Structural, hydrogeological and hydrochemical characterization of aquifers in the Paraná Basin: An integrated literature review

Caracterização estrutural, hidrogeológica e hidroquímica de aquíferos da Bacia do Paraná: Uma revisão integrada da literatura

Caracterización estructural, hidrogeológica e hidroquímica de los acuíferos de la Cuenca del Paraná: Una revisión integral de la literatura

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Abstract
The Paraná Basin in Brazil is of vital importance and because of a large groundwater reservoir and the high exploitation of this resource by the population a structural and hydrogeochemical knowledge is needed. Objectives: 1) Analyze studies that address the structural, hydrogeological and hydrochemical characterization of aquifers in the Paraná Basin; 2) Highlight the main techniques used in the respective studies and the scientific development arising from the use of these techniques for a better hydrochemical and structural understanding of the Paraná Basin. Methodology: Tracing lineaments from satellite image and field work are the main techniques used for structural characterization. For hydrochemical analyses, factorial methods physical-chemical analyses are used. Results: the most common chemical types of groundwater that circulate in the sedimentary and volcanic units of the Paraná Basin, which include the Pirambóia, Irati, Rio Bonito, Botucatu and Serra Geral formations are calciumbicarbonates, calcium-magnesian bicarbonates, calcium-sodium bicarbonates and sodium-sulphate-chloride bicarbonates. Sodium-sulfated waters are not found in the Serra Geral Formation, except when they come from the sedimentary units. Sodium and sulfate are not expected ions in basalt weathering, and therefore a greater understanding is needed on structural communication by means of faults that occur between the Serra Geral Aquifer System (SGAS) and the mesozoic and permian sedimentary aquifers and aquitards that contribute for unexpected ions in the SGAS. Conclusion: The Paraná Basin is a reason for interest in geological studies in Brazil because of its link to several areas of interest in geosciences, which include hydrochemistry, stratigraphy, paleontology and hydrogeology.
Keywords: Paraná Basin; Hydrochemistry; Structural geology.

Resumo
A Bacia do Paraná no Brasil é de vital importância e devido ao grande reservatório de água subterrânea e ao aproveitamento desse recurso pela população, é necessário um conhecimento estrutural e hidrogeoquímico. Objetivos: 1) Analisar estudos que abordem a caracterização estrutural, hidrogeológica e hidroquímica de aquíferos da Bacia do Paraná; 2) Destacar as principais técnicas utilizadas nos respectivos estudos e o desenvolvimento científico decorrente da utilização dessas técnicas para um melhor entendimento hidroquímico e estrutural da Bacia do Paraná. Metodologia: Traçar lineamentos a partir de imagens de satélite e trabalhos de campo são as principais técnicas utilizadas para caracterização estrutural. Para análises hidroquímicas, métodos fatoriais e análises fisíco-químicas são usadas. Resultados: os tipos químicos mais comuns de água subterrânea que circulam nas unidades sedimentares e vulcânicas da Bacia do Paraná, que incluem as formações Pirambóia, Irati, Rio Bonito, Botucatu e Serra Geral são cálcio bicarbonatadas, bicarbonatas cálcico-magnésianas, bicarbonatas cálcico-sódicas e bicarbonatas cloretadas

sulfatadas com sódio. Águas sulfatadas com sódio não são encontradas na Formação Serra Geral, exceto quando provêm de unidades sedimentares. Sódio e sulfato não são íons esperados no intemperismo de basalto, portanto, é necessário um maior entendimento sobre a comunicação estrutural por meio de falhas que ocorrem entre o Sistema Aquífero Serra Geral e os aquíferos sedimentares mesozóicos, permianos e aquitardos que contribuem para íons inesperados na Formação Serra Geral. Conclusão: A Bacia do Paraná é um motivo de interesse para os estudos geológicos no Brasil devido à sua vinculação com diversas áreas de interesse das geociências, que incluem a hidroquímica, estratigrafia, paleontologia e hidrogeologia.
Palavras-chave: Bacia do Paraná; Hidroquímica; Geologia estrutural.

Resumen
La Cuenca del Paraná en Brasil es de vital importancia y debido a un gran reservorio de agua subterránea y la alta explotación de este recurso por parte de la población, se necesita un conocimiento estructural e hidrogeoquímico. Objetivos: 1) Analizar estudios que aborden la caracterización estructural, hidrogeológica e hidroquímica de los acuíferos de la Cuenca del Paraná; 2) Destacar las principales técnicas empleadas en los respectivos estudios y el desarrollo científico derivado del uso de estas técnicas para un mejor conocimiento hidroquímico y estructural de la Cuenca del Paraná. Metodología: Trazar lineamientos a partir de imágenes de satélite y trabajo de campo son las principales técnicas utilizadas para la caracterización estructural. Para los análisis hidroquímicos se utilizan métodos factoriales e analisis fisico-quimicas. Resultados: los tipos químicos más comunes de aguas subterráneas que circulan en las unidades sedimentarias y volcánicas de la Cuenca del Paraná, que incluyen las formaciones Pirambóia, Irati, Rio Bonito, Botucatu y Serra Geral son cálcio bicarbonatos, bicarbonatos calcio-magnesianos, bicarbonatos calcio-sodicas y bicarbonatos cloruras sulfuradas de sodio. Las aguas sulfuradas de sodio no se encuentran en la Formación Serra Geral, excepto cuando provienen de las unidades sedimentarias. El sodio y el sulfato no son iones esperados en la meteorización del basalto, por lo que se necesita una mayor comprensión de la comunicación estructural mediante fallas que ocurren entre el Sistema Acuífero Serra Geral y los acuíferos sedimentarios del Mesozoico y Pérmico y los acuitardos que contribuyen a iones inesperados en la Formación Serra Geral. Conclusión: La Cuenca del Paraná es motivo de interés en los estudios geológicos en Brasil por su vínculo con varias áreas de interés en geociencias, que incluyen hidroquímica, estratigrafía, paleontología e hidrogeología.
Palabras clave: Cuenca del Paraná; Hidroquímica; Geología estructural.

1. Introduction

The valorization of groundwater occurs at a global level because it is essential for the maintenance of life. Groundwater is an important reserve because it is available at any time, in addition to low storage costs, being an alternative to surface water, subject to more frequent changes in its natural quality. Groundwater is also a source supply in periods of drought for rivers and surface water sources such as springs, lakes and wetlands. In turn, the increase in industrialization, urbanization and population has created many problems. Overuse has been the cause of deteriorating water quality and is also responsible for chemical changes in water (Bonotto, et al., 2012). The use of aquifers as a source of drinking water for agricultural and industrial activities is often poorly managed by government authorities in general, especially in underdeveloped countries. As a consequence, the extent and severity of groundwater contamination has increased in many regions. However, the knowledge and information-base to better manage and care of this resource is also increasing (Belletinni, et al., 2019).

For this use, it is significant to have the knowledge of the structural and hydrogeochemical characteristics of the aquifers that make up the Paraná Basin. Not taking into account the structural aspects of the Paraná Basin aquifers can bring unpleasant surprises in terms of water quality (Filho, et al., 2005). Structural understanding has evolved in the last 20 years, the result of intense fieldwork by several authors (Strieder, et al., 2017; Rostirolla, et al., 2001). Large structures are capable of transmitting water. Many of these structures were generated in the Precambrian and were later reactivated during the Mesozoic or at the end of the Cretaceous as a product of plate movements. These large structures, in addition to allowing the storage of water, allow the mixing of waters from different aquifers, as they cross all the sedimentary units of the Paraná Basin.

The knowledge of chemistry of the Paraná Basin was more strongly developed from the beginning of the 21st century (Meng & Maynard, 2001; Sracek & Hirata, 2002). Multivariate statistical techniques classify and separate samples containing the signature of the places they have passed (Teixeira & Viero, 2017; Teixeira & Viero, 2021; Freitas & Roisenberg, 2016).

Therefore, the objectives of this integrative literature review are: 1) the evolution of the structural and hydrogeochemical understanding developed in the last 20 years about the main units that make up the Paraná Basin; 2) Highlight the main techniques used in the respective studies.

2. Methodology

An integrative literature review (ILR), which aims to sumarize knowledge through a systematic and rigorous process and the conduct must be guided by the same principles recommended for methodological rigor in research development. The steps of this method are: 1) elaboration of the review question; 2) search and selection of primary studies; 3) extraction of study data; 4) critical evaluation of the primary studies included in the review; 5) summary of the results of the review and 6) presentation of the data (Mendes, et al., 2019).

In the first stage the following research question was asked: What is the national and international scientific production about the structural aspects and the hydrogeological and hydrochemical characterization of the aquifers of the Paraná Basin, between 1999 and 2019?

In the second stage a search was carried out in the database, which consisted of: GeoScience World (Georef), Scientific Electronic Library Online (Scielo), Scopus and Web of Science. In addition, a search for CAPES journals was carried out, considering the possibility that some journals (and their respective articles) may not be indexed in Georef, Scielo, Scopus and Web of Science. The database search was performed with descriptors according to the developed Integrative Review Protocol, containing search strategies, organized in conjunction with the librarian, considering descriptors, and synonyms, resulting in the following syntax: ((“Paraná Basin” OR “Paraná Basin Tectonica” OR “Aquifero Guarani System” OR OR “Serra Aquifero System” OR OR “Paraná Geological Basin” OR OR OR“ Rio Bonito ”OR Palermo OR Botucatu OR“ Paraná Basin ”OR“ Paraná Basin Tectonics ”OR“ Guarani Aquifer System ”OR“ Paraná geological basin ”OR“ Paranaica basin ”) AND (Hydrochemistry OR“ Diagenesis of sedimentary aquifers ”OR“ Groundwater ”OR Aquifer OR“ Geological structure ”OR hydrogeological OR “Chemical composition of water” OR “Stable isotopes” OR “Interaction of water rock” OR “Fractured aquifer” OR “Fractured aquifer” OR “Stable isotopes” OR “Water-rock-interaction” OR “Cluster analyzes” OR Hydrogeochemistry OR Hydrogeological OR hydrochemical OR aquifer OR “Geological structure” OR diagenesis OR groundwater OR “Subterranean water” OR “chemical composition of water” OR “groundwater esoz oicos ”)). The following were considered for the search on the Web of Science TS = title, abstract and keywords; in Scopus the title, abstract and keywords; in GeoRef All and advanced search and in Scielo and CAPES journals, all indexes.

The following criteria were established for inclusion of the researched studies: a) Studies published between 1999 and 2019 and that contain the established search terms. The exclusion criteria for studies were: a) Studies in the form of letters, reviews and editorials and theses and dissertations; b) Duplicate studies; c) Studies that do not contemplate the scope of the research; d) Studies not available in full.

In the third stage carried out on August 31, 2019, the databases were searched using the descriptors, finding 837 references (Chart 1). In the fourth stage, the selection of studies began by reading the title and abstract, totaling 328 articles. With the application of the exclusion criteria, 37 duplicate studies were detected, 221 studies that did not consider the scope of the research, 21 studies that were not available in full, resulting in 34 studies selected to be read in full. In addition, in the fourth stage, the selected studies were organized and analyzed using Microsoft Excel®. The fifth stage, discussion of the results and presentation of the ILR will be addressed in the next sections of this article. There are 10 exceptions from the main methodology adopted. Two books (Feitosa, et al., 2008 & Milani 2004); a book chapter (Teixeira, et al., 2019); an old article from 1994 (Turner, et al., 1994); a Congress (Reginato, et al., 2004); a Thesis (Machado, 2005); an article taken by other means (Freitas & Roisenberg, 2016), the methodology of search (Mendes, et al., 2019) and two recent works (Mancuso, et al., 2021; Teixeira, et al., 2021).

Chart 1 - Chart of the methodological itinerary.

	Selected articles from the database	Selected articles with summary title analysis	Articles selected after applying the exclusion criteria
Georref	87	22	1
Periódicos Capes	105	93	14
Scielo	28	14	4
Scopus	272	125	9
Web of Science	350	83	6
Total	839	329	34

Source: Authors.

3. Hydrogeological Setting

The Paraná Basin (Fig.1) is located in four countries (Brazil, Argentina, Uruguay and Paraguay). Thus, it is an intracratonic basin covering about 1,500,000 km^2, developed between the Devonian and the Cretaceous. The sedimentary sequence is 7.5 km thick and is composed of six supersequences: Rio Ivaí, Paraná, Gondwana I, II and III and Baurú (Milani, et al., 1994). The sedimentary filling comprises five large stratigraphic units, which make up 6000 m in thickness. It is a flexural, polycyclic basin, with deposition beginning in the Devonian. The Paraná Basin is considered a single basin, although it was subjected to disturbances of varying origin, which include: 1) vertical movements, 2) flexural subsidence from the margins of the plate during the Paleozoic. The basin rocks are essentially siliciclastic generated in the Paleozoic and Mesozoic, in addition to occurrences of sporadic carbonates in the Permian (Rostirolla, et al., 2000). After the deposition of sedimentary units, the volcanism of Serra Geral Formation occurred. Volcanism was associated with the generation of the Atlantic Ocean. Turner, et al., (1994) placed volcanism between 137 and 127 Ma.

The Rio Bonito Formation is contained in sequence I of Paraná Basin. The history is linked to subsidence in the Carboniferous, accompanied by the deposition of the Aquidauana-Itararé units, with records exceeding 1500 m in thickness. Overlapping the Itararé group, there are sandstones, siltstones and layers of coal from the Rio Bonito Formation. The deposition of the Itararé Group and the Rio Bonito Formation was influenced initially by the subsidence phase attributed to the overload of the continental glaciers, followed by the weight of the sediments deposited during the subsequent transgressive-regressive cycle. In Rio Grande do Sul, the Rio Bonito Formation is closely associated with the Palermo Formation (Milani, et al., 2007).

The Rio Bonito aquifer, wich has a fine to medium sandstone composition, has drinking water only at low depths. In some portions there may be intercalated layers of shales and coal that behave like aquitards with aquiferous sandstones. Average flow rates can reach up to 20 m^3/h. In a study carried out in the municipality of São Gabriel, the specific capacities of the Rio Bonito wells are less than 0.5m^3/h and the salinity of water varies between 800 and 1500 mg/L of total dissolved solids, (Goffermann, et al., 2015). Its transmissivity and storage capacity depend on local structural characteristics, mainly open faults. NE and NW faults are the main open fault directions (Belletinni, et al., 2019).

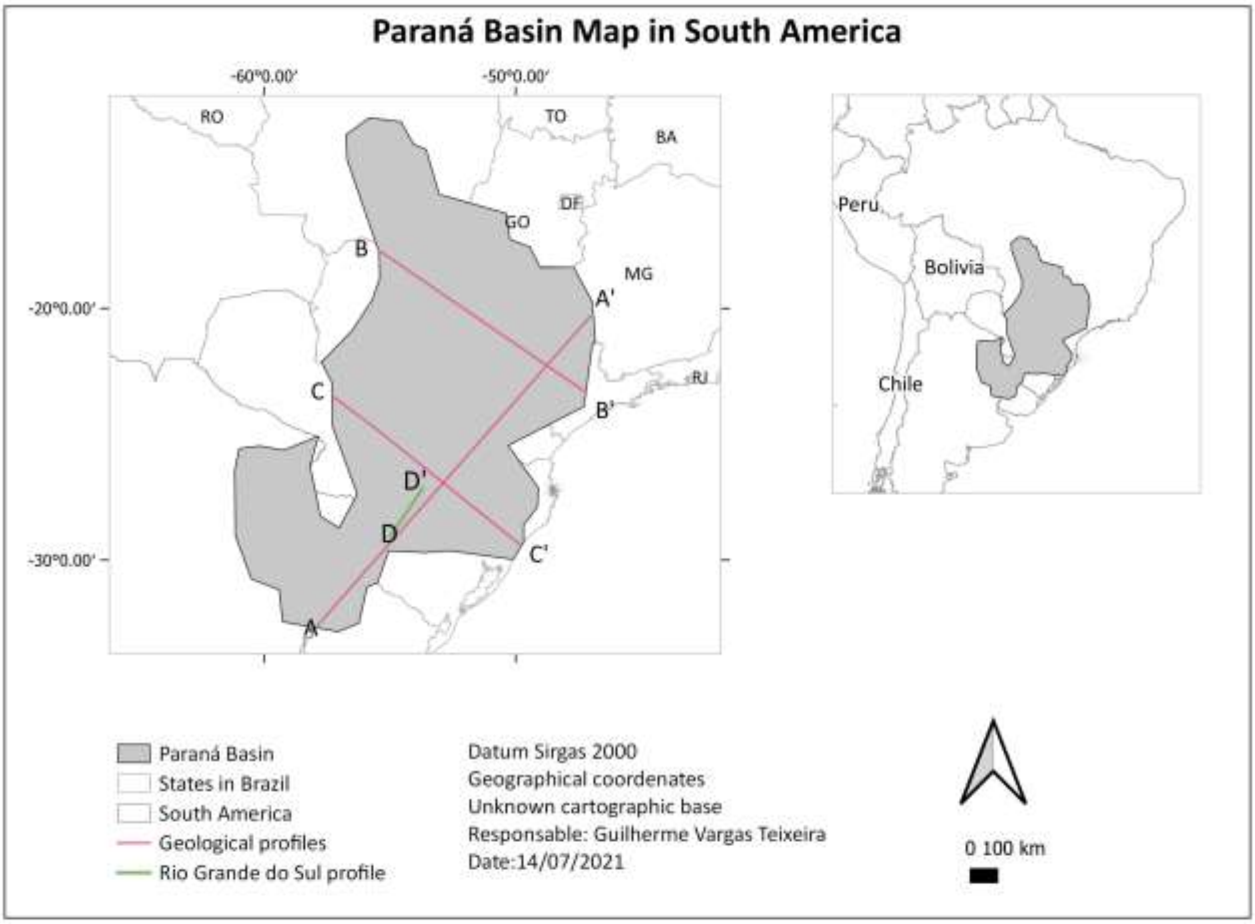
The Irati Formation, also in Sequence I, documents a unique movement in the evolution of the basin: an effective restriction on the circulation of water between the syneclysis and the Panthalassa Ocean culminated in the development of a hypersaline environment in the interior basin and the last marine incursion in the Paraná Basin (Milani, et al., 2007). The Irati is classified as a Permian equitard. The specific capacities of the wells that capture water from this system are usually low, <0.1m^3 / h.m (Machado & Freitas, 2005). These units overlie the Rio Bonito aquifer and because they are essentially made of rocks fine sedimentary are considered as aquitards, and do not have groundwater transmission capabilities. However, limestone lenses and flat layers of sandstone between shales and fractures can promote the circulation of water in these units

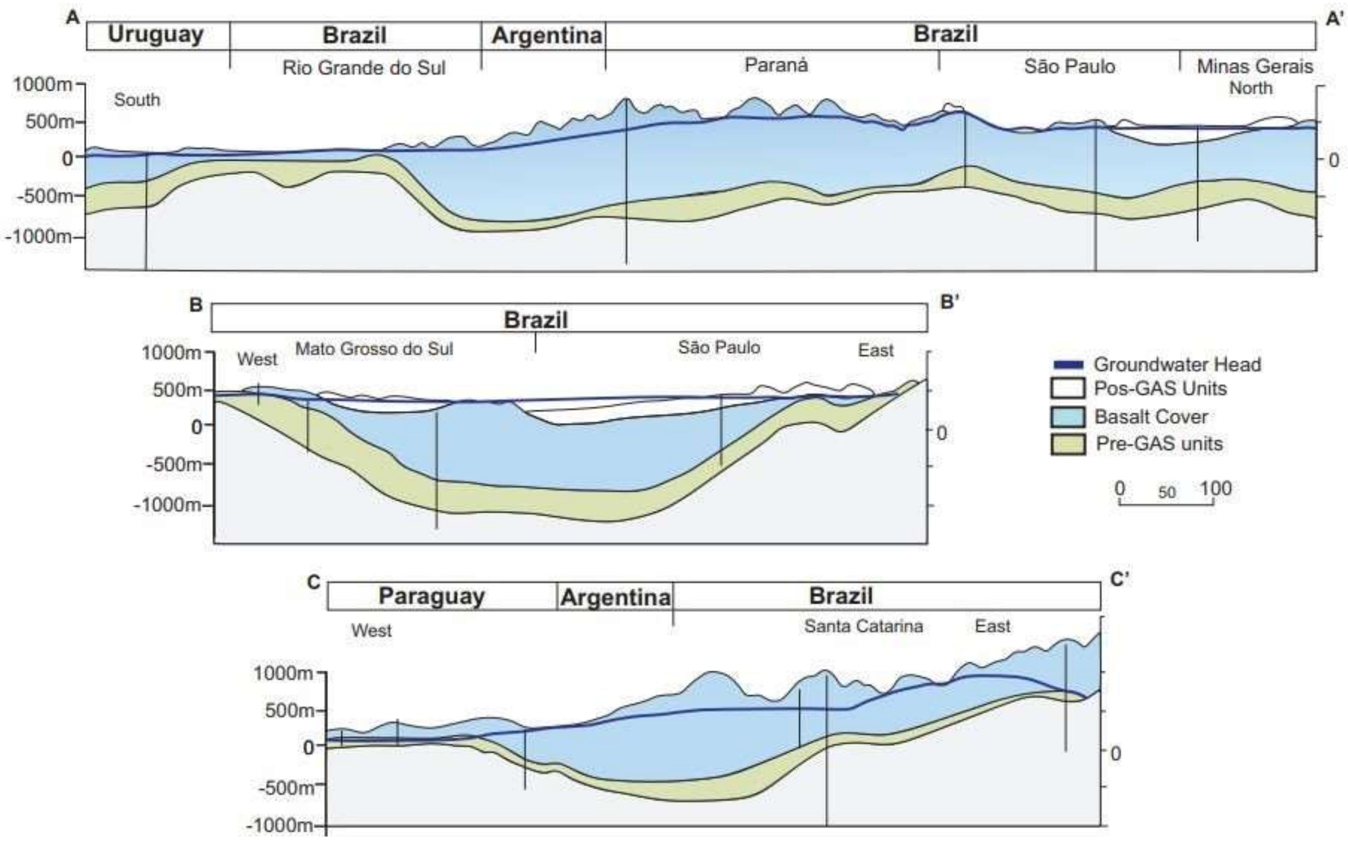
The Gondwana III supersequence named Jurassic-Ecretaceous Sequence in the conception of Milani, et al., (1994) comprises the interval of the stratigraphic record of the Paraná Basin in which the eolian sediments of the Botucatu Formation together with fluvial Pirambóia Formation and the magmatism of the Serra Geral Formation are positioned. In some locations, the thickness of the Pirambóia Formation layer is three times greater than the Botucatu Formation, as in the state of Paraná, showing the significance of this subunit of Gondwana III (Soares, et al., 2016). The volcanic rocks of the Serra Geral Formation correspond to the SGAS of fractured nature constituted by the discontinuities present in the volcanic rock. Such rocks emerge in practically the entire Paraná Basin and are of great hydrogeological relevance due to their high exploitation. Its waters are explored through tubular wells and public supply, with flow rates up to 220 m3/h (Freitas & Roisenberg, 2017). The strategic importance of the SGAS is proportional to the exploratory difficulty. Cases have been described in which two tubular wells that are less than 10 m apart have specific antagonistic capabilities (Athayde, et al., 2012). Therefore, in recent years there has been an increase in public interest about the enormous potential of the Paraná sedimentary basin in South America, and a large number of issues related to the correct management of this resource have been raised.

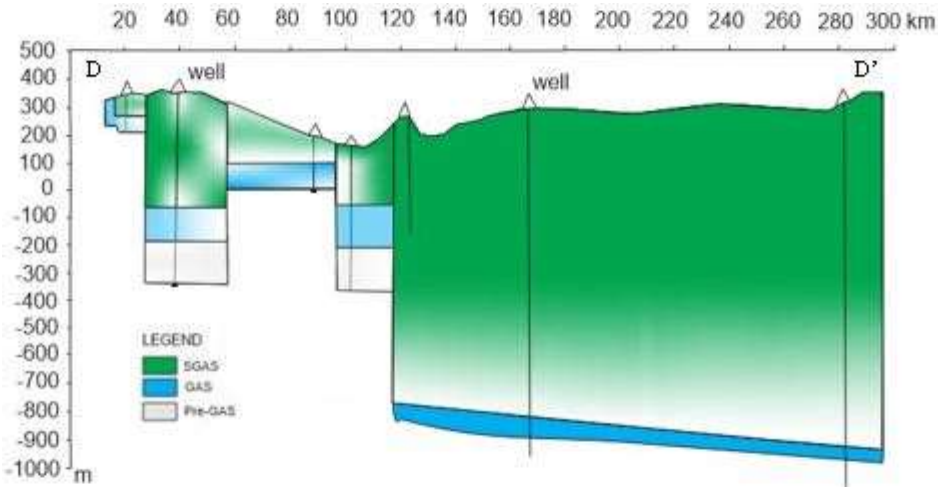
The Serra Geral Aquifer System (SGAS) is characterized by great storage capacity and circulation of water because of fractures and faults amplified by vesicular and amygdaloidal crusts and horizontal discontinuities between lava flows. Such structures can store and transmit large volumes of groundwater. The SGAS confines large aquifers such as the GAS and deeper units (Pre-GAS). The SGAS recharge and interaction mechanism with the aquifers below depend on structures that connect them (Freitas & Roisenberg, 2016).

Higher Ca^{+2}, Na^{+} and sulfate values found in the GAS in relation to the SGAS indicate the dissolution of eodiagenetic calcite that fills the pores of the sandstones of the Botucatu Formation. Water richer in total dissolved solids and sodium indicates a mixture of GAS with overlapping aquifers (Gastmans, et al., 2010; Filho, et al., 2006). The clearest influence of the GAS and other sedimentary aquifers on the SGAS occurs in wells where the values of total dissolved solids range from 1000 to 2000 mg/L, with chloride and sulfate contents above bicarbonate and predominance of sodium over calcium (Filho, et al., 2006). When the amounts of salinity between the GAS and the SGAS are the same, there is a hydraulic connection between these two aquifers, with a vertical extension of 400-500 m which allow the ascent of aquifer waters under the SGAS with mineralized waters originating from mixture (Scheibe & Hirata, 2008).

Figure 1. Location of the Paraná Basin in Brazil and geological profiles that cross the Paraná Basin.







Source: Geological profiles and Paraná Basin Map adapted from (Kirchheim, et al., 2019; Machado, 2005).

As shown in the Rio Grande do Sul profile which is not so evident in the large extension profiles of the Paraná Basin, faults play a prominent role in the connection between different units of the Paraná Basin because horizontally deposited layers are displaced by the movement of faults. These movements also allow the mixing of groundwater from these units as well as the rise of deep groundwaters to the surface. This pattern is seen throughout the Paraná Basin. Chart 2 shows the columnar stratigraphy of the Paraná Basin and the large discordances that occurred due to major tectonic movements.

Chart 2. Stratigraphic units of the Paraná Basin (adapted from Kirchheim, et al., 2019).

Sedimentary Basin/ Aquifer Units"	**Uruguay**	**Argentina**	**Paraguay**	**Brazil**	
	North	**Chaco-Paraná**	**Paraná**	**Paraná** **South**	**North**
Post-GAS	**Arapey**	**Serra Geral Posadas/Solari**	**Alto Paraná**	**Serra Geral**	
GAS	Taquarembó Itacumbú	Missiones Tacuarembó	Missiones	Botucatu Guará	Pirambóia
	Jurassic regional discordance			Caturrita Santa Maria Sanga do Cabral	
	Permo-Triassic discordance				
Pré-GAS	Buena Vista Yaguari	Buena Vista	Tacuary Independencia	Irati Rio Bonito	

Source: Authors.

4. Evolution of Structural Studies

Hydro-stratigraphic units in the Paraná Basin are controlled by diverse tectonic structures which include major faults and associated secondary faults. Many of the larger faults are reactivations of ancient basement weaknesses located below the first depositional sequences of the Paraná Basin. Rostirolla, et al., (2000) mentioned the response of hydrostratigraphic units to tectonic events in the southern Paraná Basin. He observed that a set of structures followed a typical transpressive tectonic regime that acted during the Mesozoic Era mainly in NE direction. Later, the extensional event at the end of the Mezosoic created NW faults and reactivated the previously generated NE faults. This same mechanism was aborded by Strieder, et al., (2017) in Rio Grande do Sul state, showing a similarity of tectonic events in the southern part of the Paraná Basin. Deep normal faults were responsible for regulating the discharge and recharge of groundwater flow and allow hydrogeochemical differentiation (Kirchheim, et al., 2019), reinforcing the connection between structural framework and hydrochemical characteristics of Paraná Basin groundwaters.

These large structures are capable of dividing the SGAS because the chemical analyses differ among compartments. In Rio Grande do Sul state, there are at least five structural SGAS compartments. Major faults tend to cause groundwater compostion differentiation from both sides of them because the hydraulic connection of the layers is interrupted by major faults and there is lateral contact of different hydrostratigraphic units (Freitas & Roisenberg, 2016; Teixeira, et al., 2021; Filho, et al., 2005).

Jacques, et al., (2014) recognized the importance of the E-W direction of σ1 paleostress caused by the compressive tectonic interaction between the Nazca and South American plates, to the generation of transpressive structures in the southern part of the Paraná Basin being nearly parallel to σ1 and perpendicular to σ3 in a compressional transpressive tectonic regime, in Santa Catarina state. Strieder, et al., (2015) also concluded that the direction of tectonic efforts represented by tectonic plates movements that were well coincident by open fault directions quite close to the E-W direction, close to σ1 direction. This author considered that a constritional regime with horizontals σ1 and σ3 were acting mainly in the Mezosoic Era and acted on all hydrostratigraphic units of the Paraná Basin.

Faults and fractures are generally not associated with specific events, and many directions appear. However, in many studies, there are preferred directions that can be identified in the field and through satellite images (Rostirolla, et al., 2001). Strieder, et al., (2015) identified different fault families of distinct orientation based on especific events. The various tectonic events verified can be summarized by: 1) Dn (Permian to the Lower Cretaceous). Deformational event prior to the rupture of Gondwana. NW oriented system (σ3). 2) Dn + 1 (Upper Cretaceous). Basalt dikes with NW direction in the Ponta Grossa arch. NE direction basalt dikes oriented according to (σ3). Dextral transcurrent movement. 3) Dn + 2 (Paleocene for the Eocene). Structural development of the Bauru Basin on the continental margin. Orientation according to NW (σ3) with sinister transcurrent movement. Paleozoic NW and NE fault orientation are present in all units of Paraná Basin, but only NW faults were reactivated after Gondwana rifting. Júnior, et al., (2013) encountered two families of faults in Serra Geral Formation in Paraná state; a family of secondary NE-SW faults have dip angles between 60-80°, while the primary NW-SE faults have high dip angle between 80° and 90°. This is the preferred orientation along the Ivaí River. The NE and NW lineaments have their origin related to the Brasiliano Orgeny (750-650 Ma) and extended to the genesis of the Paraná sedimentary basin in Devonian period and went through more pronounced reactivations after the separation between the South American and African plates. The E-W lineaments, as well as the more recent, newly formed N-S structures, are associated with the opening of the South Atlantic Ocean (130 Ma) and with the crustal flexure of the South American Plate. However, these lineaments have a secondary influence in the Paraná Basin, and rosette diagrams from several works show that the E-W and N-S directions are less frequent (Sordi, et al., 2017).

Chart 3 shows the evolutions of structural knowledge through time. Teixeira, et al., (2021) showed that orientation close to 90° is relevant for the permeability of fractured aquifers, and that the presence of higher density of smaller faults close to large faults is pertinent for the distribution of groundwater that comes from deep aquifers to shallow aquifer depths and should be considered (Soares, et al., 2016). The understanding of local stress is important to assess the geometry of faults as stress orientation can vary from place to place mainly closer to the surface where the neotectonics can act more intensely in opposition to the great depths, where the inheritance of tectonic events is more pronounced (Fernandes , et al., 2016).

Large faults are also responsible for vertical movements of blocks on both sides of the fault, causing lateral discontinuity of units that were previously deposited horizontally. In the state of Rio Grande do Sul, the displacement of GAS between structural compartments in the Western Rio Grande do Sul state close to Jaguari Mata fault system is up to 100 m (Teixeira, et al., 2019). In Paraná state, the towns of Foz do Iguaçu and Itaipulândia have elevation differences of 274 m. These increases are caused by regional uplifts represented by major faults (Filho, et al., 2006).

Techniques dealing with tectonic issues are often linked to satellite images and the tracking of structures in these images. Fieldwork identified these structures in more detail. The tectonic analysis around the Ijuí municipality in Rio Grande do Sul was developed through the treatment of shaded relief satellite images. These images were used to trace lineaments based on escarpments and valleys, as well as existing drainages. The lines were classified, according to their length, in small (<2 km), medium (2-4 km) and large size (2-4 km) (Tomasi & Roisenberg, 2019). A similar procedure was adopted by Mancuso and Santos (2021) in the municipality of Frederico Westphalen. The scale chosen was 1: 50,000, and the rosette diagrams were subsequently extracted using a geoprocessing software. The density of lineaments in the municipality was extracted with the frequency of lineaments in a specific direction, with the area of the municipality as a pixel. Soares, et al., (2016) compared six classes of lineaments to identify directions of highest lineament density towards the south of the Paraná Basin, while Teixeira et al., (2021) used four classes to identify the directions of higher lineament density present in cells of 1 by 1 km. This author came to the conclusion that minor faults in which the density lineament direction of S60-S90E had the highest correlation with high salinity and TDS values in SGAS of Rio Grande do Sul state. In the western region of Paraná state groundwater wells with high salinity were sampled. These cases demonstrate that there is a physical possibility of mixing water from the SGAS with the GAS due to favorable potentiometric isolines. The lowest potentiometric levels of the SGAS are recorded in the extreme west of Paraná state close to the Paraná River, which is a mixing zone (Athayde, et al., 2012). Bongiolo, et al., (2011) showed that there are compositional differences between distinct compartments in the state of Paraná. Fieldwork (Reis, et al., 2014; Strieder, et al., 2015) led to collection of structural data to complement satellite image tracing as some minor faults cannot be verified; striations caused by field scale tectonic movement are also measured.

Chart 3. Evolution of structural understanding of Paraná Basin through time.

Authors	Main contribution
Rostirolla, et al., (2000)	Reactivation review of paleolineaments by tectonics acting in Mesozoic and by neotectonics.
Filho, et al., (2005)	Topographic chart scanning for digital terrain model.
Athayde, et al., (2012)	Analysis of potentiometric elevations to determine the degree of mixing between aquifers and possible compartmentalization of the GAS in the state of Paraná and division of SGAS in Paraná state in two members.
Jacques, et al., (2014)	Extraction of linear features (faults) from satellite images and generation of rosette diagrams from these lineaments.
Strieder, et al., (2015)	Intensive measurement of lineaments in field work for the generation of rosette diagrams in the Serra Geral Aquifer System.
Sordi, et al., (2017)	Understanding the relationship of fault direction with specific periods of South American tectonic evolution.
Teixeira, et al., 2021	Direct relationship of regional faults with high salinity using a stochastic simulation method.

Source: Authors.

5. Hydrochemistry Evolution

The field of sodium bicarbonated waters is not common in typical SGAS groundwaters, and two situations arise for the SGAS salinization. The first is related to the greater confinement of the SGAS, which can occur in certain localities, where the SGAS reaches great depths due to the thick volcanic layer, while the second is related to the possible existence of a connection between the GAS and the SGAS, which is the most plausible alternative. SGAS groundwaters that do not have calcium or magnesium bicarbonate composition represent different rates of water mixtures from aquifers under the SGAS. The hydraulic pressure between the top Formation (SGAS) and bottom Formation (GAS) is almost always ascending and allows deep water to rise towards the surface. (Teixeira, et al., 2021; Bittencourt, et al., 2003; Freitas & Roisenberg, 2016; Mocelin & Ferreira, 2009; Filho, et al., 2005).

Back in 2001, Meng and Maynard were pioneers in carrying out geostatistical analysis in hydrochemical studies in groundwaters in the Paraná Basin. Their analyses showed that there is a tendency for $SO_4^{-2}$and Cl^- enrichment at great depths in the basin while surface groundwater is richer in Ca^{+2} and HCO_3^-. Samples richer in some variables that had similar characteristics to each other were associated with a specific component in the R-mode (variable grouping) cluster analysis. The same factorial technique for analyzing a complex data set that needed to be reduced in terms of variables was used in Bongiolo, et al., (2011). The main component technique was applied to a set of 45 samples studied for nine variables: pH, STD, HCO_3^-, Cl^-, SiO_2, Ca^{+2}, Mg^{+2}, Na^+ and K^+. Three main components were obtained from this data set. STD and HCO_3^- were the main variables for component 1, while for components 2 and 3, the main components were Cl^- and K^+ and STD and Cl^-, respectively, with three new variables being generated from three factors. Sracek & Hirata, (2002) came to the same conclusions as Meng and Maynard about the hydrogeochemical evolution of GAS groundwaters, but the author preferred to use the traditional mass balance and saturation índices to reach the same results. They corroborated the statement regarding the role of the cation exchange and carbonate dissolution mechanisms as GAS flow evolved downgradient to more salinized groundwaters and cation exchanges improved as the evolution proceeded.

This same evolutionary pattern described previously based on hierarchy cluster analyses, confirming the existence of three major groups. One belongs to deep confined groundwaters of alcaline, SO_4^{-2}, Cl^- composition, another to the intermediate zone of high pH and Na^+-HCO_3^- composition and the last one in the recharge zone of Ca^{+2}-HCO_3^-composition with acidic pH (Hirata, et al., 2011; Bongiolo, et al., 2011). In Rio Grande do Sul state, through K-means technique, there are typically three groundwater chemical groups in each of the five SGAS compartments in the state, and the most salinized of the groups had influence of GAS and Pre-GAS units (Teixeira, et al., 2021).

Alternatively to clustering, other techniques are used for hydrochemical studies in Paraná Basin. The exploratory data analysis (AED) technique is also an option to analyze data that do not follow a normal distribution and has the advantage of not making many demands on the statistical distribution of data, as with other methods. EAD emphasizes the original exploration with the aim of simplifying the description of data and obtaining a view of its nature (Freitas & Roisenberg, 2016). Belletinni, et al., (2019) separated Rio Bonito groundwater in Criciúma in Santa Catarina state in four groups mainly according to their sulfate, sodium, alkalinity, calcium, electrical conductivity and magnesium concentrations using EQ3 software to predict the saturation index of minerals and variable concentrations. This study was carried out in samples collected in nine Rio Bonito deep wells at six month intervals since 2008.

The origin of Na^+ in GAS and SGAS is an old debate. Only recently has it been taken into account that exchange processes between Ca^{+2} and Na^+ could be the cause of the increase in the amounts of Na^+ found in groundwater in several units in the Paraná Basin. In the state of São Paulo, Sracek and Hirata (2002) noted that Na^+ is probably derived from the dissolution of albite or halite, related to evaporites from the Pirambóia Formation or surrounding aquitards. However, this process alone is not enough to explain all the Na^+ input and cation exchange with calcium. The Ca^{+2} removed from solution by this process promotes more calcite dissolution and could explain the decrease in Ca^{+2} with increased concentration of HCO_3^- and Na^+ along the evolutionary path. Eodiagenetic smectite occurs in both Pirambóia and Botucatu formations in addition to the presence of mesodiagenetic betumen and calcite cementation and the higher pH accompanies the chemical facies more enriched in sodium and sulfate (Sracek, et al., 2003).

The δ13C enrichment indicates dissolution of calcite in the Guarani aquifer. The high concentration of sodium and the high concentration of bicarbonate, associated with low concentration of calcium, suggest an exchange of these ions in clays (Gastmans, et al., 2010). This exchange process prevents saturation of calcite and allows more calcite to be dissolved. The SGAS groundwater is mainly calcium or magnesium bicarbonates representing the chemical composition of the volcanic rocks that correspond to the SGAS aquifer unit. The original source of the elements calcium, magnesium and sodium is associated with changes in the silicates present on these rocks. The SGAS tends to present Ca> Mg> Na and an enrichment of calcium and magnesium at the top (acid rocks) in relationship to the base (basic rocks) of the volcanic rock stratification. Calcium bicarbonated waters are typical waters of the SGAS with calcium being the most abundant cation resulting from the alteration of plagioclase and ferromagnesian minerals of basalt (Reginato, et al., 2010). However, calcium is related to bicarbonate which indicates its origin mainly from the hydrolysis of amygdale calcite, because the basalt feldspars have low solubility and no interaction with water (Teixeira & Viero, 2017).

Studying the Rio Bonito Aquifer in Candiota and Bagé towns in Rio Grande do Sul state, Goffermann, et al., (2015) stated that the Palermo Formation, which is stratigraphically above the Rio Bonito Formation, is considered an aquitard and does not store water. The Rio Bonito aquifer has greater salinity at great depths. Only in regions of small depths where salinity is lower, the groundwater can be used for human consumption. The Rio Bonito aquifer may have an aquitard or aquiclude nature dependent of specific mineralogical composition. Most of the time, Rio Bonito Formation has direct direct contact with the basement and inherited the tectonic structures. In the region of Criciúma, the dissolution of gypsum is an important source of sulfate as well as pyrite oxidation of coal layers in the Rio Bonito aquifer. They also concluded that the sodium source whose contents are high in some wells resides in the cationic exchange with Ca and also in the dissolution of halite (Belletinni, et al., 2019). Filho, et al., (2006) were the first authors to directly relate the increase in salinity found in the west of the SGAS in the state of Paraná to the west of the Ponta Grossa arch as a structural factor, and major faults would be responsible for the communication of several units in the Paraná Basin and would take SO_4^{-2} and Cl^- to the surface. Samples located near the Paraná River in the Paraná state have a higher probability of mixing water from different aquifers (Athayde, et al., 2014). The same was with respect to the Uruguai River in Rio Grande do Sul state, indicating that the same faults where the rivers are embedded are responsible for salinizing the SGAS (Teixeira, et al., 2021). Chart 4 shows the evolution of structural understanding of the Paraná Basin through time.

Chart 4. Evolution of geochemistry understanding through time.

Authors	Main contribution
Meng & Maynard, (2001)	Principal components analyses technique applied to Guarani Aquifer System in São Paulo.
Sracek & Hirata, (2002)	Presence of sulfate and chloride associated with the mineral halite in deep areas of the Paraná Basin.
Filho, et al., (2006)	Importance of major faults in bringing chloride and sulfate to shallower areas of the crust.
Hirata, et al., (2011)	Identification of a pattern of hydrogeochemical evolution.
Athayde, et al., (2014)	Clear hydrogeochemical modification of samples to the west of the Ponta Grossa arch in Paraná, showing the importance of major faults in hydrogeochemical differentiation.
Kirchheim, et al., (2019)	Contextualization of the evolution of the study of the Guarani aquifer in history and the recent .importance of stable isotopes in the current understanding of the Paraná Basin.

Source: Authors.

6. New Trends in Hydrochemical and Structural analyses

Currently, hydrochemical studies in Brazil depend on cluster analysis and the analytical techniques of structural analysis depend on satellite image analysis in a numerical model of the terrain (MNT) and subsequent extraction of rosette diagrams in various software and structural mappings carried out in field.

A possible progress in the field of hydrochemical study of aquifer systems in the Paraná Basin will be in the field of geostatistics, which uses kriging and simulation as the main means of visualizing the geological phenomenon both in two dimensions and in three dimensions. Stochastic simulation applied to groundwater in Brazil is currently very scarce. Normally, traditional methods are used as numerical models (finite elements and finite differences), and their most common use is to determine the hydraulic conductivity of the studied aquifers.

The finite element method, such as that adopted for the study of the Cabeças aquifer in the Vale da Gurguéia-PI (Feitosa, et al., 2008) is an improvement from these two methods because it allows the modeling of heterogeneous and anisotropic geological phenomena and irregular contours. However, this method, in addition to the advantages of determining the hydraulic head values at different points, does not allow the visualization of the geological phenomenon, which is required to have a real idea of the structure of the aquifer both in physical parameters (permeability, porosity and load hydraulics), as well as hydrochemically (concentration of important ions in aquifers). This visualization is possible thanks to the analysis of covariance between the samples that are later inserted in the adopted stochastic simulation or kriging model. An important work in this field of stochastic simulation was done by Teixeira, et al., (2021) in the hydrochemical study of the Serra Geral aquifer system, in the state of Rio Grande do Sul, who used chemical samples collected by the CPRM of Rio Grande do Sul at SGAS. The simulation showed that the major faults that cut the SGAS coincide with high salinity values in this aquifer, and that these same faults collaborate to allow the SGAS potentiometric elevation values to be lowered in many of these faults.

Another improvement to look at in the future is the use of programming techniques in the study of aquifers, since more powerful company computers and even personal computers allow new tools to be applied. For this, programming platforms like python and R are the best known in academic environments.

7. Conclusions

The Paraná Basin was mainly subject to a constrictional regime in Mesozoic and extensional regime in Early Cenozoic. The constritional transpressive regime was responsible for the development of NW and NE structures that crosscuted all the units of Paraná Basin and later the NW faults were reactivated preferentially to NE structures during Pangea fragmentation. There is a typical structural control over the salinization phenomena in SGAS, where the regional faults act to transport sodium, sulfate and chloride to shallow environments and cation exchange processes are important to increase Na^{+} concentrations in detriment of Ca^{+2} in clays of GAS and pre-GAS. The major faults act as barriers for lateral communication in hydrostratigraphic units of Paraná Basin and are responsible for compartmentalization of them.

The last 20 years were significant for the development of a new concept in the understanding of Paraná Basin hydrogeology thanks to techniques like lineament tracing in satellite image and hydrochemical clustering analyses. New methods like programming and simulation could result in some improvement for future research. Many questions were answered in the last few years but still others remain, like the correct assessment of calcium, sulfate and chloride origin in each of the clustering groups, since both GAS and pre-GAS are capable of supplying it; the degree of GAS, SGAS and pre-GAS mixing within each compartment of Paraná Basin; in which unit the cation exchange process is more important; the real role of each individual regional fault in the ascent of ions to SGAS and its relationship with minor faults around them.

Again, it is important to highlight that the programming tools and the use of stochastic simulations applied to the study of groundwater in the world and in Brazil, combined with geoprocessing tools, which nowadays use friendly interfaces to perform various tasks that go beyond the simple construction of maps and that connect well with other softwares, can very well raise the level of knowledge in structural, hydrogeology and hydrochemistry subjects in geology.

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