

Research Article

Fluoride in the Serra Geral Aquifer System: Source Evaluation Using Stable Isotopes and Principal Component Analysis

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Groundwater with anomalous fluoride content and water mixture patterns were studied in the fractured Serra Geral Aquifer System, a basaltic to rhyolitic geological unit, using a principal component analysis interpretation of groundwater chemical data from 309 deep wells distributed in the Rio Grande do Sul State, Southern Brazil. A four-component model that explains 81% of the total variance in the Principal Component Analysis is suggested. Six hydrochemical groups were identified. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were analyzed in 28 Serra Geral Aquifer System samples in order to identify stable isotopes patterns and make comparisons with data from the Guarani Aquifer System and meteoric waters. The results demonstrated a complex water mixture between the Serra Geral Aquifer System and the Guarani Aquifer System, with meteoric recharge and ascending water infiltration through an intensive tectonic fracturing.

1. Introduction

In the last several decades, the global water consumption has dramatically increased, especially for agriculture, water supply, and industrial uses. This paper examines the fluoride content in water from the southernmost region of the fractured subcontinental Serra Geral Aquifer System (SGAS), an important aquifer that supplies a large amount of water for an economic developed region in Southern Brazil.

Fluoride content in water is beneficial to human health and in a moderate concentration (0.7–1.2 mg/L) prevents dental cavities. When used in excess can be toxic causing human and animal dental and skeletal fluorosis, which has been detected in China [1, 2], India [3], Kenya [4], and Israel [5], among other countries. The drinking water limit recommended by the World Health Organization for fluoride

is 1.5 mg/L [6]. In the study area, the SGAS fluoride average concentrations are around 0.24 mg/L, with a minimum value of 0.02 mg/L and the highest at 3.03 mg/L.

The SGAS overlies the Guarani Aquifer System (GAS; [7]), which has been the focus of several recent studies due to its spatial extent and storage potential as a transboundary aquifer [8]. The area covered by the SGAS in Brazil, Uruguay, Argentina, and Paraguay is equivalent to 1,200,000 km² (Figure 1). In Brazil, these groundwater resources should be efficiently managed to protect its water potential and quality. The climate in the study area ranges from subtropical to temperate, with precipitation average of 1,550 mm/year.

The SGAS reaches its maximum thickness of about 1,800 m along the central axis of the Parana Basin, located in the Sao Paulo State. In the Rio Grande do Sul State, this aquifer has a wedge shape, ranging from 1,000 m in the eastern

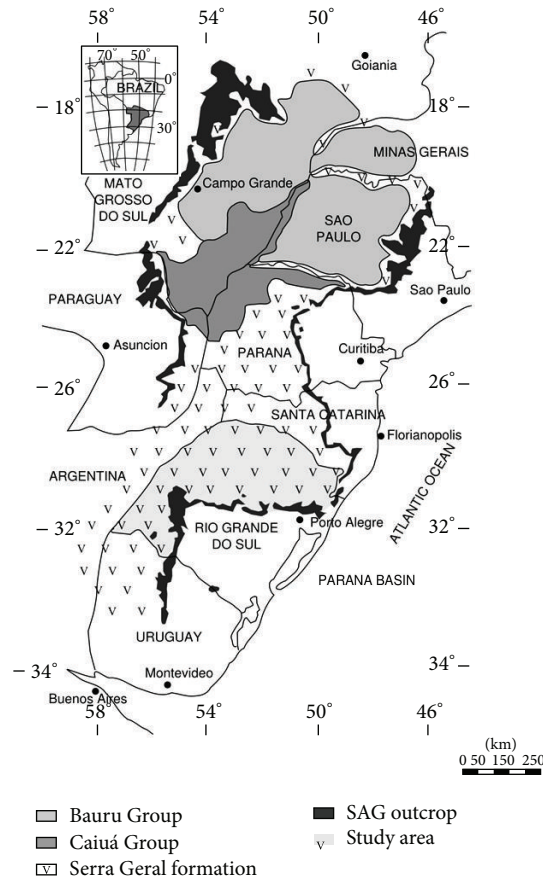


FIGURE 1: Location map showing the Serra Geral Formation (SGF) in South America (modified from [9]).

area bordering the Santa Catarina State to thickness of 200 m in the western area adjacent to Argentina Border.

The aim of this study is to understand the spatial distribution and geologic control of fluoride content in the SGAS, identifying hydrochemical groups with high fluoride. Physicochemical analysis, geostatistics, and stable isotopes approaches were used along with a Geographic Information System (GIS) in order to identify the spatial distribution of the different water types.

1.1. Geologic and Hydrogeologic Framework. The study area is located in the Rio Grande do Sul State, Southern Brazil, and underlies 164,200 km², extending from 27°S to 31°S and from 50°W to 57°W. The volcanic sequence has an average thickness of about 550 m and consists of basaltic to rhyolitic units of Mesozoic age; the last ones occur on the Serra Geral Formation (SGF) top sequence. The clayish soil thickness in the SGF ranges from few decimeters in the eastern area to several meters in the west and northwest. This soil controls water infiltration and, as a consequence, the SGAS recharge by meteoric waters [10].

Studies have suggested groundwater mixing processes between the SGAS and older confined sedimentary aquifer

systems from the Parana Basin, including the GAS, through ascending groundwater infiltration [11–16].

Distinct tectonic fracturing occurs in the study area, controlling geomorphological features and groundwater circulation. These structures are directly related to the opening of the South Atlantic Ocean, which is reflected in the major NE and NW fault and fracture directions. Neotectonics is considered to play an important hydrogeological role in the eastern region. Major tectonic systems define individual hydrochemical sectors, which are considered as individual hydrogeological blocks [15, 17, 18]. The tectonic block limited by the Terra de Areia-Posadas and Mata-Jaguari Fault Systems (Figure 2) is uplifted with respect to the neighboring blocks. In the north, the adjacent block is divided into smaller units with a gradual terrain lowering from east to west, influenced by NE normal faults, parallel to the Leao and Perimpo Fault Systems.

The identification of hydrochemical groups in the SGAS is an important tool for the definition of tectonic structures, supporting the fluoride ascending circulation hypothesis in the aquifer [22]. The meteoric recharge pattern as Ca²⁺HCO₃⁻ waters and also ascending infiltrations by Na⁺HCO₃⁻ waters with SO₄²⁻ and Cl⁻ in the GAS, resulting in a complex water mixture [15]. Several authors have pointed

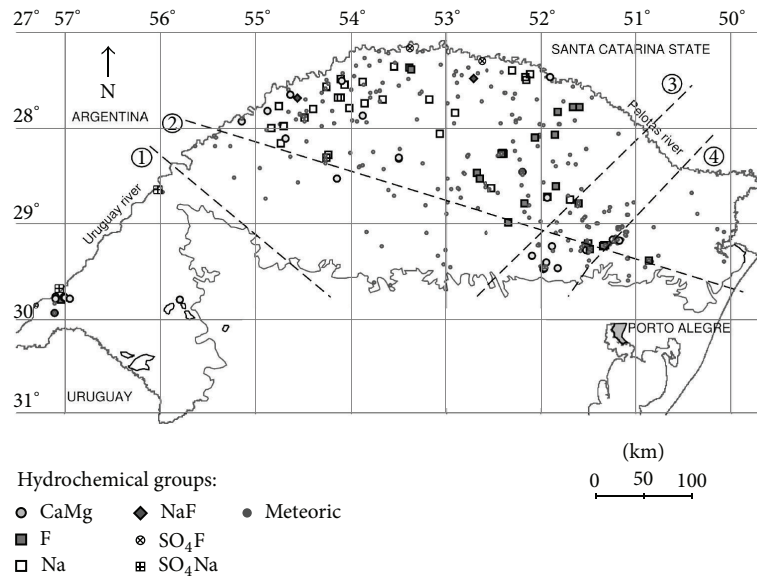


FIGURE 2: Sample points, hydrochemical groups distribution on SGAS, and major tectonic fault systems: (1), Mata-Jaguari, (2) Terra de Areia-Posadas, (3) Perimpo, and (4) Leao.

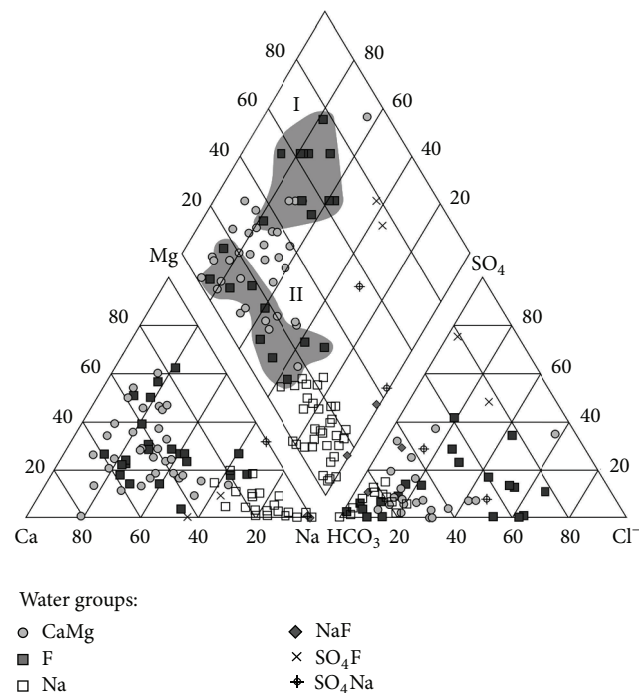


FIGURE 3: Hydrochemical groups distribution in the piper diagram, showing two fluoride hydrochemical types (I—sulfated and II—bicarbonated, [19]).

out that high fluoride content in groundwater can be related to $\text{Na}^+\text{HCO}_3^-$ ascending infiltrations waters [11, 15, 22–24]. Such mixing and hydrochemical groups can both result from $\text{Ca}^{2+}\text{HCO}_3^-$ and $\text{Na}^+\text{HCO}_3^-$ waters [25].

2. Materials and Methods

2.1. Multivariate Statistics. Principal components analysis (PCA) was used to discriminate hydrochemical groups in

the 309 physicochemical analyses of the SGAS in order to systematize the interpretation of a large number of variables through the maximization of differences between them [26].

The PCA was performed to 2, 3, and 4 principal components and normalized to a value of “1,” minimum eigenvalue accepted [27]. Subsequently, the outliers were cut by visual analysis in boxplots and dispersion charts for F^- , Na^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , and Cl^- , considering water classification. This statistical procedure restricts the analysis

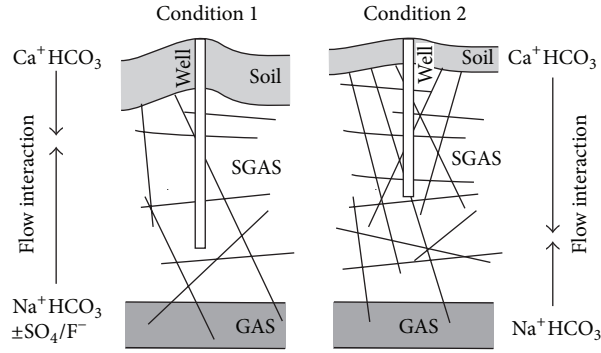
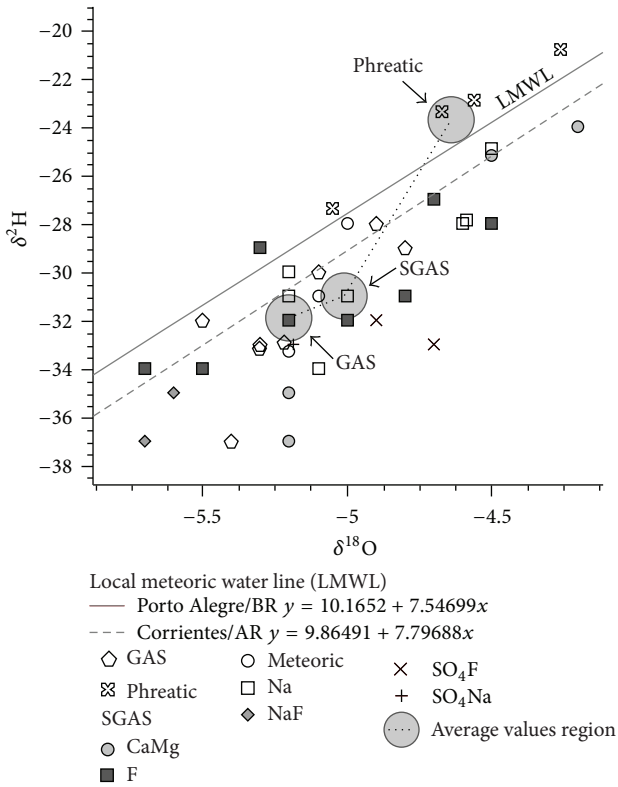


FIGURE 4: Water flow interactions to different geological conditions.

FIGURE 5: $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) in GAS, SGAS, and phreatic aquifer.

towards the fluoride focus, avoiding interferences from other parameters. The spatial distribution and interpretation of principal components defined by PCA were performed with a GIS environment.

2.2. Stable Isotopes. Stable isotopes were analyzed in the Geochronological Research Center of the Sao Paulo University. The analysis for oxygen was accomplished through the balanced isotopic reaction between water and CO_2 over 24 hours.

The CO_2 extraction was done in a vacuous line offline and subsequently was read in a Thermo Finnigan Delta Plus/Advantage spectrometer with dual-inlet installed.

TABLE 1: Rotated matrix with four components and characteristic parameters. Data from [21].

Parameters	Components			
	1	2	3	4
Mg^{2+}	.874	.063	.072	.139
Ca^{2+}	.811	.231	-.045	-.043
Na^+	-.143	.188	.870	.271
Cl^-	.353	.707	.206	-.051
HCO_3^-	.572	.095	.699	-.091
SO_4^{2-}	.030	.872	.074	.237
F^-	.067	.145	.150	.956
Explained variance	37.433	20.260	12.694	10.770
Cumulative % of variance	37.433	57.693	70.386	81.156

The hydrogen was analyzed through the reaction of water with pure zinc at 500°C for liberation of the H_2 gas.

Twenty seven samples were selected in order to establish stable isotope patterns in the SGAS. These results were considered together with eight additional ones belonging to the GAS (seven data from [28] and one from this study) and four from phreatic waters from an adjacent area [28]. This procedure is appropriate for understanding water mixture features between aquifers and to estimate their relative ages.

Unfiltered water samples were collected and stored in 100 mL polypropylene bottles to provide adequate volume for separate analyses of $\delta^{18}\text{O}$ and $\delta^2\text{H}$. All data considered in this paper are expressed in ‰ with respect to Vienna Standard Mean Ocean Water (VSMOW) on the Delta scale:

$$\delta = \left[\frac{(1000 + R_{\text{sample}})}{(1000 + R_{\text{standard}})} - 1 \right] * 1000, \quad (1)$$

where R_{sample} is the $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ ratio of the sample and R_{standard} is the corresponding ratio in VSMOW. Analytical precisions were better than $\pm 0.5\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 2\text{‰}$ for $\delta^2\text{H}$.

The altitude and the distance from the ocean can influence stable isotopes patterns. The average altitude of the SGAS in the area is 500 m, and the spatial position ranges from the coast in the eastern sector to 800 km inland in the western sector.

TABLE 2: Cluster central scores, dominant components and hydrochemical groups. Data from [21].

Component	Cluster								
	1	2	3	4	5	6	7	8	9
CaMg	1.614	-0.613	-0.228	0.511	-0.152	-0.724	2.042	-0.722	-1.720
SO ₄	0.987	4.411	-0.377	-1.198	-0.113	9.303	-0.236	-0.260	-0.348
Na	-0.892	3.032	-0.881	-0.667	-0.305	-0.845	1.092	1.653	2.691
F	-0.330	-1.357	1.244	6.986	-0.250	2.849	0.285	-0.034	4.786
Cases	22	2	19	3	212	2	11	36	2
Hydrochemical group	CaMg	SO ₄ Na	F	F	Meteoric	SO ₄ F	CaMg	Na	NaF

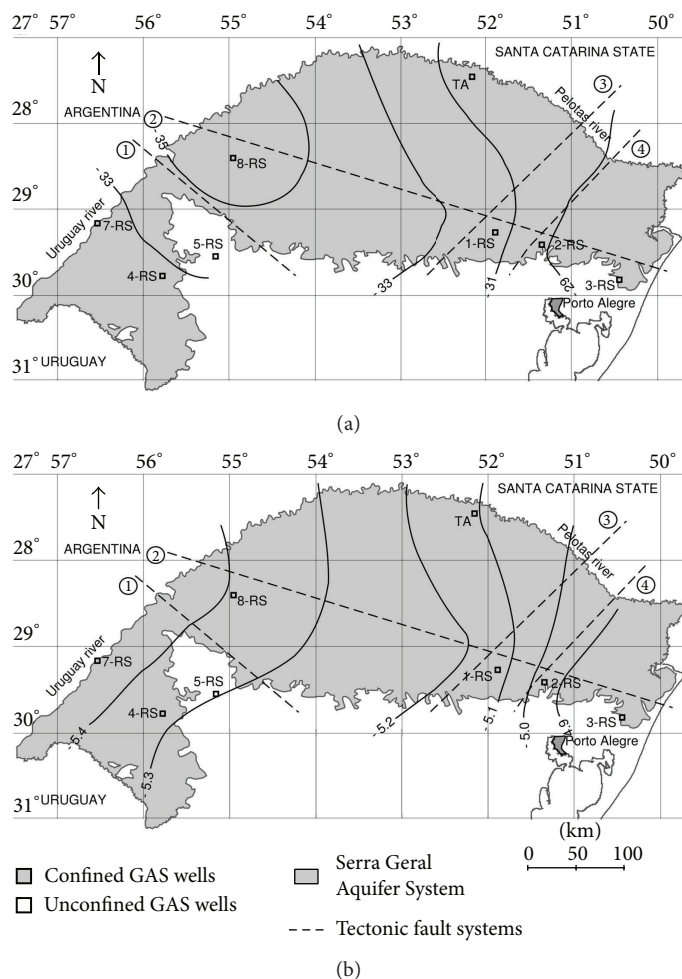


FIGURE 6: Hydrogeological spatial trends of $\delta^2\text{H}$ (a) and $\delta^{18}\text{O}$ (b) in the GAS (data from [20]) and major tectonic fault systems: (1) Mata-Jaguari, (2) Terra de Areia-Posadas, (3) Perimpo, and (4) Leao.

Due to this, ISOHIS [29] isotope data from the precipitation sampling stations were selected both in Porto Alegre, Southern Brazil, located in coastal and low altitude condition (GNIP code 8396700) and Corrientes, Argentina, located in interior and low altitude (GNIP code 8716600) area showed to compare data obtained in this research.

3. Results and Discussion

3.1. Principal Components Analysis. The PCA results show the correspondence of each component to the analyzed

parameters. The solution using the eigenvalue criterion results in four components that explain 81% of the total variance. Component 4 is highly weighted by fluoride (Table 1).

Component 1 contains HCO_3^- , Ca^{2+} , and Mg^{2+} , typical for calcium and magnesium bicarbonated waters with short to medium residence time. In Component 2, SO_4^{2-} and Cl^- prevail, indicating calcium and sodium-chlorinated and sulfate waters. Component 3 is distinguished by HCO_3^- and Na^+ , representing sodium bicarbonated waters. The F^- followed by Na^+ and SO_4^{2-} defines Component 4, which

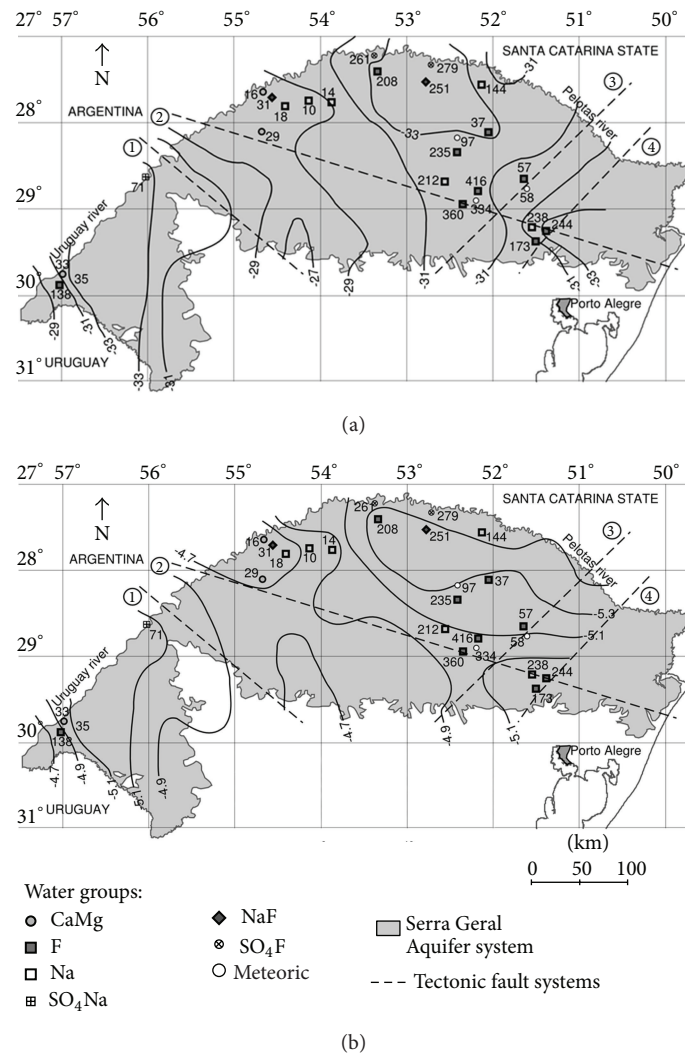


FIGURE 7: Hydrogeological spatial trends of $\delta^2\text{H}$ (a) and $\delta^{18}\text{O}$ (b), hydrochemical groups in the SGAS and major tectonic fault systems: (1), Mata-Jaguari, (2) Terra de Areia-Posadas, (3) Perimpo, and (4) Leao.

comprises the high F^- group linked to sodium-sulfated waters.

Based on these components, the solution for nine clusters was selected, and it shows the best approach to the hydrochemical groups. Subsequently, a cluster interpretation was performed based on central scores of each cluster. In order to assist the interpretation, each cluster was renamed according to the predominant ion (Table 2), defining hydrochemical groups. Thus, Component 1 has been renamed to CaMg, Component 2 to SO_4 , Component 3 to Na, and Component 4 to F.

Clusters 3 and 4 are composed predominantly by the F group. Clusters 1 and 7 comprise the CaMg group. Cluster 8 is composed by the Na group. Other clusters show prevalence of two components, resulting in the groups SO_4Na , SO_4F , and NaF. Cluster 5 comprises the Meteoric waters and other samples with no relationship to the four principal components.

3.2. Hydrochemistry. The geochemical data based on PCA results were plotted in a piper diagram (Figure 3), with the four renamed clusters defined by the PCA. The majority of wells (212 out of 309 wells) have a composition close to *meteoric waters* with $\text{Ca}^{2+}\text{HCO}_3^-$ nature and do not include high fluoride waters. Due to this, 212 samples are not represented in the diagrams in order to obtain a better fit by the other groups.

The CaMg group represents a predominant HCO_3^- water type where Mg^{+2} appears in more than 50% of the wells (Figure 3).

The Na group shows their typical distribution in the piper diagram, representing $\text{Na}^+\text{HCO}_3^-$ waters.

SO_4Na , SO_4F , and NaF groups appear only in two wells each. Both wells compose distinct groups as shown in Figure 3.

F distribution in the piper diagram maintains an association with sulfated and bicarbonated groundwaters. These

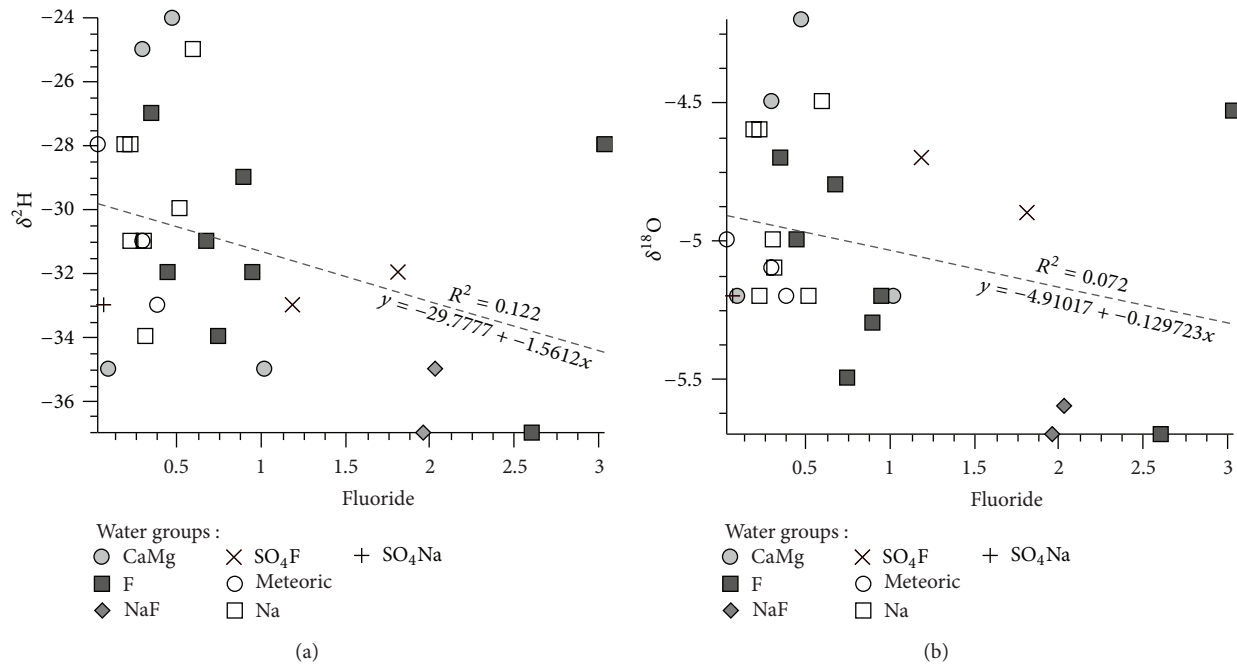


FIGURE 8: Fluoride versus $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and the SGAS hydrochemical groups.

hydrochemical characteristics are also related to different groundwater sources or point out to mixture features during groundwater ascending infiltration, where ionic enrichment including increasing fluoride content can result from the interaction of ascending/descending water recharge due to longer residence time in the Na and CaMg hydrochemical groups [19]. Thus, the SO_4F , NaF, F, and SO_4Na hydrochemical groups have a closed relationship interaction with two or more fracture directions (Figure 4), where SO_4^{2-} , Na^+ , and fluoride can ascend.

3.3. Stable Isotopes. The 27 analyzed samples from SGAS are distributed among the six water groups defined in the PCA. For GAS waters, one sample was analyzed and aggregated other 7 results [20]. Another 4 results to phreatic waters [28] were aggregated as mentioned. The $\delta^{18}\text{O}$ (‰) ranges from -5.0 to -4.2 (phreatic waters), from -5.7 to -4.2 (SGAS), and from -5.5 to -4.8 (GAS), while the $\delta^2\text{H}$ (‰) varies from -27.4 to -20.8 (phreatic waters), from -37 to -24 (SGAS), and from -37 to -28 (GAS; Table 3). The SGAS shows a scattered distribution compared to the GAS (Figure 5). Nevertheless, the average of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in both aquifer systems is similar, and the SGAS is located in an intermediate position but nearer to GAS when compared to phreatic waters. This reinforces the hypothesis of water circulation through the SGAS to the GAS, with minor influence of phreatic/meteoric waters in the sampled field.

The GAS data plotted in a map (Figure 6) show decreasing $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values from east to west, reflecting the distance from the ocean and the groundwater flow direction through the GAS. The lowest $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the GAS are related to the highest confinement and distance from direct recharge areas. In this sense, tectonic fractures can provide

meteoric to medium residence time waters to the GAS across the Serra Geral Formation, indicating descending water recharge processes, corresponding to Condition 2 described into Figure 4.

The SGAS $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results plotted in the same map show a different arrangement from the GAS, with the lowest values in the northern, western, and eastern portions (Figure 7). These differences are related to the influence of tectonic fractures and, as a consequence, to the hydrochemical groups distribution [19].

In the northern region, the lowest $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values coincide with a greater volcanic sequence thickness and thicker soils, providing for an increase in groundwater residence time and reduced meteoric water recharge. The prevalence of SO_4F , NaF, and F hydrochemical groups in this portion confirms the long residence time and older relative age to this waters.

In the western sector of Figure 6, samples with the lowest $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are located along the Uruguay River Fault System in an NE-SW direction. In this area, the SGAS is thinner, and the intense tectonic fracturing favors to the groundwater ascension through the confined GAS.

In the eastern area, the lowest $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (samples 238 and 244) are related to the Leao and Terra de Areia-Posadas Fault Systems, which allow for groundwater ascension through the confined GAS.

The scatter diagram of fluoride versus $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Figure 8) reveals, in a broad sense, that lower isotope ratios (most negative values) are associated with higher fluoride content, reflecting water-rock interaction during a long residence time. Similar conditions were also described by [24] in the GAS in the Sao Paulo State, Southern Brazil. This behavior can be associated with ascending infiltration GAS waters.

TABLE 3: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of phreatic waters (a), GAS (a), and SGAS (b). Data from [28] (*) and [20] (**). TA is a code to Tres Arroios City (sampled by author). Fluoride content is exclusive to SGAS.

(a)			
Sample code	Aquifer	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
PMT1*	Phreatic	-4.67	-23.4
PMT2*		-4.26	-20.8
PMCG3*		-5.05	-27.4
PMBF7*		-4.56	-22.9
Averages		-4.64	-23.7
TA	GAS	-5.1	-30.0
1-RS**		-5.2	-33.0
2-RS**		-4.9	-28.0
3-RS**		-4.8	-29.0
4-RS**		-5.3	-33.0
5-RS**		-5.3	-33.0
7-RS**		-5.5	-32.0
8-RS**		-5.4	-37.0
Averages		-5.28	-33.2
(b)			
Sample code	SGAS water group	F^- (mg/L)	$\delta^{18}\text{O}$ (‰)
35	CaMg	0.1	-5.2
33	CaMg	1.02	-5.2
29	CaMg	0.3	-4.5
16	CaMg	0.47	-4.2
416	F	0.45	-5.0
360	F	0.68	-4.8
235	F	0.95	-5.2
208	F	0.75	-5.5
173	F	0.9	-5.3
138	F	3.03	-4.5
57	F	0.35	-4.7
37	F	2.6	-5.7
244	Na	0.32	-5.1
238	Na	0.52	-5.2
212	Na	0.31	-5.0
144	Na	0.23	-5.2
18	Na	0.23	-4.6
14	Na	0.19	-4.6
10	Na	0.6	-4.5
251	NaF	1.96	-5.7
31	NaF	2.03	-5.6
279	SO_4F	1.19	-4.7
261	SO_4F	1.81	-4.9
71	SO_4Na	0.07	-5.2
334	Meteoric	0.39	-5.2
97	Meteoric	0.3	-5.1
58	Meteoric	0.03	-5.0
Averages		0.81	-5.01

4. Conclusions

In the Rio Grande do Sul State, extensive groundwater mixing processes operate between the SGAS and GAS through defined and intense tectonic fractures. Six hydrochemical groups were distinguished in the SGAS, three of them containing substantial fluoride contents in combination with Na^+ and SO_4^{2-} . Ascending recharge processes are considered to define ionic enrichment, especially in Na^+ , F^- , SO_4^{2-} , and Cl^- .

The comparison between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ spatial distribution in the SGAS demonstrates a different scenario concerning the GAS. The differences are probably explained by the interference of different tectonic structures than those in the GAS which are responsible for the defined hydrogeological blocks. The combination of deep fault zones and high pressure and temperature conditions in a confined GAS supports the hypothesis of ascending groundwater infiltration.

The depleted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values suggest that fluoride enrichment in the SGAS is related to percolation through the GAS in confinement and long residence time conditions. The similar values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the two aquifer systems suggest, in some regions, that ascending recharge processes are more intense than meteoric recharge. In the Rio Grande do Sul State, this behavior increases from east to west, which is the groundwater flow direction in the GAS. Similar behavior is observed in the SGAS, except in some scarps and valleys, as is demonstrated by the distribution of the CaMg water group. The fluoride input to the groundwater is probably related to water-rock interaction in the GAS and in older aquifer systems below it.

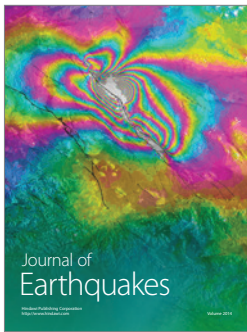
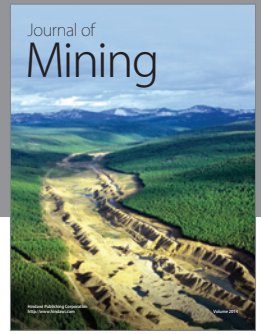
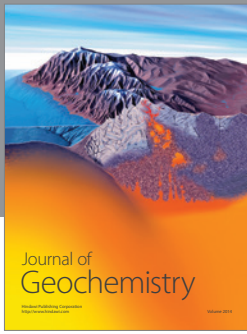
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