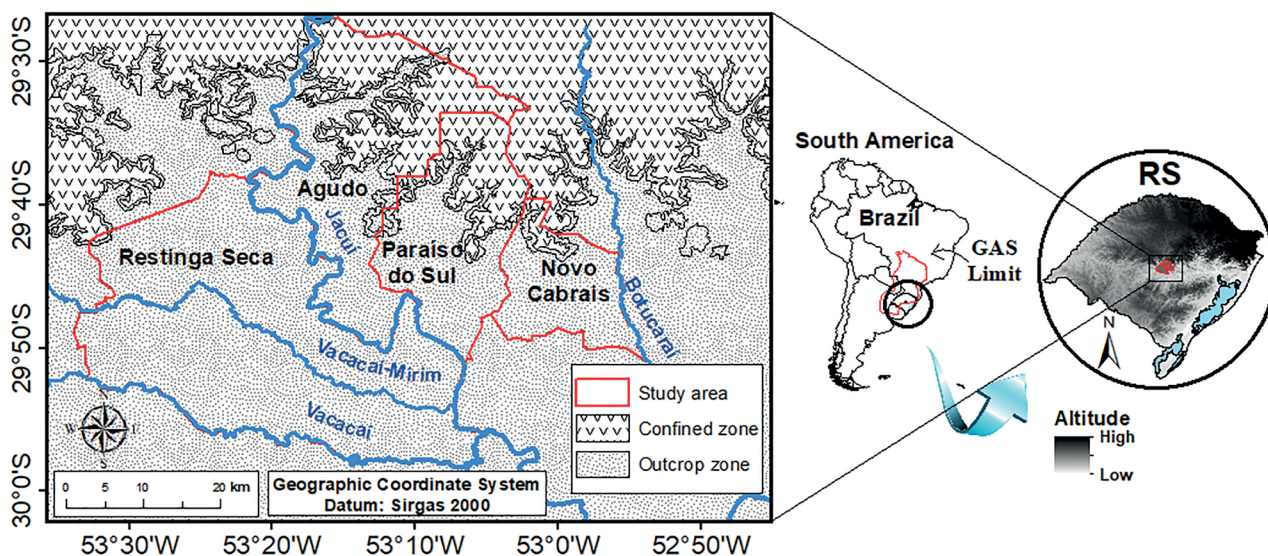

Figure 1. Map of study area with Guarani Aquifer System (GAS) limit and management zones.

Table 1. Stratigraphic profile in the study area.

Group	System	Formation	Geologic features
São Bento (Cretaceous)	Serra Geral Aquifer System	Serra Geral	Basalt layers with acid and/or basic composition (andesites, riodacites and rhyolite). The groundwaters circulate through fractures or small fissures
Rosário do Sul (Triassic and superior Permian)	Guarani Aquifer System	Botucatu	Aeolian sandstone, dominant quartz and feldspars and carbonates, cemented by silica or iron oxide.
		Caturrita	Sandstone, conglomerate, arenaceous silty and shale, containing fossil tetrapods and conifer trunks, continental environment, fluvial deposits and lacustrine deltas
		Santa Maria	**Alemoa Member:** floodplain facies rich in vertebrates **Passo das Tropas Member:** Sandy fluvial facies
		Sanga do Cabral	Predominant siltstone and claystone

variable, and may be locally sandy from medium to coarse granulometry or very fine interdigitated, with siltstones and clayey sandstones.

In Santa Maria Formation, Silvério da Silva et al. (2014) observed outcrop rocks that may be related to the formation of dikes or other discordant forms of outcropping volcanic rock. The authors reported the occurrence of 19 intrusive dikes of basic and/or alkaline composition, which are probably related to fault zones. The dikes that split the sedimentary rocks in outcrop area of GAS were observed in the sample collection campaign in Agudo municipality (shown in Figure 2), close to Jacuí river.

The groundwater flow in the studied area was previously evaluated through the potentiometric surface analysis, which demonstrated regional flow directions in southward direction, mainly to the south of the city of Restinga Seca (Luiz, 2017). However, the intrusive dikes (Figure 2) that split some layers of the sandstone eventually alter local flow directions and increase the residence time of these waters. In this study, the hydrogeochemical modeling was proposed from geological homogeneous blocks inferred by lineaments that took into account the geological features and main river stream alignments.

The characterization of the structural context of the land was made through the analysis of lineaments, with the aim of integrating the hydrogeochemical results and visualizing the tectonic features of the studied area. The lineaments identified in radar image were recognized according to their extent and orientation, using the shaded relief of the digital elevation model (DEM) (USGS, 2016) with 90 m for pixel of resolution and the geologic map (CPRM, 2007) of the investigated area.

The lineament traces were done in a 1:500.000 scale, and the structural lineaments resulted in a vector file in *shp* format extension with geographic coordinates of their extreme points. Subsequently, the data were exported to a spreadsheet for the calculation of the angles and production of the rosette diagram with the predominant directions of the lineaments.

The lineaments were interpreted as well as the used directions of luminosity for the shadings are illustrated in Figure 3. Thus, the lineaments analyses sought to infer the basic regional structures that define the main tectonic features and that may be related to fractures or contact between different layers. In total, 76 lineaments were drawn and 45 reached the area of interest of the research.

The rosette diagram shows the predominant directions N20º-50ºW and N60º-70ºE, demonstrating consistency with other studies carried out in the Paraná Basin. For Zalán et al. (1990), the Paraná Basin is dominated by lineaments and/or linear tectonic elements that are oriented in three main directions: N45º-65ºW, N50º-70ºE and E-W. In accordance to Soares et al. (2007) and Descovi Filho (2015), the NW and NE lineaments are highly recurrent in Paraná Basin among different spatial data sources, revealing large tectonic blocks that are able to restrict water flow and the formation of hydrogeological cells. Thus, the structural blocks in sedimentary rocks characterize certain stratigraphic
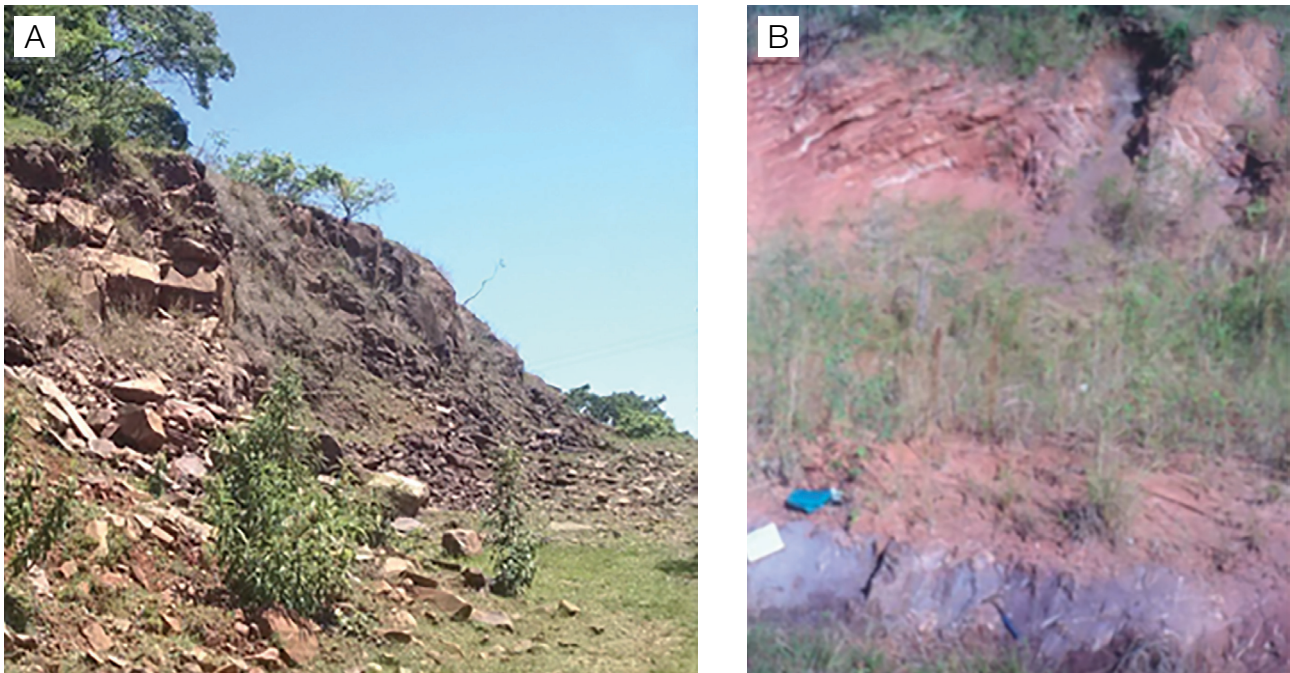
Source: Luiz (2017) and Silvério da Silva et al. (2014).
Figure 2. Dikes splitting the Santa Maria Formation in (A) Passo das Tropas Member and (B) Alemoa Member.

homogeneity (Da-Rosa and Faccini, 2005), which allows to establish hydrochemistry correlation on geologic conditions. In accordance to Kim and Jeong (2005), the geologic structure is an important factor that control the occurrence of high F⁻ groundwaters.

From the mapping of the lineaments and analysis of the main directions, aiming to establish the fundamental characteristics of hydrogeochemical evolution of the samples with high fluoride contents, it was chosen to execute the simulations of the data through A-A', B-B' and C-C' transects.

The A-A' and B-B' transects follow the direction patterns (NW-SE) of the Vacacaí-Mirim and Jacuí rivers, respectively, and were also observed by studies of Da-Rosa and Faccini (2005), once these lineaments are responsible for the delimitation of large structural blocks of the study area, which can be visualized in Figure 3. The C-C' transect crosses the municipality of Novo Cabrais, following the NE-SW direction.

A database of groundwater quality of 13 wells was obtained. The used hydrochemical values were obtained from pre-existing data of the Mineral Resources Survey of Brazil (CPRM, 2016), and from sample of the studied area. *In situ*, a global positioning system (GPS Garmin Colorado 400T) was used for locating wells in the area. Also, temperature and electrical conductivity (EC) (Hanna HI 933000) were taken.

The collected samples were submitted for analysis at the Laboratory of Chemical and Industrial Environmental Analysis (LAQIA) of Universidade Federal de Santa Maria (UFSM). The technical procedures used to determine hydrochemical concentrations were inductively coupled plasma optical emission spectrometry (ICP-OES), flame atomic absorption spectrometry (FAAS) and potentiometric titration. The fluoride was determined by a selective ion electrode. All procedures followed the *Standard Methods for the Examination of Water and Wastewater* (APHA, 1998).

Aqueous speciation modeling

In general, the modeling of chemical interactions can be described with approaches based on thermodynamics or kinetics. In the thermodynamic approach, assuming the equilibrium of the system, the reactions are expressed by the law of mass action, that is in thermodynamically reversible theory and independent of time.

To characterize the dynamics of hydrogeochemical processes in groundwater, speciation calculations were performed using the chemical parameters of the analyses. Speciation calculations use chemical water data to calculate the distribution of species distributed in solution through a model based on ionic associations and expressions of Debye Hückel (Parkhurst and Appelo, 1999; Drever, 1997; Merkel and Planer-Friedrich, 2012). The most important results of the calculations of speciation in the hydrogeochemical studies are the indexes of mineral saturation, that
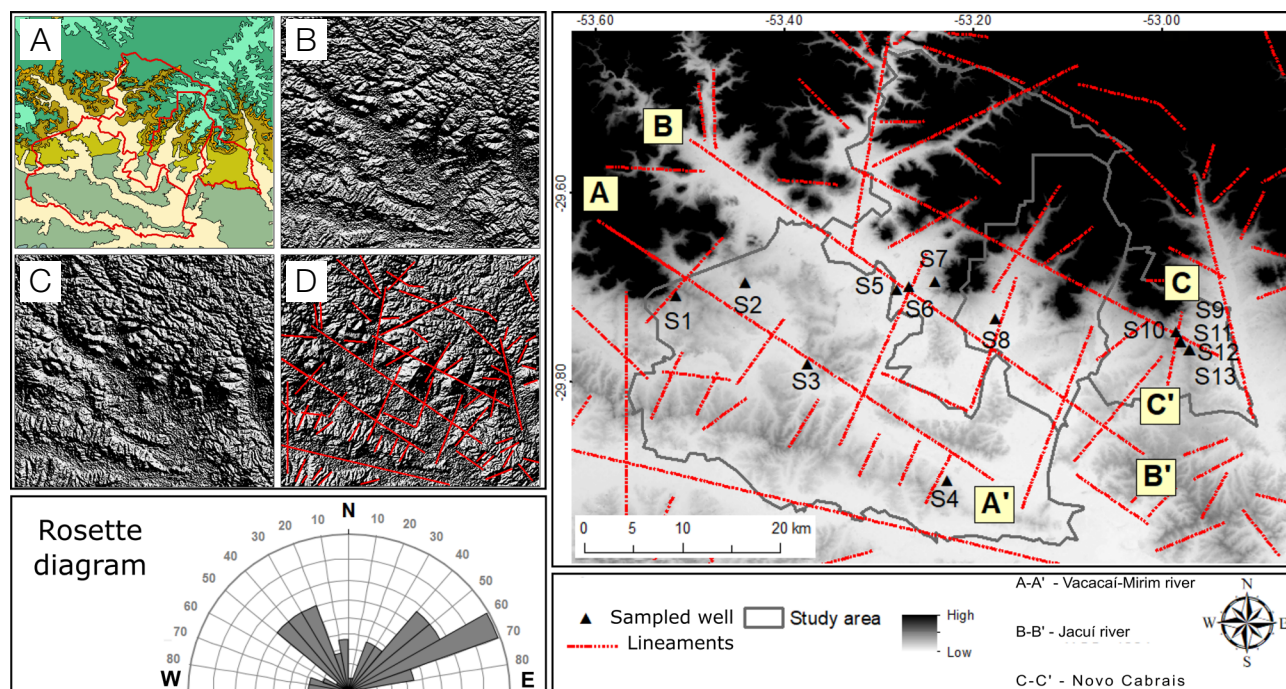

Figure 3. Sample location with mapping of the structural lineaments from the geological map (A) and shading of digital elevation model (DEM) in the (B) N (0º), (C) NE (45º) and (D) NW (315º) directions. On the right side, the lineaments are presented with the proposed main transects.

relate the characteristic ionic activity of the solute and its respective solubility.

The saturation index (SI) close to zero indicates equilibrium of the respective mineral in solution. When negative, it indicates undersaturation and tendency for dissolution; when positive, it indicates saturation and possible precipitation (Ball and Nordstrom, 1991; Merkel and Planer-Friedrich, 2012).

Based on the law of mass action, it is possible to obtain the product of solubility K as being the maximum possible solubility (based on solubility equilibrium data obtained experimentally at 25ºC and 1 atm) and being equivalent to the product of ionic activity product (IAP). The IAP values depend on mineral, solvent, pressure, temperature, pH and the ions previously dissolved in water (Merkel and Planer-Friedrich, 2012). From the logarithm of the quotient between the calculated IAP and the solubility product K, the SI of each sample is obtained as follows in Equation 1:

$$SI = \log IAP/K_{mineral} \qquad (1)$$

According to Custodio and Llamas (2001), natural changes in chemical composition of groundwater are strongly characterized by the reactions of dissolution of the surfaces of rocks and precipitation of dissolved substances in water, highlighting the etching mechanisms minerals (hydration and hydrolysis) that promote dissolution and precipitation. These weathering reactions are generally reversible and heterogeneous, and the solubility of a mineral is defined as the mass of mineral that can be dissolved in a standard volume of solvent.

The calculations were made by the geochemical modeling code PHREEQC 3.3.5 (Parkhurst and Appelo, 1999), indicating the possible mineral distributions that are found in these waters. The thermodynamic database *phreeqc.dat*

was used, trying to evaluate if the mineral balance would be favorable for the occurrence of dissolution or precipitation processes. Several studies have successfully applied geochemical modeling to study fluoride origin, as Carrillo-Rivera et al. (2002), Kim and Jeong (2005), Guo et al. (2007) and Coetsiers et al. (2008).

The main mineral contributions analyzed and evaluated in this study were halite (NaCl) and sylvite (KCl) halides, sulphated minerals gypsum [$Ca(SO_4)H_2O$] and anhydrite ($CaSO_4$), carbonate minerals calcite ($CaCO_3$) and dolomite ($MgCO_3$), as well as the mineral fluorite (CaF_2). Thus, in this paper, hydrogeochemical modeling was used to determinate the main control of geochemical processes that are determinant in underground environment. Finally, the correlation of the ionic strength on the mineral dissolution capacity in these waters was evaluated.

RESULTS AND INTERPRETATION

Field and experimental investigations

The obtained concentrations of groundwater physical-chemical parameters of 13 wells from sample collection and CPRM (2016) database are shown in Table 2. The ionic parameters are in milliequivalent per liter (meq/L) and present low error of cations and anions balance, demonstrating quality in the analytical results. The water type for each sample is mainly Na-HCO_3, Na-SO_4-Cl and Na-Cl-SO_4^{-2} types.

From the analytical results observed in Table 2, it can be seen that these waters have alkaline characteristics with pH ranging from 8.1 to 8.9. Fluoride concentrations ranged from 0.12 to 0.29 meq/L (2.2 to 5.6 mg/L), demonstrating the high concentrations of this element.

Table 2. Analytical results of groundwater of 13 tubular wells with high fluoride contents.

Sample	City	pH	F⁻	Na⁺	K⁺	Ca²⁺	Mg²⁺	Cl⁻	SO₄²⁻	HCO₃	EC (µS/cm)	Water type
S1	Restinga Seca	8.5	0.12	7.79	0.02	0.25	0.05	1.35	2.25	3.67	804	Na-HCO₃
S2	Restinga Seca	8.8	0.14	8.31	0.02	0.10	0.05	1.72	2.58	3.47	847	Na-HCO₃
S3	Restinga Seca	8.9	0.29	10.53	0.03	0.15	0.03	3.27	2.81	3.54	1080	Na-HCO₃-Cl
S4	Restinga Seca	8.8	0.13	44.59	0.06	0.85	0.08	22.85	9.83	3.03	4257	Na-Cl
S5	Agudo	8.1	0.17	23.71	0.00	1.65	0.25	11.37	11.93	2.95	3740	Na-SO₄-Cl
S6	Agudo	8.1	0.22	28.01	0.10	3.51	0.38	16.50	15.05	2.97	4208	Na-Cl-SO₄
S7	Agudo	8.2	0.22	36.19	0.02	3.89	0.58	19.13	20.65	1.54	2735	Na-SO₄-Cl
S8	Paraíso do Sul	8.3	0.26	43.37	0.08	2.51	0.12	25.47	24.34	1.75	5206	Na-Cl-SO₄
S9	Novo Cabrais	8.8	0.16	10.79	0.02	0.16	0.05	2.93	2.08	4.28	1076	Na-HCO₃
S10	Novo Cabrais	8.6	0.15	14.36	0.02	0.27	0.03	5.30	4.66	3.52	1522	Na-Cl-SO₄
S11	Novo Cabrais	8.7	0.16	12.79	0.03	0.18	0.03	5.81	3.93	4.68	1630	Na-Cl-HCO₃
S12	Novo Cabrais	8.6	0.17	13.05	0.00	0.31	0.18	4.77	3.73	4.36	1470	Na-Cl-HCO₃
S13	Novo Cabrais	8.6	0.19	13.44	0.05	0.21	0.03	5.30	3.29	5.37	1470	Na-HCO₃-Cl

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The analyzed EC of groundwater ranged from 804 to 5,206 µS/cm, indicating waters from moderate to advanced process of salinization. On the side of the cations, the sodium as major ion is evidenced, predominating in the evaluated waters. Also, low concentrations for potassium, calcium and magnesium were observed. Generally, the calcium is an abundant element in most natural waters and rocks, occurring mainly in the minerals calcite, aragonite and dolomite (Hem, 1985). Santos (2008) points out values ranging between 0.5 to 5.0 meq/L in groundwater and can reach up to 24 meq/L in ocean waters. The low concentrations of this ion that has been found in this study, allied to high alkalinity, may indicate the occurrence of carbonate dissolution processes or cation exchange with sodium.

On the side of the anions, the meq/L analysis shows the predominance of bicarbonate in less mineralized waters (EC between 804 and 1,080 µS/cm) and predominance of chloride or sulfate in more mineralized waters (EC > 1,080 µS/cm). The origin of these elements may be linked to the oxidation of sulfur present in the deeper rocks and the leaching of sulfate compounds such as gypsum and anhydrite, mainly due to the dissolution of minerals associated with sulfate and chloride rich in evaporite minerals (Manzano and Guimaraens, 2009).

Thus, it is possible to infer that these waters are being enriched, mainly, with the elements sodium, calcium, sulphate and chloride, probably, from upward flows of water from deeper aquifers, evidencing mixing patterns. From the physical-chemical data of Table 1, the hydrogeochemical modeling of these waters was carried out with the purpose of evaluating the possible mineral contributions of the aquifers adjacent to the GAS at each point.

Hydrogeochemical modeling

The first stage to carry out the chemical speciation calculations was done by constructing an algorithm with the command blocks required by the PHREEQC 3.3.5 modeling code. The analyses of hydrochemical mineral saturation and of other calculations of speciation with fluoride anomalies were performed from the traced transects (Figure 3), according to the direction of the main lineaments. Therefore, the modeling results are discussed through the profile of transects A-A', B-B' and C-C'. Each digital cross section presents a transversal view of the transects, correlating the terrain surfaces that were obtained by means of the DEM with their respective well depths in the GAS sandstone framework.

A-A' Transect: Vacacaí-Mirim River

The A-A' transect, in the NW-SE direction, which initially covers the confined zone of the GAS, is represented in Figure 4 by means of its geologic cross section. Its topographic dimensions extracted from the DEM were in the order of 470 meters in the highest parts (confined zone) and range between 30 to 50 meters in the lower parts where the Vacacaí-Mirim river flows (outcrop area).

The depths of the tubular wells reached -19 to -83 meters below sea level, showing that the S3 and S4 capture the waters of deeper zones of the sandstone. Hydrochemically, the tendency of salinity growth in the southeast direction of this lineament is observed, evidenced by its increasing electrical conductivities. It is important to note that the salinity of
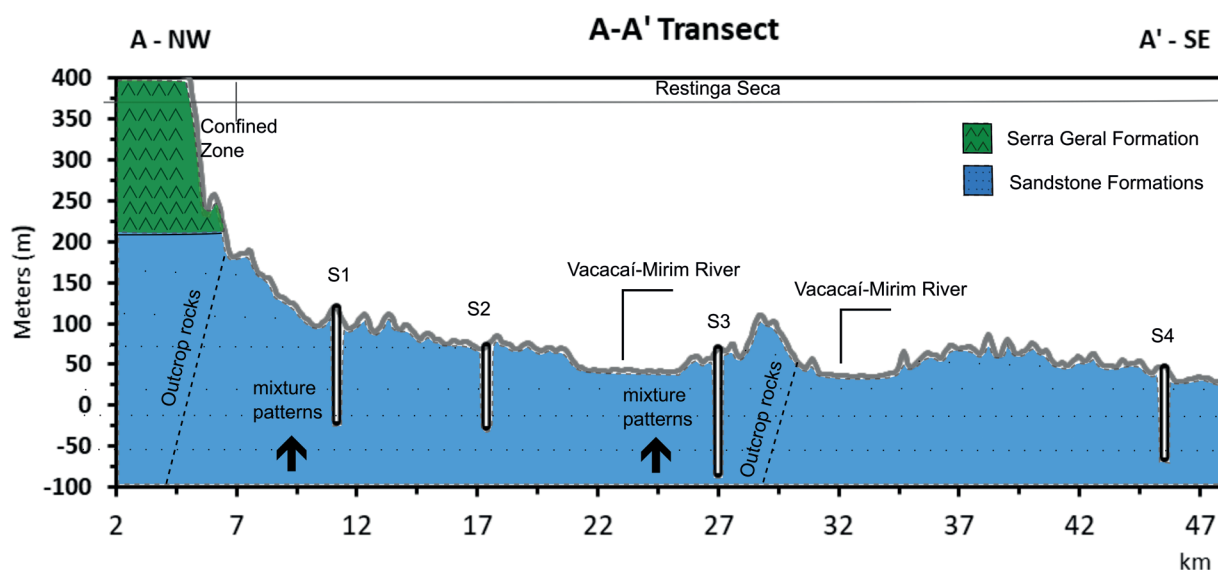

Figure 4. Geologic cross section in A-A' transect with well depths. Topographic profile obtained by digital elevation model (DEM).

the waters increased according to the well depth and the S3 sample had the highest concentration of fluoride (5.6 mg/L).

The mineral speciation calculations of the samples with fluoride anomalies illustrated in the graphs of Figure 5, executed by the modeling code PHREEQC 3.3.5, present the distinct tendencies of dissolution and mineral precipitation along the A-A' transect. The dissolution of gypsum, anhydrite, halite and sylvite minerals is evident with increasing chloride and sulphate concentration in groundwater over bicarbonate until chloride be the dominant anion in the water.

All SI calculated on the Figure 5A graph indicates undersaturated state for gypsum, anhydrite, halite and sylvite minerals, and their tendency to equilibrium direction in the most salinized waters along the A-A' transect became evident. The increase in sulfate, chloride, calcium and sodium concentrations along A-A' transect may be influenced by the dissolution of these minerals in deeper layers of the GAS or by the pre-GAS. For Manzano and Guimaraens (2009), the SI for gypsum and halite increase at points where there are upward flows of deep salt water, but no water saturated with these minerals was found at any point in the study.

For the calcite mineral ($CaCO_3$), the calculated SI was very close to the equilibrium with values ranging from 0.06, -0.08, 0.14 and 0.55 respectively, showing trends for the saturation of this carbonate mineral. Dissolution processes of carbonated minerals in less mineralized groundwaters are recurrent at GAS, since these minerals are common in the aquifers that compose it. Calcite dissolution consumes CO_2 and could control the saturation index with respect to other minerals. As the water salinizes during its course, the tendency is to enter into a mineral equilibrium and, subsequently, precipitate.

For the fluorite, the samples presented undersaturated mineral with different dissolution tendencies for this mineral. The S3 sample showed the highest tendency for saturation conditions since it has the highest fluoride concentration detected. When looking at the types of groundwater in A-A' transect line, the hydrochemical evolution, in which

$Na-HCO_3$ dominates in the tubular well S1 and S2, in the S3 sample dominates the $Na-HCO_3-Cl$, and in sample S4 becomes strictly Na-Cl.

B-B' transect: Jacuí River

The hydrogeochemical modeling in B-B' transect was performed from the samples S5, S6 and S7, going southeast of the municipality of Paraíso do Sul, where the sample S8 is located (Figure 6). The groundwater of these localities was the most salinized (EC between 2,735 and 5,206 µS/cm), demonstrating hydrochemical types with dominant sulfate or chloride by the anions and sodium by the cations side.

Along B-B' transect, outcrop rocks that may be related to the formation of discordant forms of outcropping volcanic rock have been observed. These dikes may be functioning as a hydraulic barrier, influencing the underground flow directions and favoring the mixing of waters. In addition, they can promote the increase of their residence time, concentrating the chloride, sulphate and sodium ions. Gouvêa da Silva (1983) points out that water mixtures can be caused by sedimentary layers split by basic dikes. These occur at various points of the studied area, such as Restinga Seca and Novo Cabrais (Silvério da Silva et al., 2014).

In the Figure 7 graphs, the SI calculated in transect B-B' for the minerals gypsum, anhydrite, halite, sylvite, calcite, dolomite, fluorite and CO_2 (g) are presented. The sulphated minerals gypsite and anhydrite showed undersaturation in the environment with tendencies for equilibrium. The SI values presented in Figure 7A demonstrate more significant contributions of these minerals. Likewise, the halite and sylvite halides presented closer values to the equilibrium than in A-A' transect, demonstrating higher possibility of contributions of these minerals in the chemical composition of the water.

Hence, it is possible to observe the mineralogical contribution of some sulfated and chlorinated minerals in the more mineralized waters of GAS. When analyzing the sulfate and chloride concentrations in the samples of B-B' transect, it is noted that they are approximately equal ($Cl^- \approx SO_4^{-2}$) and
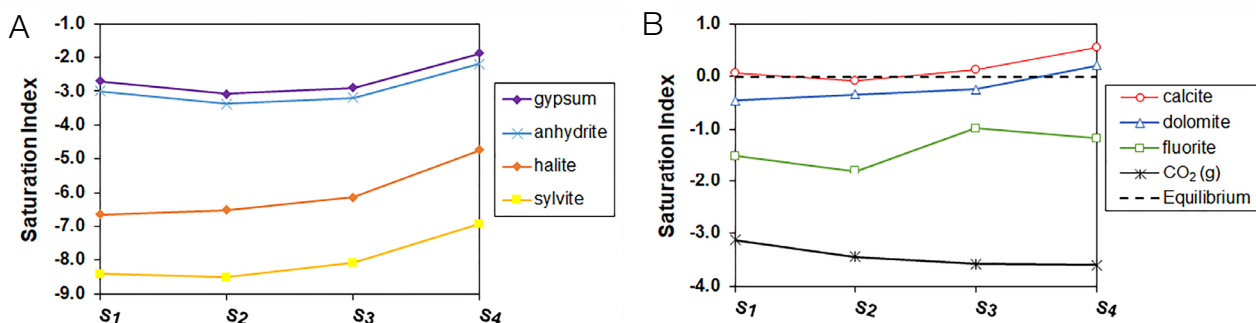

Figure 5. Graph of saturation index (SI) mineral in transect A-A' for gypsum, anhydrite, halite, sylvite, calcite, dolomite, fluorite and CO_2 (g).

this provides a possible indication of influence of chlorinated and sulphated evaporite rocks (Manzano and Guimaraens, 2009) in a process of concentration of salts in the direction of the groundwater flow, indicating the advance in the saline concentration process.

For the calcite mineral, in each well, saturation tendencies in solution were presented, with calculated SI of 0.26, 0.41, 0.15 and 0.17 respectively, indicating the occurrence of calcite precipitation in the environment. Gaciri and Davies (1993) demonstrate through literature research that the concentration and availability of Ca^{2+} influence the F^- level of water, but mention that the way fluoride is present in carbonate and phosphate structure has not been solved.

For Genxu and Guodong (2001), alkaline conditions may cause carbonate minerals to precipitate, favoring the dissolution of fluorite and the decrease of Ca^{2+} content in solution. Thus, the low Ca^{2+} concentration in water and their alkaline environment could explain the increase of F^- in

groundwater. If Ca^{2+} precipitates first as carbonate (higher solubility), the waters become rich in F^-, since the solubility of the fluorite is lower. In other words, calcite precipitation can reduce the Ca^{2+} concentration in groundwater and promote the dissolution of fluorite. This case has already been observed in several other geochemical studies (Fraga, 1992; Kim and Jeong, 2005; Chae et al., 2007; Guo et al., 2007; Marimon et al., 2013).

The fluorite mineral presented the indexes closest to the chemical equilibrium in this study, with SI that varied from -0.58, -0.07, -0.08 and -0.16 respectively, demonstrating the reactions in the fluorite equilibrium direction. However, calcite precipitation occurs before the fluorite precipitation due to its higher solubility, removing the fluoride ions from the environment.

Thus, considering the saturation pathways for calcite, both in A-A' and B-B' transects, it is possible to affirm that the calcium concentrations in these waters are strongly influenced
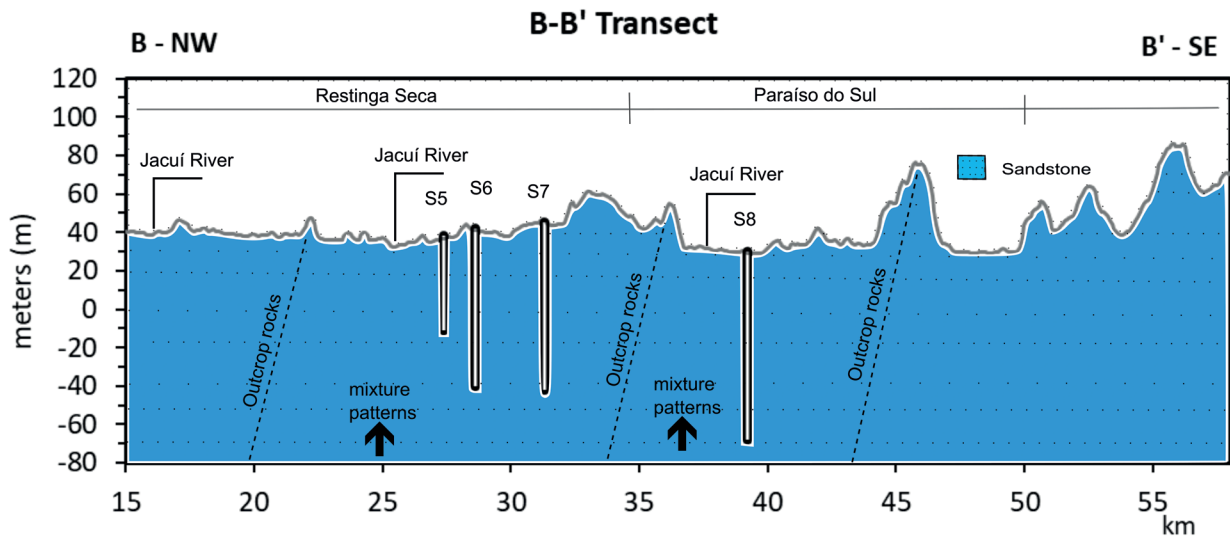

Figure 6. Geologic cross section of B-B' transect with well depths. Topographic profile obtained by digital elevation model (DEM).
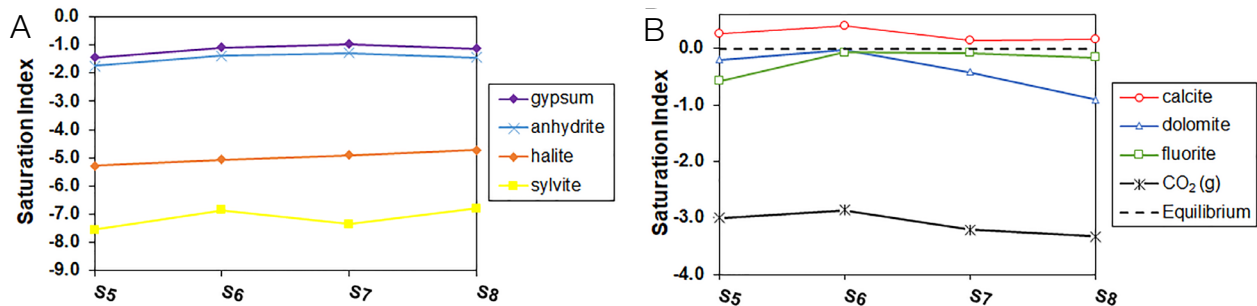

Figure 7. Graph of saturation index (SI) mineral in B-B' transect for gypsum, anhydrite, halite, sylvite, calcite, dolomite, fluorite and CO_2 (g).

by calcite, which, in the process of precipitation, removes calcium from the system. In addition to these processes, studies carried out in other portions of the GAS suggest the occurrence of cation exchange, mainly between sodium and calcium, evidenced by the high concentration of sodium in relation to chloride and calcium (Sracek and Hirata, 2002; Manzano and Guimaraens, 2009; Gastmans et al., 2010). The low concentrations of calcium generate favorable conditions for the dissolution of fluorite (Hem, 1985) (evidenced by the SI calculated for fluorite) causing the release of fluoride in the water, raising its concentration in solution.

C-C' transect: Novo Cabrais municipality

The hydrogeochemical modeling in the C-C' transect was performed from the samples S9, S10, S11, S12 and S13 in the NE-SW direction (Figure 8), close to the Botucaraí river, in Novo Cabrais municipality. These wells are linked to lineaments between the tectonic blocks formed by the Botucaraí river and the Jacuí river. The EC of groundwater analyzed in this transect, ranged from 1,076 to 1,630 µS/cm, and

fluoride contents ranged from 2.9 to 3.6 mg/L. The depths of the tubular wells reached -15 to -60 meters below sea level.

In Figure 9, the SI calculations for the main minerals were performed. Hydrochemically, no large trends variation was observed, since these wells are very close to each other. The water types become mostly Na-HCO$_3$ and Na-Cl-SO$_4$ or Na-Cl-HCO$_3$, showing the increments in chlorate and sulfate.

The results of the SI calculation for the sulphated and chlorinated minerals gypsite, anhydrite, halite and sylvite present undersaturation for all the evaluated minerals, in which small variation of SI was evidenced between the tubular wells with fluoride anomalies of the municipality.

In general, the calculated SI remained constant, especially for halite and sylvite halide salts which had SI average of -5.8 and -7.8, respectively. For gypsum and anhydrite, the SI averages were around -2.7 and -3.0, respectively.

As in the A-A' and B-B' transects, groundwater with fluoride anomalies in the municipality of Novo Cabrais presented precipitation trends for calcite with SI in the order of 0.22, 0.12, 0.04, 0.12 and 0.26, respectively. For the mineral dolomite, the SI presented saturation pathways in the samples S9
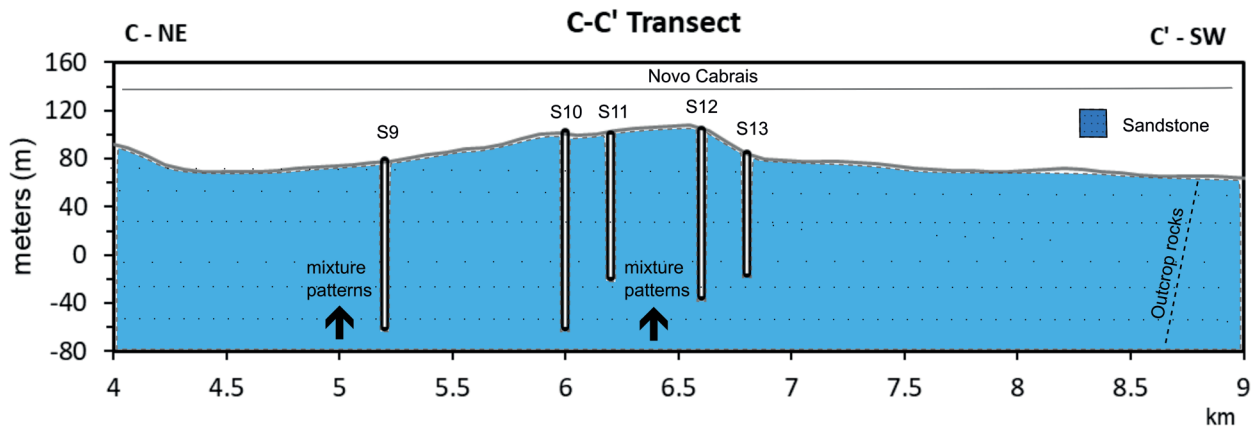

Figure 8. Geologic cross section of C-C' transect with well depths. Topographic profile obtained by digital elevation model (DEM).
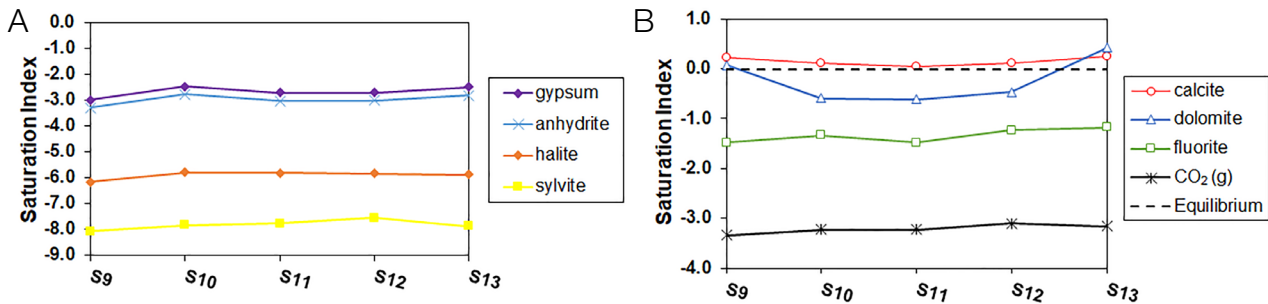

Figure 9. Graph of saturation index (SI) mineral in C-C' transect for gypsum, anhydrite, halite, sylvite, calcite, dolomite, fluorite and CO$_2$ (g).

and S13 and undersaturation in the remaining wells. The SI for the mineral fluorite remained between -1.48 (S9) and -1.18 (S13), indicating that these waters are undersaturated for this mineral, so it would not precipitate in the solid form.

Hydrochemistry and geochemical features

From the results presented in the proposed transects, some intrinsic processes of the system can be highlighted. All SI calculated for calcite in groundwater with fluoride anomalies were positive, indicating saturation trend of this mineral in these waters. Previous studies on less mineralized GAS water in this region have diagnosed calcite undersaturation and cation exchange (Luiz and Silvério da Silva, 2017). In addition to this characteristic, the authors reported the super-saturation of the clay-minerals illite, smectite and kaolinite, and the alkalinization of the waters (pH range reached 10.1).

Calcium concentrations in groundwaters with fluoride anomalies are strongly regulated by the precipitation of calcite and by cationic exchanges with sodium, causing calcium to be removed from the system, and its concentration decreased and sodium concentration increased. This fact generates favorable conditions for the dissolution of fluorine minerals, which causes the release of fluoride into the water.

The SI calculated for the fluorite were all negative, demonstrating undersaturation of this mineral in these waters. Fluorite saturation indexes below zero were diagnosed in many parts of the GAS (Sracek and Hirata, 2002; Manzano and Guimaraens, 2009; Marimon et al., 2013). No saturated groundwaters were found with this mineral in any location. However, according with Hem (1985), in thermal springs, positive SI values of fluorite can be found.

Thus, it is possible to affirm that fluorite does not precipitate, because it does not find favorable conditions to do so, since the geochemical processes of calcite precipitation and cation exchange occur before, being alkalinity and pH fundamental conditioning factors of the process. In fact, by observing the relationship of alkalinity and pH with the SI calculated for the fluorite shown in Figure 10, we can see

this finding, in which the SI of the fluorite approaches equilibrium in waters with lower alkalinity and pH.

To Hem (1985), in waters with higher amounts of calcium, the maximum concentration that the fluoride can reach before precipitation, based on its characteristic of ionic activity and normal conditions of temperature and pressure, is around 3.1 mg/L. It also emphasizes that higher concentrations of fluoride in natural waters can be influenced by ionic strength of the solution and complexing effects.

In this perspective, the ionic strength was considered as being a total parameter of the ionic interactions, since it is calculated as the half of the sum of the moles products of each species and their respective charge. The ionic strength was calculated in each sample based in the concentration of electrolytes in solution (Figure 11A). It's known that ionic strength affects important properties such as ion dissociation or solubility of salts. There are several potential solubility controls that can limit the dissolved fluoride concentration in water in which calcium concentration is one of the most important.

In the A-A' transect, the graph of Figure 11A demonstrates an increase in ionic strength in the southeast direction, especially at the most southerly point of the transect (S4), reaching a value of 0.045. Likewise, a trend of ionic strength growth along transect B-B' was observed. In this transect, the highest calculated values of ionic strength were identified in this study, varying from 0.031 to 0.051. In the C-C' transect, the ionic strength of the samples remained relatively constant, ranging from 0.012 to 0.019.

Gouvêa da Silva (1983), in her hydrochemical study in northern GAS, reported the increase of ionic strength and sodium concentration as a function of the increase of fluoride concentrations. For the author, raising the ionic strength could result in a greater ability to dissolve trace minerals. In fact, when evaluating the graphs of Figures 11B and 11C, an increase of the sodium and fluoride concentrations was observed as a function of the ionic strength.

The alkalinity, on the other hand, presented smaller values of ionic strength as a function of increments of its concentrations (Figure 11D). This fact is related to the
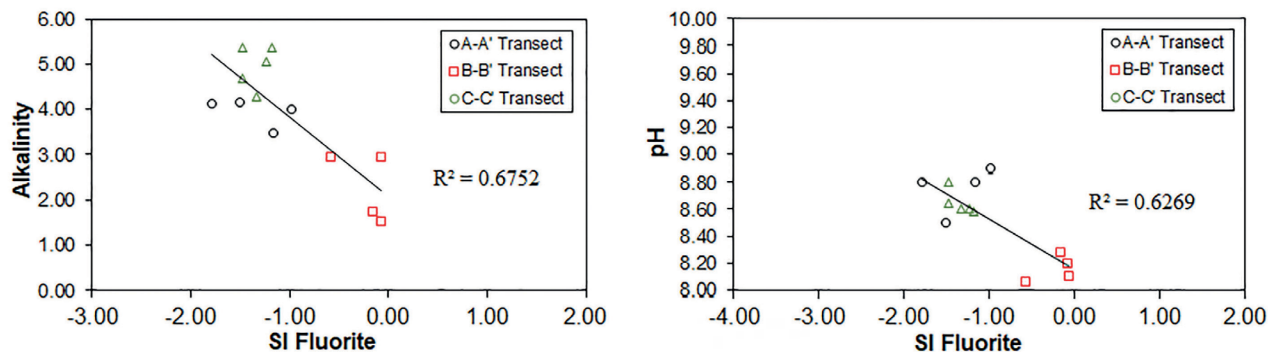

Figure 10. Graphs of the saturation index (SI) calculated of fluorite and relation with alkalinity and pH.

precipitation processes of calcium carbonate minerals, which generate decrease in the alkalinity of the water and control the concentrations of the smaller ions in the hydrogeochemical processes.

High values of ionic strength may be related to hydrochemical alterations of the groundwater, since they affect important properties in the environment, such as to facilitate the processes of ionic dissociation or alter the mineral solubility. So, it is possible that minerals not evaluated in this work may be contributing to the groundwater chemistry in the aquifer. However, the analysis used in this study allowed us to evaluate the hydrochemical evolution of groundwater with fluoride high contents and its relationship with the main minerals found in the underground environment.

CONCLUSIONS

The integration of hydrogeochemical and structural lineament analyses of the aquifer allowed the evaluation of the geochemical processes resulting from the mixing of groundwater in outcrop area of the GAS. The occurrence and the direction of large tectonic blocks of the Vacacaí-Mirim and Jacuí rivers showed association with the hydrochemical data evidenced both by the increase of the salinization of the groundwaters and by the ionic strength along the underground

flow. The blocks have a tectonic control with predominant lineaments according to directions N60º-70ºE and N20º-50ºW.

The results of hydrogeochemical modeling of the main minerals, analyzed from A-A', B-B' and C-C' transects, allowed the determination of the dissolution characteristics of chlorinated and sulphated minerals, releasing sodium, chloride, sulfate and calcium ions in groundwater. Calcium free ions precipitate in the form of calcite, decreasing alkalinity and making water poor in calcium, favoring a conducive environment for the elevation of fluoride contents.

Considering the fluorite, all the analyses presented undersaturated mineral with different dissolution tendencies. However, the most saline waters, especially those of transect B-B', have presented greater tendencies to mineral equilibrium, evidenced by the calculated SI values. Also, a correlation between ionic strength and fluoride contents was noted, especially in B-B' transect, where groundwater reaches high concentration of this ion.

ACKNOWLEDGEMENTS
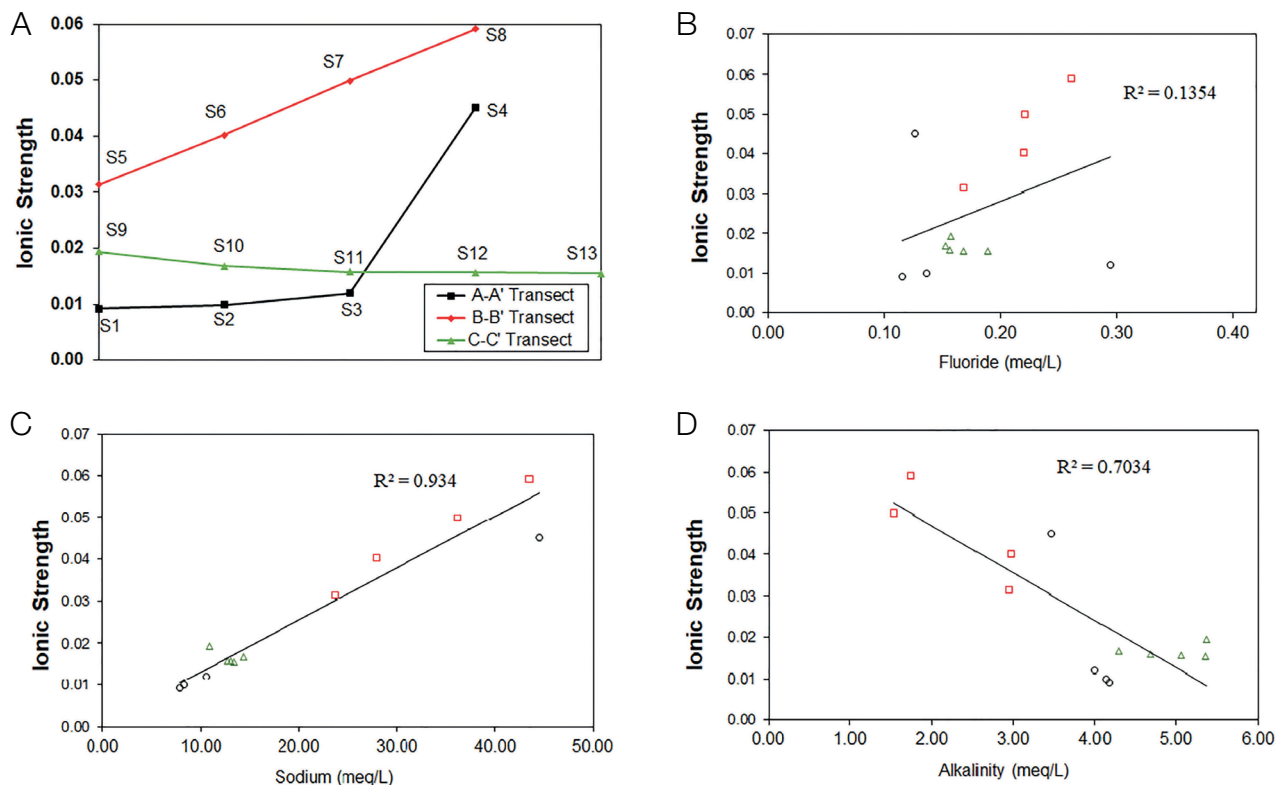
Figure 11. Graphs of the ionic strength calculated for the hydrochemical and its relation with major ions.

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