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Fluoride characterization by principal component analysis in the hydrochemical facies of Serra Geral Aquifer System in Southern Brazil

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ABSTRACT

Principal component analysis is applied to 309 groundwater chemical data information from wells in the Serra Geral Aquifer System. Correlations among seven hydrochemical parameters are statistically examined. A four-component model is suggested and explains 81% of total variance. Component 1 represents calcium-magnesium bicarbonated groundwaters with long time of residence. Component 2 represents sulfated and chlorinated calcium and sodium groundwaters; Component 3 represents sodium bicarbonated groundwaters; and Component 4 is characterized by sodium sulfated with high fluoride facies. The components' spatial distribution shows high fluoride concentration along analyzed tectonic fault system and aligned on northeast direction in other areas, suggesting other hydrogeological fault systems. High fluoride concentration increases according to groundwater pumping depth. The Principal Component Analysis reveals features of the groundwater mixture and individualizes water facies. In this scenery, it can be determined hydrogeological blocks associated with tectonic fault system here introduced.

Key words: fractured aquifer, geostatistics, GIS, groundwater, hydrogeology.

INTRODUCTION

Water scarcity and increasing human consumption requires new sources of water with adequate potability. Therefore, an emergent necessity to understand groundwater resources is evident. Low cost treatment and technical advances in exploration turns groundwater into a vital and precious natural resource.

Fluoride content in water, like other chemical species, is beneficial to human health but can be toxic when in excess. High fluoride contents in groundwater are responsible for human and animal health problems causing dental and skeletal fluorosis, which is detected worldwide, like in China (Lin et al. 2004, Genxu and Guodong 2001), India (Kumar et al. 2001), Kenya (Moturi et al. 2002), and Israel (Kafri et al. 1989), among other countries. In the Rio Grande do Sul State, southern Brazil, the endemic fluorosis has been detected in several districts (e.g. Venancio Aires, Santa Cruz do Sul, Pantano Grande, General Camara). It is accepted that fluoride anomalies in groundwater could be related to anthro-

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pogenic contamination (fertilizer application, brick and aluminum smelters, sewage piles and other sources) or to a natural origin, such as prolonged water-rock interactions (Nordstrom et al. 1989). The drinking water limit recommended by the World Health Organization for fluoride is 1.5 mg/L (WHO 2002), and in a moderate concentration (0.7-1.2 mg/L) prevents dental cavities.

The main aim of the current study is to understand the distribution of high-fluoride waters in the Serra Geral Aquifer System (SGAS) and to identify the hydrochemical types and their spatial distribution, using the Principal Component Analysis (PCA). PCA is an important tool for understanding the large quantity of data involved in extended aquifer studies (Invernizzi and Oliveira 2004). This aids to define geological sources and pathways for high fluoride, consequently, assisting future well locations and management of SGAS waters. Investigations about the source of high fluoride concentrations in previous studies had shown a relationship with tectonic structures and with pumping of deep groundwater.

GEOLOGY AND HYDROGEOLOGY OF THE STUDY AREA

The study area is located in the Rio Grande do Sul State, southern Brazil and extends from 27°S to 31°S and from 50°W to 57°W, corresponding approximately to 164.207 km^2 in the Parana Basin. The region is covered by a basaltic to rhyolitic Mesozoic volcanic sequence belonging to the Serra Geral Formation (SGF), whose thickness varies from 50 to 1000 meters (average of 550 meters), constituting a fractured aquifer that provides public water supply to more than 80% of the cities in the area.

SGAS hydrochemical characteristics indicate the influence of water mixing with other sedimentary aquifer belonging to the Parana Basin (Szikszay et al. 1981, Fraga 1992, Portela Filho et al. 2002, 2004). This aquifer is directly superimposed by the Guarany Aquifer System/GAS (Campos 2000) that has been the focus of several studies in the last few years, due to its spatial extent and storage potentiality as a transnational aquifer.

Tectonic structures cut the SGF controlling terrain surface and hydrochemical characteristics of the related aquifer. These structures are connected to the South Atlantic Ocean opening, causing NE and NW dominant directions (Fig. 1). The main fault systems define sectors that may be considered as hydrogeological blocks (Lisboa 1996, Lisboa and Menegotto 1997, Machado 2005). The tectonic block limited by the Terra de Areia-Posadas Fault System and Mata-Jaguari Fault System is uplifted in the south-central area. The adjacent block to the north shows a gradual terrain lowering from east to west, conditioned by NE normal faults, parallel to the Leao and Perimpo fault systems.

The identification of different water facies for SGAS focused on tectonic block separations is important to define structures where high fluoride groundwater can ascend from deep levels to SGAS. This tectonic control for the high fluoride groundwaters has been reported in other regions (Licht 2001). 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. Machado (2005) describes the influence of $Ca^{2+}HCO_3^-$ meteoric recharge on the SGAS and mixture mechanisms between the SGAS and the GAS inputing $Na^+HCO_3^-$ with SO_4^{2-} and Cl^- water to SGAS.

MATERIALS AND METHODS

HYDROCHEMICAL DATA

Hydrogeological data represent a network of 309 deep wells (Fig. 1) that exposes only SGAS groundwater used in public and private water supply. All data information was provided by governmental groundwater management agencies.

This study regarded only seven major parameters to evaluate hydrochemical facies in the piper diagram, namely fluoride, Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-} and Cl^-.

STATISTICAL ANALYSIS

The PCA was performed using SPSS version 8 software (Nie et al. 1975) and tested for two, three and four principal components using the eigenvalue equal to 1 criterion (Kaiser 1958). Before this procedure, outlier suppression was carried out through boxplots and dispersion charts for all variables. The Varimax orthogonal rotation was used (Kaiser 1958), in order to facilitate Factor Analysis interpretation (Invernizzi and Oliveira 2004). Principal component scores performed in the Cluster Analysis (K-Means Method) allow to group wells into homogeneous clusters.

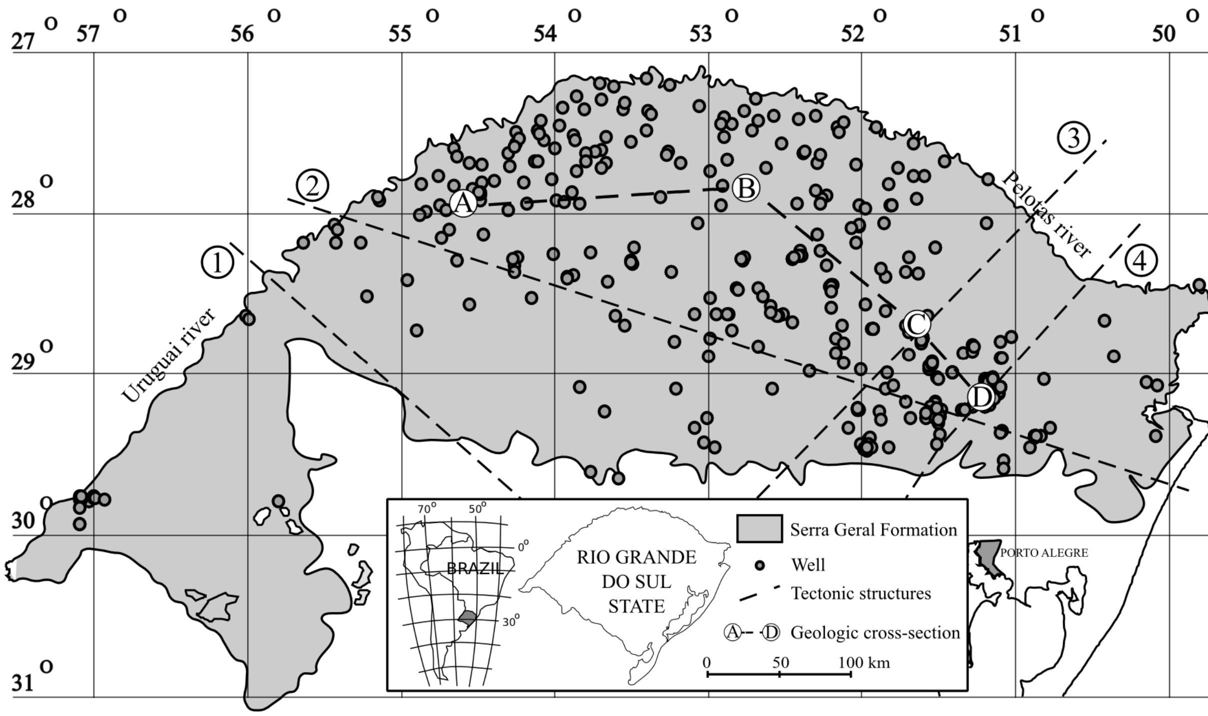

Fig. 1 – Location map of SGAS(gray) in Rio Grande do Sul State, sampling wells and main tectonic fault systems: (1) Mata-Jaguari, (2) Terra de Areia-Posadas, (3) Perimpo, and (4) Leao.

Spatial Analysis

Spatial distribution and interpretation of principal components defined by PCA was performed on Geographical Information System (GIS) with Quantum GIS version 0.7.4 software (Sherman et al. 2005). Cluster results were classified, considering the most important chemical parameter as an identification name.

The relationship between depth and fluoride concentration considers the maximum absolute groundwater pumping depth in each well. This procedure was carried out with Labplot version 1.5 software (Gerlach 2004) in order to investigate whether fluoride concentration in SGAS increases with depth.

RESULTS AND DISCUSSIONS

Principal Component Analysis

Table I presents the correlation coefficient matrix for hydrochemical data in SGAS.

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 II).

Component 1 is mainly influenced by HCO_3^-, Ca^{2+}, and Mg^{2+}, and explains 37.43% of the total variance, representing calcium-magnesium bicarbonate groundwaters with long residence time, evidenced by Mg^{2+}. Component 2 is defined by SO_4^{2-} and Cl^-, and represents sulfated and chlorinated, calcium and sodium groundwaters.

Component 3 is explained by HCO_3^- and Na^+, defining sodium bicarbonated groundwaters.

Component 4 is defined by F, followed by Na^+ and SO_4^{2-}, corresponds to sodium sulfate with high fluoride facies.

Fluoride participates with similar intensity on Components 2 and 3, suggesting two groundwater sources that contain relatively high fluoride concentration. Therefore, fluoride was associated with sulfated and sodium bicarbonated groundwaters.

Based on the above, cluster analysis was performed and selected a solution with nine clusters, since it showed the best water facies individualization. Using this criterion the results pointed out a minimum number of wells with meteoric water facies (212).

TABLE I
Correlation coefficient.

Parameter	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	F^-
Na^+	1.0	0.0069	–0.043	0.235	0.263	0.46	0.339
Mg^{2+}		1.0	0.549	0.351	0.093	0.457	0.096
Ca^{2+}			1.0	0.273	0.207	0.4	–0.012
Cl^-				1.0	0.457	0.352	0.198
SO_4^{2-}					1.0	0.196	0.385
HCO_3^-						1.0	0.094
F^-							1.0

TABLE II
Rotated matrix with four components and characteristic parameters.

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 cluster interpretation was based on final center scores. Thus, each cluster was renamed using related ion predominance (Table III). In order to facilitate the reading it was decided to designate Component 1 as **CaMg**, Component 2 as **SO4**, Component 3 as **Na**, and Component 4 as **F**.

It can be defined that clusters 3 and 4 are composed predominantly by **F** component groundwaters. Clusters 1 and 7 comprise the **CaMg** water facies. Cluster 8 is composed by **Na** component. The remaining groups show more than one component in high concentration.

In the water facies, components **SO4**, **Na**, and **F** were added to the main water facies. Therefore, these clusters were called **SO4Na**, **SO4F**, and **NaF**, due to their final centroid intensities. This components combination is a result of the interference of different geochemical water sources and/or mixture features.

HYDROCHEMISTRY

The geochemical data were plotted in a piper diagram (Fig. 2), with the four renamed cluster defined by the PCA. The majority of wells (212 out of 309 wells) have a composition related to **meteoric waters** with $Ca^{2+}HCO_3^-$ nature and do not include high fluoride waters. In this case, 212 samples are not represented in the diagrams, in order to obtain a better fit by the other groups.

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

The **Na** group shows their typical distribution in the piper diagram, representing $Na^+HCO_3^-$ waters.

F distribution in the piper diagram maintains an association with sulfated and bicarbonated groundwaters. These hydrochemical characteristics are also related to

TABLE III
Components final cluster centers and clusters name reclassification.

Component	Cluster								
	1	2	3	4	5	6	7	8	9
CaMg	**1.6143**	–0.6137	–0.228	0.511	–0.152	–0.724	**2.042**	–0.722	–1.720
SO4	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
Water Facies	**CaMg**	**SO4Na**	**F**	**F**	**Meteoric**	**SO4F**	**CaMg**	**Na**	**NaF**

different groundwater sources or point out to mixture features during groundwater ascending recharge.

SO4Na, **SO4F**, and **NaF** facies appear only in two wells each. Both wells compose distinct groups as showed in Figure 2.

The spatial distribution of water facies confirms that fluoride has a relationship with the analyzed fault systems Mata-Jaguari, Terra de Areia-Posadas, Perimpo, and Leao (Fig. 3).

Meteoric Waters occurs in all SGAS, but more significantly in the tectonic block limited by Terra de Areia-Posadas, Jaguari-Mata and Perimpo Fault Systems, due to the uplift condition of this block.

The **CaMg** facies is spatially related to discharge zones of SGAS in the west, northwest, and southeast regions, representing waters at the final percolation stage under long time residence.

The **Na** facies is dominant in the northwest region, where SGF achieves the maximum thickness in the study area, suggesting a hydrogeological tectonic block. This characteristic indicates that ascendant waters in this region present only Na^{+} enrichment, as a result of water-rock interaction in SGF. Thus, the non-interference of GAS in this scenery is evident, probably due to the maximum thickness of SGF.

SO4Na facies appears only in the northeast alignment direction of the Uruguay River, showing a close relationship to this regional alignment. **SO4F** facies presents a similar behavior, but occurs only in the east-west section of the Uruguay River.

NaF facies is spatially linked to the Na hydrogeological block which has a poor fluoride content. The **NaF** with high fluoride appears only in two wells at a similar distance from the Uruguay River, suggesting a particular hydrogeological condition.

The **F** group related that high fluoride groundwaters are distributed in the central-northeast portion of SGAS. Aligned wells associated with the main tectonic fault systems (Terra de Areia-Posadas, Leao and Perimpo) suggest a water ascension recharge. New tectonic fault systems are introduced in the present study, corresponding to the linear distribution of wells belonging to **F** facies in the central portion of SGAS, which receive the nomination Fontoura Xavier-Parai and Victor Graeff-Barracao hydrogeological alignments (Fig. 3). It must be stressed that the introduced structures are parallel to Leao and Perimpo Fault Systems.

The distribution of **NaF** facies is similar to the **Na** facies (Fig. 3). Both are chemically very similar and distinguished by a more intensive fluoride participation in the **NaF** facies.

The **SO4F** and **SO4Na** facies are scarce and closely associated with major regional structures that delineate the Uruguay River (Fig. 3). The **SO4F** facies occurs in the north sector while the **SO4Na** facies occurs preferentially in the west sector of the study area.

The composition of the volcanic rocks belonging to the SGF does not comprise fluorine rich minerals to provide anomalous fluoride content in the SGAS. This enrichment could be better explained by the ascending groundwater recharge crossing older Parana Basin sedimentary sequences combined with long residence time and extreme confination conditions.

The A-D geological cross-section (Figs. 1 and 4) demonstrates the east-west gradual terrain lowering, due to tectonic block accommodation, where hydrogeological ascension structures are represented. Near the well "B" (Fig. 1) the **Na** block limit is registered.

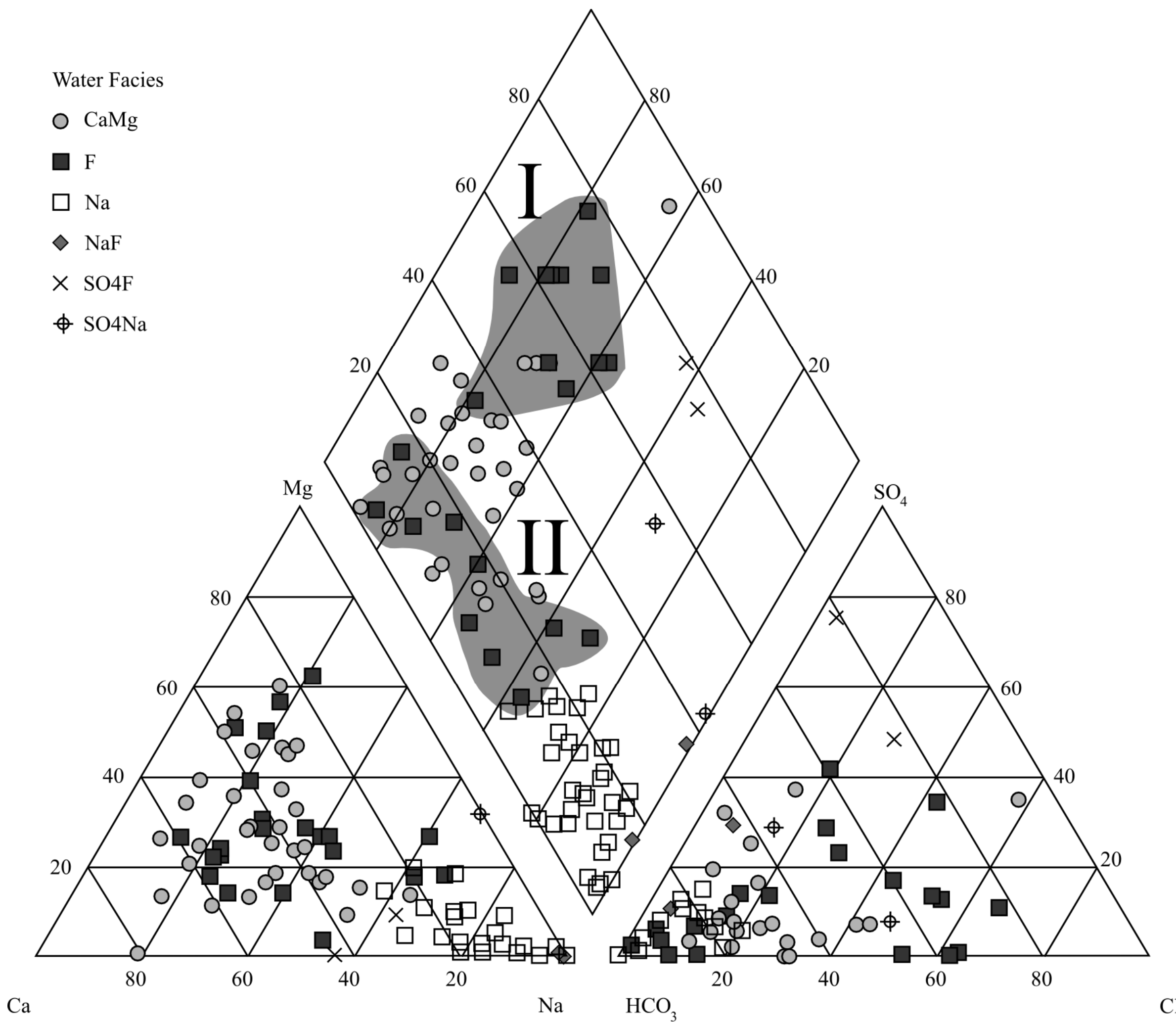

Fig. 2 – Water facies distribution in the Piper Diagram, showing two fluoride hydrochemical types (I – sulfated; II – bicarbonated).

The depth variation shows fluoride concentration increase according to groundwater pumping depth (Fig. 5). It can be demonstrated that beyond **F** facies, all the other facies increase the fluoride content with the depth. This behavior probably is related to the influence of confined GAS and the proximity of other older aquifer systems.

CONCLUSIONS

The PCA methodology was efficient to discriminate hydrochemical water facies in a collection of more than 300 wells located in the SGAS in Rio Grande do Sul State, southern Brazil, with special emphasis to the fluoride content. As a result a comprehensive spatial model was achieved, using seven chemical components that validate six hydrochemical facies were distinguished in the SGAS, three of them containing substantial fluoride contents in combination with Na^+ and SO_4^{2-}. The spatial distribution of these facies confirms the presence of hydrogeological blocks limited by tectonic alignments.

Two tectonic structures are apparently present in the central area, indicated by linear distribution of high fluoride groundwater wells. An aquifer system status for SGAS is reaffirmed, considering complex chemical mixtures, recharge processes and percolation through the fractured reservoir. The ascending recharge processes are considered to define ionic enrichment, especially in Na^+, F^-, SO_4^{2-} and Cl^-.

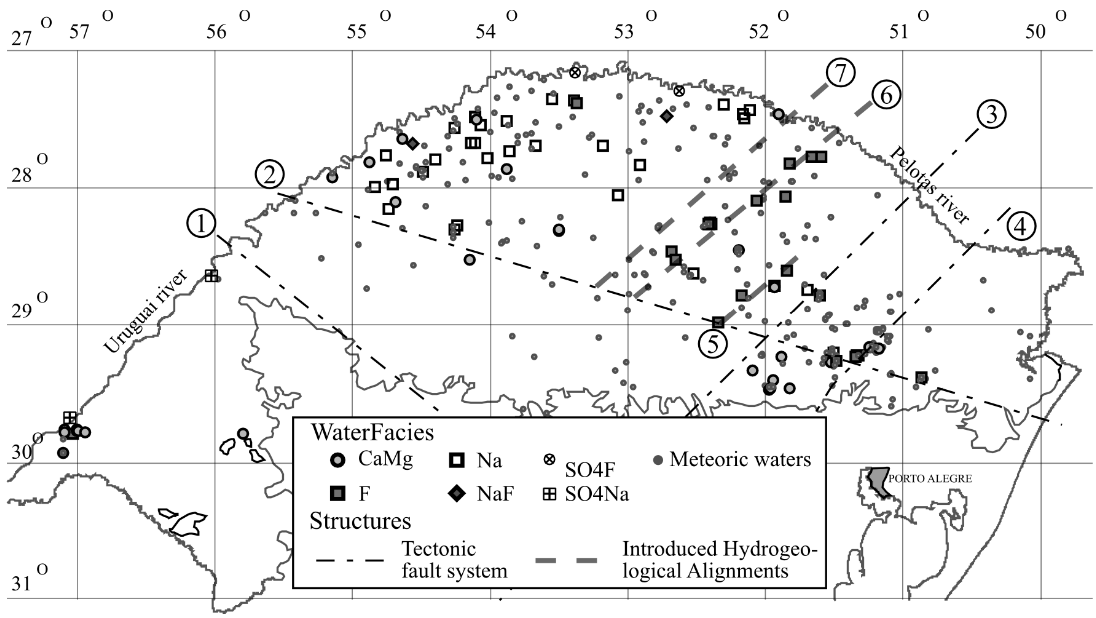

Fig. 3 – Water facies distribution and tectonic fault systems: (1) Mata-Jaguari, (2) Terra de Areia-Posadas, (3) Perimpo, and (4) Leao. Introduced hydrogeological alignments are (5) Fontoura Xavier-Parai, (6) Victor Graef-Barracao and (7) that indicates a tectonic block limit.

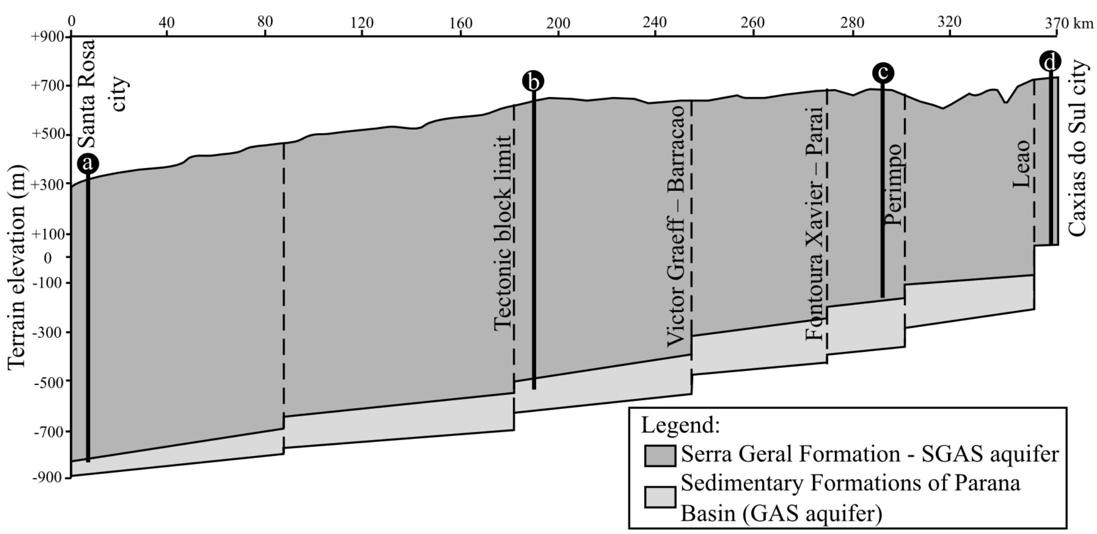

Fig. 4 – Geological cross-section showing the main tectonic structures responsable for high fluoride groundwater ascension. Modified from Machado, 2005.

The results were able to point out the influence of deeper confined aquifers on fluoride contents of the SGAS and add elements to minimize the costs for well location with better water quality.

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RESUMO

A Análise de Componentes Principais foi aplicada em 309 dados químicos de águas subterrâneas de poços do Sistema Aqüífero Serra Geral. Correlações entre sete parâmetros hidroquímicos foram examinadas através da estatística. O modelo

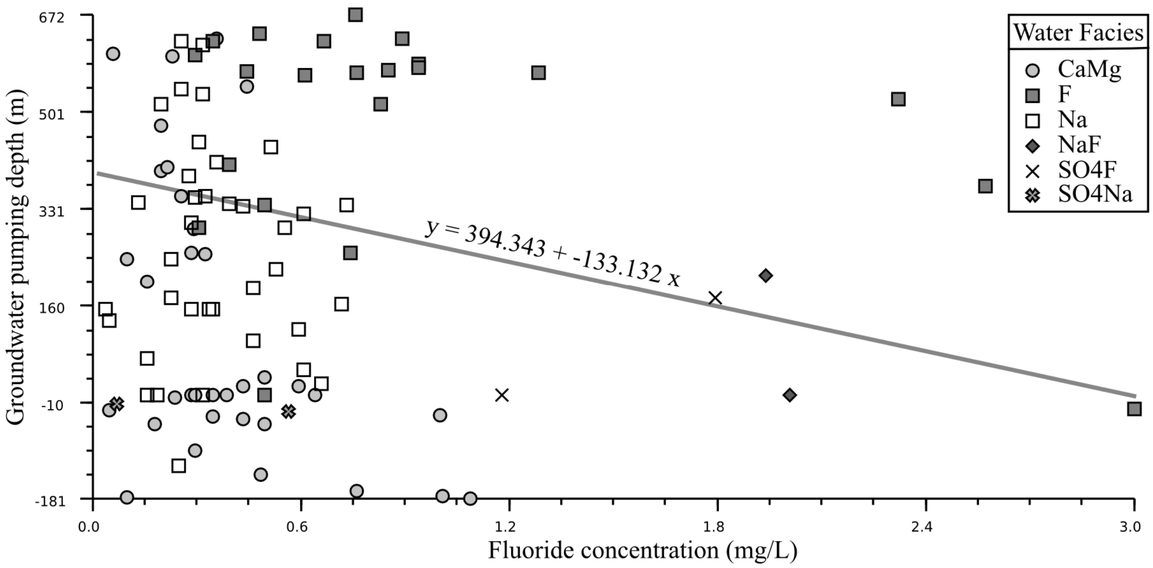

Fig. 5 – Relationship between fluoride concentration and groundwater pumping depth.

de quatro componentes foi utilizado por explicar 81% da variância total. A Componente 1 é representada por águas cálcio-magnesianas com longo tempo de residência, a Componente 2 representa águas bicarbonatadas sulfatadas e cloretadas, a Componente 3 representa águas bicarbonatadas sódicas e a Componente 4 é caracterizada por águas de fácies sódica e sulfatada com alto fluoreto. A distribuição espacial das componentes mostra águas com concentrações anômalas ao longo dos sistemas tectônicos de falhas, analisados e alinhados a NE em algumas áreas, sugerindo outros sistemas de falhas hidrogeológicos. As concentrações de fluoreto aumentam de acordo com a profundidade de bombeamento das águas. A Análise de Componentes Principais revelou feições de mistura e individualizou diferentes fácies de águas subterrâneas. Neste cenário, é possível determinar blocos hidrogeológicos associados com os sistemas tectônicos de falhas introduzidos no presente trabalho.

Palavras-chave: aqüífero fraturado, geoestatística, SIG, águas subterrâneas, hidrogeologia.

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