

15th Water-Rock Interaction International Symposium, WRI-15

## Hypothesis of Groundwater Flow Through Geological Structures in Guarani Aquifer System (GAS) Using Chemical and Isotopic Data

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### Abstract

Guarani Aquifer System (GAS) is one of the most important in South America shared by more than 9 million people living in Argentina, Brazil, Paraguay and Uruguay. Groundwater flow through GAS is controlled by the geological framework of the Paraná and Chacoparanense sedimentary basins, dividing the aquifer in four groundwater flow compartments. The limit between north and southern compartment of the GAS is represented by the Rio Grande-Asunción Arch (RGAA), a megastructure that represents a regional uplift. During long time the role played by this important geological structure over groundwater flow has remained a controversial question. Groundwater from the northern portion of the RGAA is characterized by elevated values of electrical conductivity ( $>1,500 \mu\text{S}\cdot\text{cm}^{-1}$ ), Na-Cl-SO<sub>4</sub> type, and oversaturated with respect to calcite. On the other hand, despite their downgradient position, samples collected south of the structure, present low values of electrical conductivity (300-500  $\mu\text{S}\cdot\text{cm}^{-1}$ ), Ca-HCO<sub>3</sub> or Na-HCO<sub>3</sub> types, and most samples are not saturated with respect to calcite. These differences allow inferring that groundwater flow through RGAA would not have continuity. Moreover, an important recharge zone could be established along the structure, partially responsible for the replenishment of the GAS in the southern compartment.

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Peer-review under responsibility of the organizing committee of WRI-15

**Keywords:** Guarani Aquifer System; Groundwater Flow; Hydrochemistry; Geochemical Evolution.

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## 1. Introduction

The Guarani Aquifer System (GAS) represents one of the most important transboundary aquifers in the world. Four countries share its groundwater: Argentina, Brazil, Paraguay and Uruguay. It is located on the eastern edge of South America (lat. 16° to 32°S; long. 47° to 60°W) and extends for more than 1,000,000 km<sup>2</sup>.

A multinational and multidisciplinary research project named “Project for Environmental Protection and Sustainable Development for Guarani Aquifer System (PSAG)”, supported by the Global Environmental Fund (GEF) of World Bank, investigated many aspects of this important aquifer. Despite the improvement of knowledge on GAS groundwater flow conditions and geochemical evolution resulting from this project, some aspects related to groundwater flow continuity through regional geological structures were not adequately addressed.

Some questions related to the role played by the Rio Grande-Asunción Arch (RGAA) on regional groundwater flow remains controversial. Does this structure represent a barrier to flow? Do geological units constitute the GAS physical continuity? Does some recharge occur along the Rio Grande-Asunción Arch?

The main purpose of this paper is to evaluate the geochemical evolution of groundwater along flow paths crossing the RGAA based on the geological framework, searching for new evidence about the connection between northern and southern GAS compartments.

## 2. General Settings

GAS encompasses Mesozoic, continental clastic units from Paraná and Chacoparanense sedimentary basins, bounded at its base by a Permo-Eotriassic regional unconformity and the top by lava flows of the Serra Geral Formation, which may be over 1,500 meters thick<sup>1</sup>. Regionally, GAS geometry is controlled by tectonic structures that match those determining the configuration of the Parana and Chacoparanense basins. These structures reflect several post-Paleozoic tectonic events that occurred in South-America and were responsible for the significant erosion of previously deposited sediments.

The Paraná Sedimentary Basin geological framework controls basin-wide groundwater flow in the GAS; aquifer recharge occurs in outcrop areas located at eastern and northern borders of GAS uplifted by the reactivation during the Gondwana break out. On a regional scale, groundwater flows from north to south following the central axis of the Parana Basin. This flow pattern allowed the recognition of four hydrodynamic domains: NE, E, W and S<sup>1,2</sup>.

The separation of NE, E and W compartments from S compartment is represented by the RGAA<sup>1</sup>, an important first magnitude tectonic megastructure that typifies a regional uplift constituted by the Rio Grande Arch in the SE portion, and the Asunción Arch in the NW portion. These megastructures represent geological highs responsible for the division of the post-Permian-Triassic sedimentation of the Paraná and Chacoparanense basins, and can act as a barrier to groundwater flow in the GAS<sup>3,4</sup>. In this work, a barrier is defined as a system which hinders or slows down the groundwater flow<sup>5</sup>. Despite the possible flow interference, the previous conceptual hydrogeological model for GAS has considered continuity of groundwater flow through the structure<sup>1,2</sup>, as presented in Figure 1.

## 3. Methods

Sixteen groundwater samples were collected directly from water supply wells in the southern compartment of GAS, whose locations are presented in Figure 1. It should be noted that wells drilled through basalts have no casing and there may be a mixture between GAS waters and basalts waters. The pH, electrical conductivity (EC) and temperature of each sample were measured in the field. The cation and anion concentrations were determined in the Laboratorio de Análisis Químicos from the Instituto de Hidrología de Llanuras – Azul, Argentina. Alkalinity was determined by titration, anions by ion chromatography and cations by ICP-AES. The quality of water analyses was checked by charge balance ( $\sum \text{meq}^+ = 100 \cdot (\sum \text{meq}^+ - \sum \text{meq}^-) / (\sum \text{meq}^+ + \sum \text{meq}^-) < 10\%$ ). Samples collected for the determination of isotopic content ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) were stored in 30mL amber glass bottles, and in order to prevent isotope fractionation, the excessive presence of air inside the bottle was avoided. Stable isotope ratios were analyzed in the Laboratório de Hidrogeologia e Hidroquímica do Departamento de Geologia Aplicada IGCE/UNESP-Rio Claro, by Laser Absorption Spectroscopy, and the results reported as ‰ relative to Vienna Standard Mean Ocean

Water (VSMOW). The geochemical computer program PHREEQC<sup>6</sup> was used to calculate saturation indices,  $P_{CO_2}$ , and activities of dissolved species in groundwater. All calculations were performed at the temperature measured in the field.

#### 4. Results and Discussion

Electrical conductivity of GAS groundwater presents a wide range of values, associated to a well-established spatial distribution. In the northern sector of the RGAA, groundwater reaches values over  $2,000 \mu S.cm^{-1}$ , while in the southern portion of the study area, EC varies from 150 to  $550 \mu S.cm^{-1}$ . Due to the extent of the uplift related to the RGAA, with many outcrops associated with it, groundwater sampled upgradient of the structure presents low EC values. Downgradient variations in EC from flow paths crossing the RGAA are not concordant with groundwater flow. In the northern portion of the structure EC values are higher than EC values observed in the southern portion. Variations in EC detected along flow paths in the southern portion indicate an increase in groundwater mineralization downgradient.

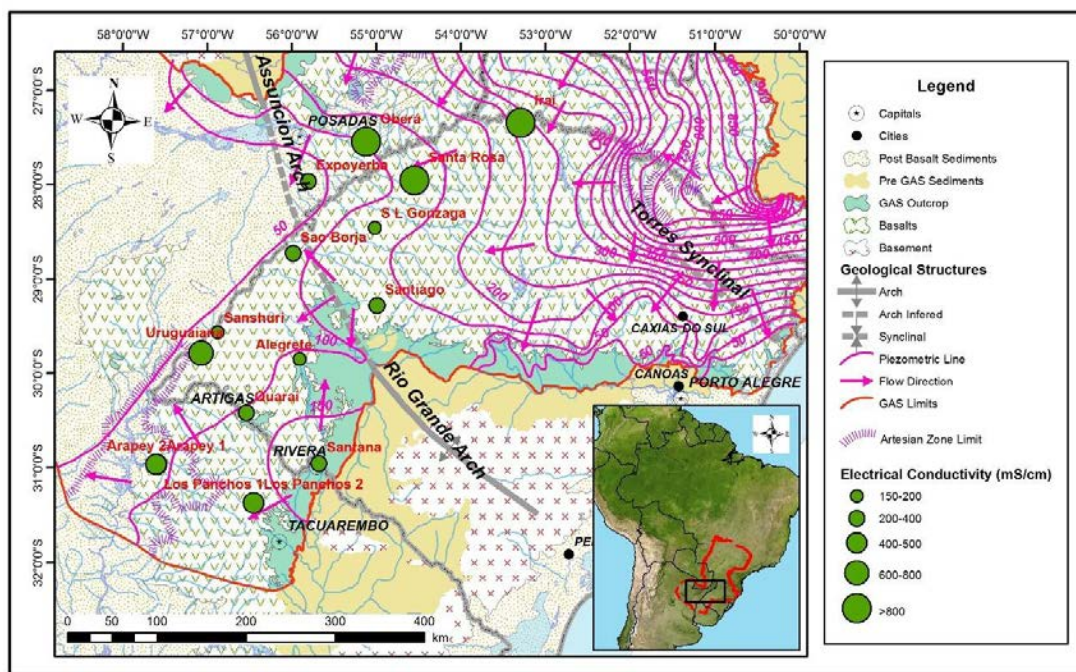


Fig. 1. Geological map of study area, showing the main hydrogeological features and EC measured in sampled wells. Regional geological and hydrogeological base map modifies from<sup>1</sup> and<sup>2</sup>.

Geochemical evolution of GAS groundwater could be summarized by the presence of  $Ca-HCO_3$  types in recharge zones that evolves to  $Na-HCO_3$  types due to dissolution of carbonate cement and exchange processes. In deeper portions of the aquifer,  $Na-SO_4-Cl$  types are observed<sup>7,8</sup>. In the northern portion of RGAA, groundwater of GAS is represented by  $Na-SO_4-Cl$  types, saturated with respect to calcite and presenting  $P_{CO_2}$  typical of confined conditions ( $\sim -5.0$ ). Meanwhile in the southern portion,  $Ca-HCO_3$  and  $Na-HCO_3$  types are observed close to outcrop areas and downgradient, respectively, indicating that groundwater in the southern sector is less evolved than in the northern portion. Evolution of calcite saturation for these samples is related directly to increase in EC values (Figure 2), and most of the samples present values of  $P_{CO_2}$  varying from  $-3.0$  to  $-4.0$ , indicating a transition from open to closed conditions. Based on this geochemical behavior and minimizing the effect of water mixing within sampled wells, it is possible to deduce the existence of recharge along the uplifted region associated to RGAA in accordance with the

GAS outcrops, . The RGAA represents a possible interference for geochemical evolution of groundwater, despite the possibility of flow continuity indicated by flow lines.

Isotopic composition of GAS groundwater varies from -25.6 ‰ to -39.0 ‰ VSMOW for  $\delta^2\text{H}$  VSMOW, and from -4.86 ‰ to -6.52 ‰ VSMOW for  $\delta^{18}\text{O}$ , indicating temporal variations in climatic conditions during recharge. No differentiation between North and South compartment has been observed (Figure 3).

Differences in geochemical evolution from these two compartments of GAS allow inferring that groundwater flow from the northern compartment would not have continuity towards the southern compartment. Moreover, the uplift of GAS in RGAA would produce a local recharge area for the southern compartment of GAS. The presence of an artesian zone along the Uruguay River, located north of the RGAA, where water discharge presenting higher temperatures is described, can explain the discharge of groundwater from the northern compartment of GAS.

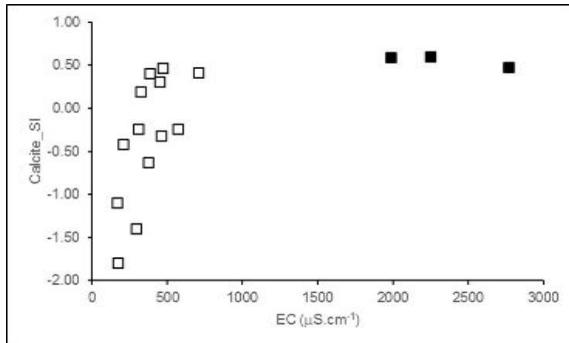


Fig. 2. Calcite\_SI versus EC. It should be noticed that groundwater from northern portion of RGAA (black filled squares) are saturated with respect to calcite, while groundwater from the southern portion of the Arch (blank squares) show a geochemical trend characterized by an increase in EC and increase in Calcite\_SI. Samples saturated with respect to calcite present values of EC about 400-500  $\mu\text{S}\cdot\text{cm}^{-1}$ .

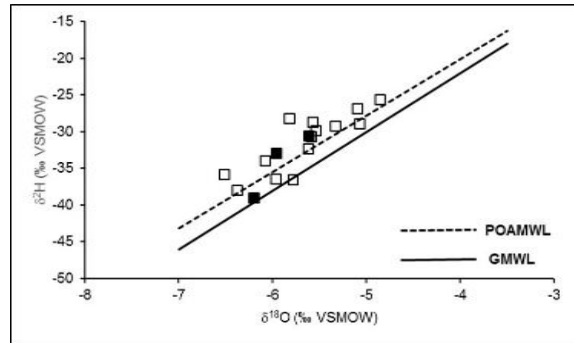


Fig. 3.  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$ . Samples are aligned according to the Meteoric Water Line from Porto Alegre GNIP station. It should be observed that there are no significant differences between north (filled squares) and south (blank squares) isotopic composition.

## Acknowledgements

The authors thank the International Atomic Energy Agency (IAEA) for the funds provided that allowed the development of this project.

## References

1. Gastmans D, Veroslavsky G, Kiang Chang H, Caetano-Chang MR, Pressinotti MMN. Modelo hidrogeológico conceptual del Sistema Acuífero Guaraní (SAG): una herramienta para la gestión. *Bol Geol Minero* 2012, **123**(3): 249-265.
2. LEBAC Informe Final de Hidrogeología do Projeto Aquifero Guaraní. *Final Report* – Consórcio Guaraní 2008. 172p.
3. Rossello E, Veroslavsky G, de Santa Ana H, Fúlfaro VJ, Garrassino CAF. La Dorsal Asunción-Río Grande: Un Altoplano Regional entre las Cuencas Paraná (Brasil, Paraguay y Uruguay) y Chacoparanense (Argentina). *Rev Bras Geociências* 2006, **36**:181-196.
4. Mira A, Veroslavsky G, Rossello E, Vives L, Rodríguez L. Subsurface geological modeling of Corrientes province (NE Argentina) and its relationships with the Guaraní Aquifer system function. *J South Am Earth Sci* 2015, **62**: 148-163.
5. Bense, V., Gleeson, T., Loveless, S., Bour, O., Scibek, J. 2013. Fault zone hydrogeology. *Earth-Science Reviews* 127 (2013) 171–192
6. Parkhurst DL, Appelo P (1999). *User's guide to PHREEQC (Version 2) – A computer program for speciation, speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations*. U.S. Geological Survey Water-Resources Investigations Report 99-4259, 1999, p.270.
7. Gastmans D, Chang HK, Hutcheon I. Groundwater geochemical evolution in the northern portion of the Guaraní Aquifer (Brazil) and its relationship to diagenetic features. *Appl Geochem*, 2010, **25**(1): 16-31.
8. Manzano M, Guimaraens M. Hidroquímica del Sistema Acuífero Guaraní e implicaciones para la gestión. *Bol Geol Minero* 2012, **123**(3): 281-295.