Using isotope data to characterize and date groundwater in the southern sector of the Guaraní Aquifer System

Luis Vives[a*], Leticia Rodríguez[b], Marisol Manzano[c], Andrés Mira[a], Luis Araguás-Araguás[d], Lucía Ortega[d], Javier Heredia[e], Takuya Matsumoto[d]

[a]*Instituto de Hidrología de Llanuras-IHLLA "Dr. Eduardo J. Usunoff", Azul, Buenos Aires, Argentina;* [b]*Facultad de Ingeniería y Ciencias Hídricas, Universidad Nacional del Litoral, Santa Fe, Argentina;* [c]*Escuela de Ingeniería de Caminos, Canales y Puertos y de Ingeniería de Minas, Universidad Politécnica de Cartagena, Cartagena, Spain;* [d]*International Atomic Energy Agency, Vienna, Austria;* [e]*Instituto Geológico y Minero de España, Madrid, Spain*

*Corresponding author: lvives@ihlla.org.ar

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Abstract

The Guarani Aquifer System (SAG) is the largest transboundary aquifer in Latin-America, extending beneath parts of Brazil, Paraguay, Argentina and Uruguay. This paper presents the results of recent hydrogeological studies in the southern portion of the SAG. Locally, the abundance of surface water bodies precluded the use of conventional hydrological tools to characterize groundwater flows. Geological, hydrochemical and environmental isotopes investigations were integrated to postulate a revised hydrogeological conceptual model. The revised geological model has provided a better definition of the geometry of the aquifer units and outlined the relevance of regional faults in controlling flow patterns. The new potentiometric map is consistent with groundwater flow from the SAG outcrops to the centre of the Corrientes Province, where upwards flows were identified. Hydrochemical and isotope data confirmed the widespread occurrence of mixing. Noble gas isotopes dissolved in groundwater (^{4}He and ^{81}Kr/Kr) provided residence times ranging from recent recharge up to 770 ± 130 ka. Groundwater age modeling confirmed the role of the geological structures in controlling groundwater flow. The southern sector of the SAG is a multilayer aquifer system with vertical flows and deep regional discharge near the Esteros del Iberá wetland area and along the Paraná and Uruguay rivers.

Keywords: Guarani Aquifer System, Corrientes and Misiones Provinces, Argentina, geology, hydrogeology, stable isotopes, krypton-81, helium 4, groundwater age

1. Introduction

The Mesozoic Guarani Aquifer System (GAS in English, known as SAG in Spanish and Portuguese literature) is one the largest transboundary hydrogeological systems in the world and extends for about 1.1 M km^2 beneath the territories of Brazil, Paraguay, Argentina, and Uruguay. Its groundwater is extensively used for water supply and many economic activities. Currently, 15 M people depend on it.

The southern sector of the SAG is studied in this paper. Groundwater resources in this portion of the SAG are poorly known, although this natural resource is strategic to Argentina and Uruguay. The study area encompasses Corrientes and Misiones provinces of Argentina (Figure 1). The relief is predominantly flat, the slope is gentle and starts to escalate towards the central part of Misiones Province. Maximum and minimum elevations are 350 and 27 m, in Oberá and near the SW border, respectively. The main surface water bodies in the area are the Paraná river, the Uruguay River, and the Esteros del Iberá Wetland (EIW), a major wetland extending over 14,000 km^2 (Figure 1). "Esteros" refers to an intricate ensemble of different wetland types with permanent and/or semi-permanent water, densely covered by marshy and aquatic vegetation. Precipitation amount decreases from 1600 mm/a in the NE to 1000 mm/a in the SW, while mean annual evapotranspiration reaches 1570 mm [1].

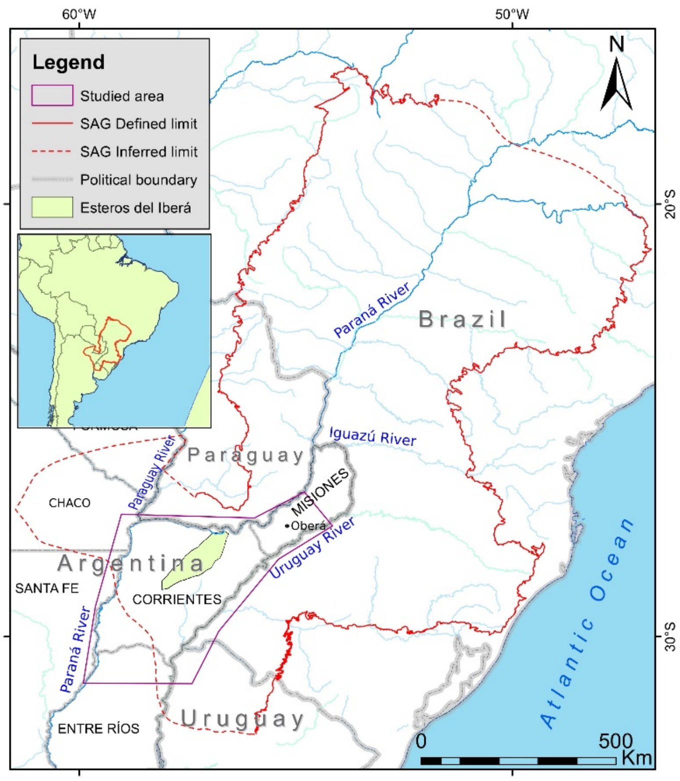

Figure 1. Study area.

Between 2003 and 2008, the four countries sharing the SAG collaboratively implemented the "Project for the Environmental Protection and Sustainable Development of the Guaraní Aquifer System", jointly funded and managed by the Global Environmental Facility-GEF, the Organization of American States-OEA, the World Bank-WB, and the governments of the four countries [2]. Among the conclusions of the project was the hypothesis that the EIW area could be a main regional discharge area of the whole SAG. But at the end of the project, there was very little knowledge about the surface hydrology of the area, and almost none about groundwater hydrology. The vast extension of the study area and the abundance of surface water bodies make difficult the identification of groundwater discharge locations and the quantification of their magnitude. Besides, geological, hydrogeological, and hydrochemical background information is scarce and unevenly distributed, turning very challenging the application of an integral hydrological approach to understanding the hydrodynamic functioning of the southern sector of this vital groundwater system. Then a myriad of questions remained unanswered or partially addressed: Where is the south-western boundary of the aquifer located? How deep is the geologic basement? Is the general stratigraphic column known for SAG valid in Corrientes Province? Is the EIW area a truly regional discharge zone? Are there local recharge/discharge systems identified within a regional context? If the SAG is confined by thick basalts, are there vertical flows between SAG and its confining units above? And between the SAG and the underlying sedimentary Pre-SAG formations? Do chemical and isotopic characteristics of groundwaters resemble those of the rest of SAG? Could groundwater age estimations, along with chemical and isotopic data, help to understand the hydrogeological functioning of the aquifer southern sector?

To address these questions, the investigation reported in this study was performed in two stages (described in Section 2) through a number of projects and field campaigns that produced several MSc and PhD theses authored or tutored by the authors of this paper.

Results of new geological, hydrogeological, hydrochemical, and environmental isotope investigations were integrated to postulate a revised hydrogeological conceptual model of the study area which introduced many novel aspects, including the estimation of groundwater mean residence time, and was tested by numerical groundwater flow and age simulations. The revised model will direct future efforts for a more detailed characterization of the SAG.

2. Materials and methods

The investigation was conducted in two distinct stages: (I) Integration and systematization of existing and new geological and hydrogeological information, leading to the postulation of a revised geological model and a new conceptual hydrogeological model; (II) Extensive field and sampling campaigns for chemical and isotopic determinations and groundwater age estimation to verify the model proposed in stage I.

The construction of the subsurface geological model of Corrientes Province and surrounding areas was based on the interpretation of 44 boreholes ranging from 50 m to 2,000 m depth, 21 geophysical surveys, and 1,366 depth data from a Bouguer gravity anomaly model. Deep geological structures that may have a significant influence on groundwater flow were identified. The proposed geological model allowed the definition of a generic lithostratigraphic column of the Corrientes Province and also provided new criteria to redraw the southwest limit of the SAG [3].

The potentiometric map of the entire aquifer [4] was revised and reconstructed in the study area. Piezometric data was verified with an improved digital elevation model for surface elevation estimation at well locations, used in conjunction with water depth data to define potentiometric surfaces. The revision process included the reevaluation of the flow directions sketched in LEBAC´s map [4], the location of proposed recharge and discharge spots, and the potential for groundwater/surface water interaction. These features, along with the regional hydrochemical characterization by Manzano and Guimaraens [5], were instrumental for the design of the water sampling campaigns.

The complexity of the mechanisms and the extension of the regional groundwater discharge area of the SAG have been a major research challenge, demanding the application of alternative methodologies. Water storage variations in the EIW were estimated by two independent procedures [6]: 1) a monthly water balance for the period 1991-2010 without considering a groundwater component; 2) a conjunctive surface water/groundwater storage fluctuation analysis for the period 2002-2010, provided by the satellite mission Gravity Recovery and Climate Experiment (GRACE). GRACE data were proven to be very representative of water level fluctuations within the EIW [6]. The differences between results obtained with both methods for overlapping years would indicate that regionally, there could be a detectable groundwater contribution to the EIW.

Seventy-four groundwater samples from 56 boreholes, complemented by another 30 surface water samples from rivers and lagoons, were collected during the dry seasons (winter) of 2009, 2010, 2011, 2012, and 2013. Some locations were sampled several times to analyze different components. Sampled wells ranged in depth from 10 to 1,250 m. Their location is presented in Section 3.3. In this work, we used data from a selected group of 54 wells and 13 surface water locations. Temperature, pH, electrical conductivity (EC), and whenever possible alkalinity, were measured in the field. The following hydrochemical parameters were determined at the Instituto de Hidrología de Llanuras (IHLLA, Azul, Argentina) following the methodology proposed by the American Public Health Association (APHA, 2005): pH, temperature, EC, alkalinity, Cl, SO_4, HCO_3, Na, K, Ca, Mg, NO_3, PO_4, F, and SiO_2, though not all the parameters were used in this work.

A selected number of samples were analyzed for environmental isotopes. Stable isotope compositions of oxygen and hydrogen ($\delta^{18}O$ and $\delta^{2}H$) in surface water and groundwater samples were measured by laser spectrometry at the IAEA laboratories. Oxygen and hydrogen contents are reported in the usual δ notation relative to the Vienna Standard Mean Ocean Water (V-SMOW) after corrections for between-sample memory and normalization to the VSMOW2-SLAP2 scale by using LIMS for Lasers 2015 [7]. Typical analytical uncertainty of the reported values is about ± 0.10 ‰ for $\delta^{18}O$ and ± 0.8 ‰ for $\delta^{2}H$.

Residence time of groundwater in the deepest parts of SAG was derived from the combined use of carbon-14 activity in total dissolved inorganic carbon (TDIC), helium-4, and radio-krypton (^{81}Kr) contents measured in groundwater samples collected in selected boreholes. Samples for carbon isotope analysis (^{14}C and $\delta^{13}C$) were collected in 500 mL HDPE bottles avoiding any contact with the atmosphere. Carbon-14 activities, expressed as percent modern carbon (pmC), were measured by accelerator mass spectrometry (AMS) at the University of Groningen (Netherlands), with a typical uncertainty of ± 0.8 pmC. Carbon-13 contents were measured in a separate aliquot of CO_2 by IRMS, and the abundance expressed in δ notation, in ‰ units with respect to the Vienna Standard Pee-Dee-Belemnite (V-PDB). Samples for helium-4 were collected in copper tubes and analysed by magnetic sector mass spectrometry at the IAEA (Vienna). For ^{81}Kr, about 20-30 $L_{(STP)}$ of dissolved gases were extracted in the field and compressed using a vacuum cylinder extraction method. Cryogenic distillation and gas chromatographic methods were used to purify radio-krypton at the IAEA laboratories, to produce 10 $\mu L_{(STP)}$ aliquots. Abundance ratios of purified ^{81}Kr/Kr were analysed by Atom Trap Trace Analysis (ATTA) at the Laboratory for Radiokrypton Dating of the Argonne National Laboratory, USA, as described in Jiang et al. [8].

The chemical and isotopic data used in this work are presented in Table 1s (groundwater samples) and Table 2s (surface water samples). For the hydrochemical and isotopic characterization, samples were grouped according to sampling depth and geological formations. Since most of the samples represented mixtures of groundwaters flowing at various depths, it was not possible to establish clear spatial patterns. The hydrochemical data was also analyzed using the modified Stiff diagram and bivariate graphical methods.

3. Results and discussion

3.1 Geological model

The study area is located in the southern part of the SAG, in a transitional zone between the Paraná and Chacoparanense sedimentary basins, where the filling of igneous and sedimentary rocks reached a mean thickness of ~2,000 m, and a maximum of 4,000 m [3]. The SAG sediments are formed by aeolian and fluvial siliceous sandstones of Upper Jurassic to Lower Cretaceous age, deposited in the Paraná and Chacoparanense basins [9]. Even though the average (165 m), maximum (600 m), and minimum (6 m) thickness of the entire aquifer were known, the thickness of SAG in Corrientes Province was very uncertain. During the course of this investigation, Mira [3] estimated an average thickness of the SAG sediments of 116 ± 63 m in this Province, thinning and disappearing westward. This finding allowed to trace a new SW limit of the SAG and build a new 3D geological model of the study area. The SAG formations lie on a Permo-Triassic discordance that separates them from sandy, clayey and silty Paleozoic formations of marine, transitional and continental environments. The continental SAG formations were deposited under warm and arid conditions. In the study area, the SAG is covered in 90% of its surface by Lower Cretaceous, fractured basalts of the Serra Geral Formation, with a range of thickness that varies between a few meters and 647 m. Aeolian dunes embedded with the first lava flows allowed the preservation of sandstone packages that constitute the Solari Member of the Solari-Serra Geral Group [11], which outcrops discontinuously in the study zone (Figure 2).

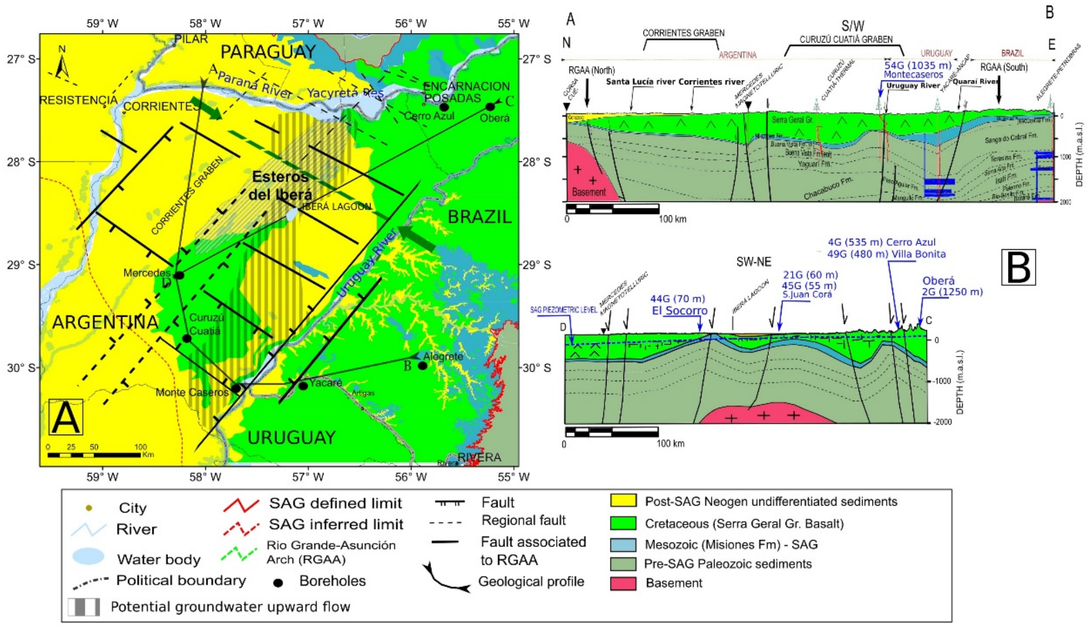

Figure 2. A. Regional geology. B. Geological profiles. (Modified from Mira et al. [2]).

Sediments ranging in age from Upper Cretaceous to the present overlay the basalts, with less than 50 m thickness in the study area. They are composed of alluvial and fluvial sedimentary rocks with interbedded calcretes (Upper Cretaceous), sandy or clay-mudstones with calcareous and silica cementation (Upper Oligocene – Lower Miocene), shallow marine marls (Miocene), and fluvial and aeolian sandstones and mudstones since then. Those sediments contain a phreatic aquifer. All these formations can be better identified in the new proposed stratigraphic column of Corrientes Province shown in Figure 3 [4].

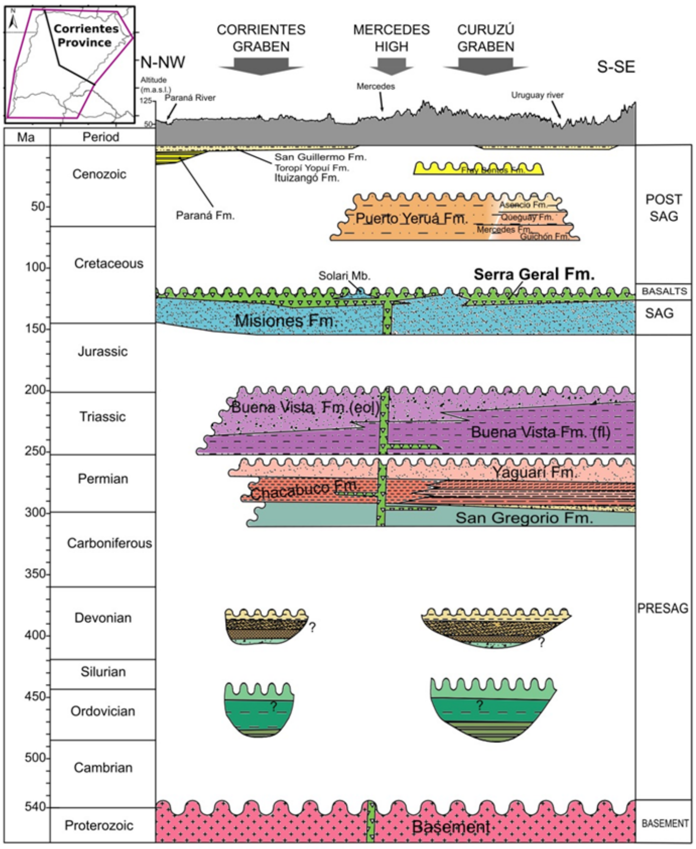

Figure 3. Stratigraphic column of the study area. (Modified from Mira et al. [3]).

Several mega-structures define the tectonic characteristics of the study area and even deform the complete stratigraphic sequence of the Paraná and Chaco-Paraná basins [12,13]. A primary structure is located in the NE sector, probably associated with the central rift of the Paraná Basin, and is likely to have regional continuity along the Misiones and Corrientes provinces. It is a wide, extensional structure formed by highs and lows of NE-SW direction, interrupted in the central sector of Corrientes Province by the layout of another mega-structure: the Rio Grande-Asunción Arch (RGAA), whose axis has been recently re-drawn [3,17]. Furthermore, two important depocenters were identified, the Corrientes and Curuzú Cuatiá grabens, filled with at least 3,500 m of sedimentary and volcano-sedimentary deposits, suggesting the existence of significant pre-Carboniferous sedimentary units associated to ancient extensional structures of the early Paleozoic (Figure 2).

3.2. Groundwater flow patterns

In the study area, the SAG is mostly confined. Groundwater regional flow originates in Brazil, and follows a predominantly NE-SW direction [14]. The revised potentiometric map of this portion of the SAG showed that regional groundwater recharge is associated with two outcropping strips, one located in southern Brazil, which extends eastward and south to the Uruguayan territory around the cities of Rivera/Santana, and another one in southern Paraguay (Figures 2 and 4). Groundwater recharged on those SAG outcrops, or near them through the basalts, flows to the W and S and converges towards the center of Corrientes Province, the northern sector of Entre Ríos Province, into selected stretches of the Uruguay and Paraná rivers, and in the EIW area, as explained below. This groundwater flow pattern is consistent with the findings of Oleaga [15] in Uruguay, Freitas [16] in Brazil and Schmidt and Vassolo [17] in Paraguay.

There are no SAG outcropping areas close to the EIW that could contribute to local recharge. Local recharge of SAG formations could occur through confining basalts in Corrientes Province between the locations of Colonia Pellegrini and Tres Cerros (Figure 4), where the basalts show their minimum thickness (< 25 m) and an important degree of fracturing [18]. The hypothesis of direct replenishment of SAG around the city of Mercedes (center of Corrientes Province) previously mapped by LEBAC [4], is not consistent with the observation that the sandstone formations outcropping in this area belong to the inter-trap Solari Member, not to the SAG.

Subtracting the potentiometric surface of the shallow aquifer from the SAG piezometric configuration allowed the identification of potential zones for upward flow, i.e., SAG regional discharge, which would take place either towards surface water bodies or shallower aquifers. Figure 4 shows the location of those zones to the E of the EIW. Regional discharge of SAG and Pre-SAG groundwater could also be expected from and explained by the hydraulic connection between SAG and older sedimentary formations through deep faults, or by SAG sandstones lying directly on top of the Paleozoic permeable formations. As explained in Section 3.3, groundwater chemistry in the study area pointed out to the contribution of dissolved salts from underlying marine Paleozoic formations.

The differences found between changes in storage at the EIW quantified with two methods was attributed to groundwater discharge. Its magnitude was estimated between 50 and 100 mm/year [1]. The small magnitude of this discharge compared to the magnitude of local precipitation (≈ 1,500 mm/yr) would prevent noticing the discharge, if it occurs.

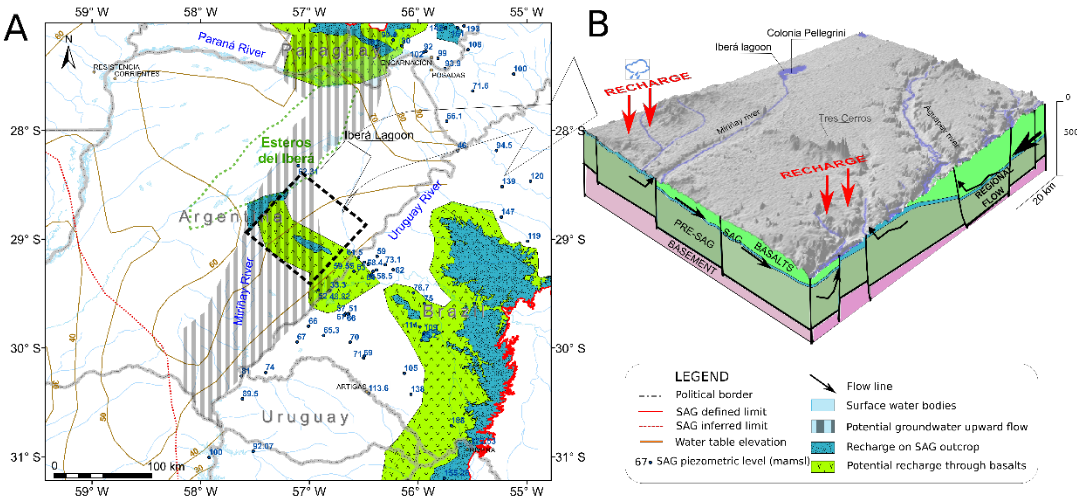

Figure 4. A: Hydrogeological map showing the potentiometric lines of the phreatic aquifer, some SAG piezometric levels, recharge zones, potential recharge zones, and potential upward groundwater flow areas. Water level data correspond to the period 2000-2014. B: Block diagram representing the conceptual hydrogeological functioning of the multilayer aquifer system (see A for block location).

3.3 Hydrochemistry and environmental isotopes

3.3.1 Groundwater and surface water chemical composition and its origin

Hydrochemical and isotopic characteristics of SAG and Pre-SAG groundwater in the Misiones Province were known from previous works of the authors [5,19]. This data was used as reference to assess the presence of SAG and Pre-SAG groundwater in the study area. The typical chemical facies of SAG groundwater was medium-mineralized sodium-bicarbonate (Na-HCO_3) waters, while the mixtures of SAG groundwater with Pre-SAG waters from Palaeozoic marine formations produced medium- to highly-mineralized sodium-sulphate/chloride and sodium-chloride facies (Na-SO_4Cl and Na-Cl).

First, the hydrochemical data from boreholes sampled in this study was used to evaluate the changes in groundwater mineralization and chemical characteristics versus depth. All collected samples clustered into four chemical facies: Na-HCO_3 (the most abundant), Ca-HCO_3 (or CaNa-HCO_3), Na-Cl, and Na-SO_4Cl. However, with the exception of the two deepest samples (2G, Oberá, 1,250 m; 54G, Monte Caseros, 1,035 m) which belonged to the Na-SO_4Cl facies, a robust correlation between chemical facies and depth was lacking: samples taken from 20 to 200 m depth displayed all the four facies, while the Na-HCO_3 facies appeared in samples collected between 200 and 600 m. Moreover, most groundwater samples collected in the depth range between 20 and 600 m presented similar EC values, varying from 0.03 to 2.0 mS/cm regardless of the sampling depth. Sample 2G showed EC = 2.1 mS/cm while sample 54G showed EC = 5.5 mS/cm.

The spatial distribution of the chemical facies did not show any correlation with the assumed main regional (horizontal) groundwater flow direction (see Section 3.2). In principle, the regional distribution of the Na-HCO_3 facies (Figure 5 and Table 1s) was consistent with the most common mineralogy of the geological units in the area: silica-dominated sandstones, silts, and clays, which usually generate waters of the Na-HCO_3 facies. The less abundant, slightly mineralized Ca-HCO_3 samples found to the NE of the study area (1G, 31G, 50G...) corresponded to recently recharged groundwater in the clayey and silty sands of the Late Pleistocene Toropí-Yupoí Formation (Figure 3; Corrientes graben area), while the medium mineralized Ca-HCO_3 samples found between the Corriente and the Miriñay rivers (samples 58G to 63G) were found in carbonated breccias of the Oligocene Fray Bentos Formation (Figure 3; Curuzú Cuatiá graben area). The two deepest samples (2G and 54G) were collected from boreholes penetrating Pre-SAG formations, thus, they were assumed to mostly represent Pre-SAG groundwater. Finally, the slightly saline to brackish Na-Cl, Na-HCO_3Cl and Na-HCO_3SO_4 facies samples found in not very deep wells (~100 m) in a small area located in the SE border of the EIW (6G, 18G, 19G, 20G and 44G) were considered, a priori, mostly mixtures of Pre-SAG and younger groundwater.

With respect to the surface waters sampled, most of them were of the Na-Cl facies and slightly mineralized waters (EC < 0.07 mS/cm; Table 2s), corresponding to rainwater-fed runoff in contact with siliceous sands and silts of the Pliocene Ituzaingó Formation (Figure 3). Only a few surface water samples from the Curuzú Cuatiá area corresponded to Na-ClHCO_3 and Ca-HCO_3 facies and were more mineralized (EC = 0.2-0.35 mS/cm); they were sampled on the carbonated breccias of the Fray Bentos

Formation. Thus, considering their level of mineralization and chemical facies, in principle none of the surface water samples could be considered as being affected – or at least, noticeably affected - by mixing with SAG or Pre-SAG groundwaters.

The presence of saline waters in some relatively shallow wells was considered questionless evidence of the presence of Pre-SAG groundwater. However, the similarity in the chemical composition between the typical Na-HCO_3 SAG groundwaters and samples from other aquifer units prevented the extensive use of hydrochemistry to identify or confirm the presence of and study the mixing patterns of SAG groundwaters. Environmental isotopes (^{18}O, ^{2}H, ^{3}H, ^{13}C, and ^{14}C) provided more valuable insight into the characterization of groundwaters of different origins and flow patterns.

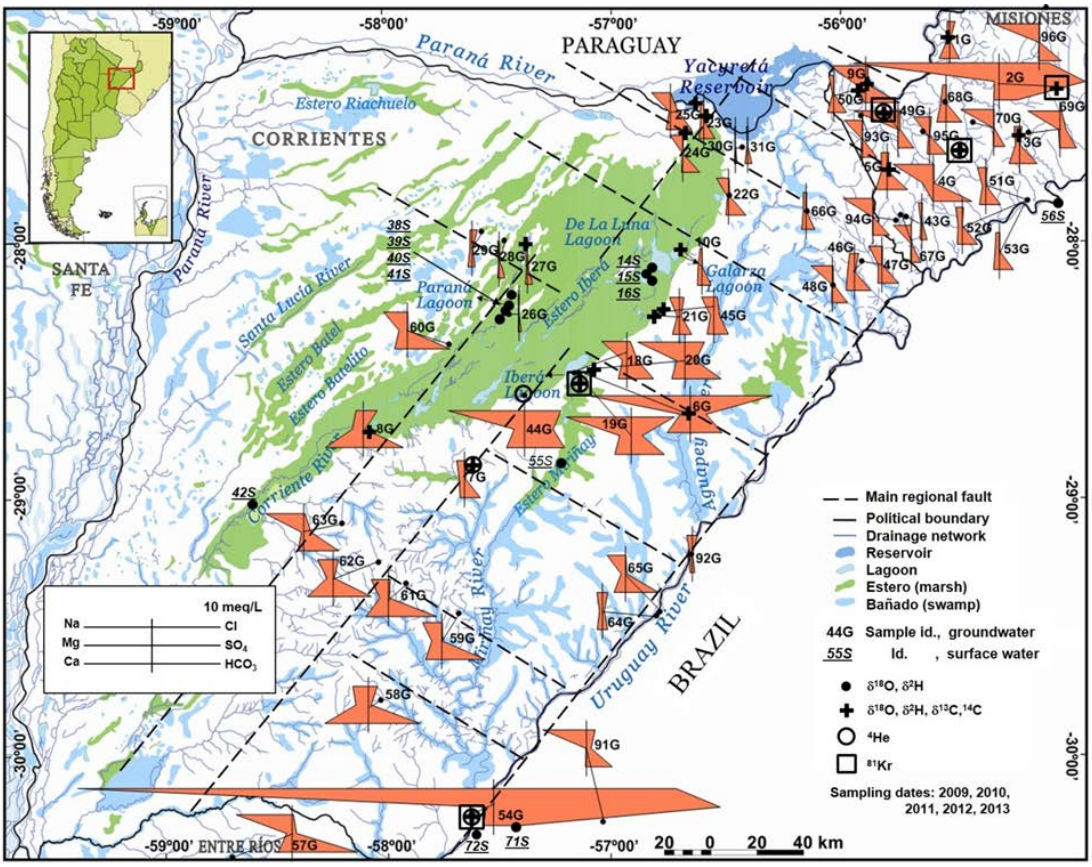

Figure 5. Location of groundwater and surface water sampling sites discussed in this study; modified Stiff diagrams of representative groundwater samples collected from 2009 to 2013, and isotopes measured in each point.

3.3.2 Groundwater isotopic composition and its origin

From previous works it was known that typical $\delta^{18}O$ values of the SAG waters in the Misiones Province were 2-3 ‰ lighter compared to the isotopic composition of present-day recharged groundwaters, and showed ^{14}C contents systematically lower than 5 pmC [20], revealing the presence of paleowaters. Stable isotopes contents in groundwater sampled in this study varied from -4.4 to -6.5 ‰ for $\delta^{18}O$ and from -23.0 to -38.2 ‰ for $\delta^{2}H$ (Figure 6). This wide range of isotopic values pointed out to the presence of waters of different origins, ages, and/or flow paths.

The characteristics of a representative meteoric water line were derived from the comparison of isotopic data from rivers, water-table wells, and historical precipitation data of several GNIP stations nearby the study area: Corrientes, within the study zone; Chaco and Santa Fe to the W and SW, respectively; Asunción to the NW, and Porto Alegre to the NE. The $\delta^{18}O$ and $\delta^{2}H$ values of river waters and shallow groundwater samples 56S (Uruguay River), 18G (a 12 m deep well nearby the Iberá Lagoon) and others in Figure 6, were assumed to represent the isotopic composition of present-day non-evaporated recharge, which is similar to the weighted long-term mean of precipitation at the Chaco monitoring site [21].

The $\delta^{18}O$ and $\delta^{2}H$ contents of the isotopically more depleted samples (2G, Oberá; 54G, Cerro Azul; 9G, Posadas; 49G, Villa Bonita, and 44G, El Socorro), representing SAG, Pre-SAG, or mixed groundwaters, corresponded to paleowaters, as confirmed by their very low ^{14}C activities (< 5 pmC) and noble gas data (Table 1s). Samples 2G, 4G, 9G, and 49G were collected from deep boreholes (500 – 1,250 m), tapping the SAG formations in the SW of Misiones Province (NE of the study area). Sample 44G, collected in a 70 m deep borehole, showed the most depleted $\delta^{18}O$ and

δ^2H contents. This borehole is located in the SE border of the EIW, where the SAG formations are very shallow (see Figure 2), suggesting an upward flow of deep groundwater. Groundwaters showing isotopic contents between these two sets of samples in Figure 6 are generally interpreted as mixtures, in various proportions, of groundwaters of different origins, although some of them might be affected by secondary isotopic enrichment by evaporation. Most surface water samples collected in lagoons and "*esteros*" are notably enriched in $\delta^{18}O$ and δ^2H due to evaporation (up to +1 ‰ in $\delta^{18}O$).

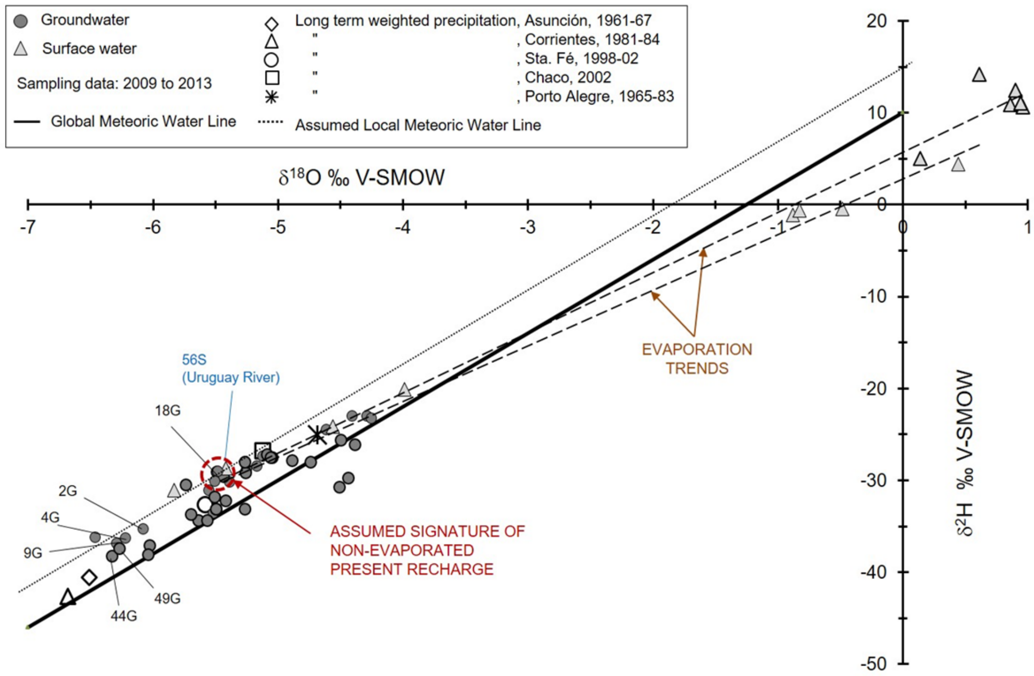

Figure 6. $\delta^{18}O$ and δ^2H contents of selected groundwater and surface water samples. The Global Meteoric Water Line, the Local Meteoric Water Line, as well as the long-term isotopic values for selected GNIP stations (Santa Fe, Corrientes, Chaco, and Porto Alegre) are shown for reference [19].

The location of wells 2G, 4G, 9G, 49G and 44G, not far from main regional faults (Figure 2, section D-C), and the prevalence of favourable hydraulic conditions for upward groundwater flow (Figure 4) may explain the presence of SAG and Pre-SAG groundwaters in boreholes at very different depths. These circumstances also induced the mixing of SAG and Pre-SAG waters with shallower groundwaters in many other wells. The combination of $\delta^{18}O$ and ^{14}C showed the existence of two distinct mixing trends (Figure 7.A), one between recently-recharged groundwater (samples labelled as R) and an old groundwater component with $\delta^{18}O \approx -5.6$ ‰ (trend O1), and another one with a second old groundwater end-member with $\delta^{18}O \approx -6.4$ ‰ (trend O2). Carbon-14 data alone could not be used to discriminate the range of ages of the samples clustering in the isotopically lighter part of both mixing trends.

On the left side of the mixing trend O1 appeared samples 6G, 19G and 20G, representing boreholes with depths around 100 m on the SE border of the Iberá Lagoon. These boreholes are located on a major NE-SW fault, and even though the presence of SAG groundwater cannot be discarded, it seemed that the old groundwater component is Pre-SAG, as indicated by their saline chemical facies and their less depleted isotopic values. This hypothesis is consistent with the position in Figures 7.A ad 7.B of the sample 54G (Monte Caseros, labelled O3), which from the lithology of the borehole is known to represent mostly Pre-SAG groundwater (see cross-section A-B in Figure 2.B).

On the left side of trend O2 appeared the samples 4G, 9G, and 44G, whose chemical facies would represent mostly SAG groundwaters. They showed the most depleted $\delta^{18}O$ values. Along this mixing trend also appeared samples 45G and 21G, which corresponded to two nearby boreholes with a depth of about 60 m, on the Eastern border of the EIW, and sample 25G, from a shallow well (20 m) close to the Yacyretá Reservoir (N border of the EIW). Mixing of SAG waters and recently recharged groundwaters in those wells can also be explained by their proximity to important regional faults (Figure 5). Sample 2G (Oberá), whose chemical facies suggested to be contributed by Pre-SAG groundwater, appeared between mixing trends O1 and O2 but closer to O2, suggesting a more significant contribution from SAG than from Pre-SAG.

Mixing trends O1 and O2 are also depicted in the $\delta^{18}O$ vs. Cl plot (Figure 7.B). In both trends, the end members representing old groundwaters are not very saline, though they are significantly different (Cl ≈ 400-500 mg/L in trend O1; Cl ≈ 100-200 mg/L in trend O2). However, the fact that their chemical facies are representative of geological formations containing evaporitic salts (e.g., sample 6G is Na-Cl; sample 44G is Na-HCO_3Cl) suggested that both mixing trends were formed not only by SAG groundwater, but also by groundwater tapping marine sediments, most probably the Pre-SAG formations. The map in Figure 7.C shows the location of the samples resulting from mixing processes, all of them in the vicinity of major regional faults. Figures 7.D and 7.E show the distribution of the $\delta^{18}O$ and ^{14}C values with sampling depth. The lack of a systematic vertical pattern supported the hypothesis that the groundwater age of each particular sample is mostly controlled by local geological and hydrogeological settings.

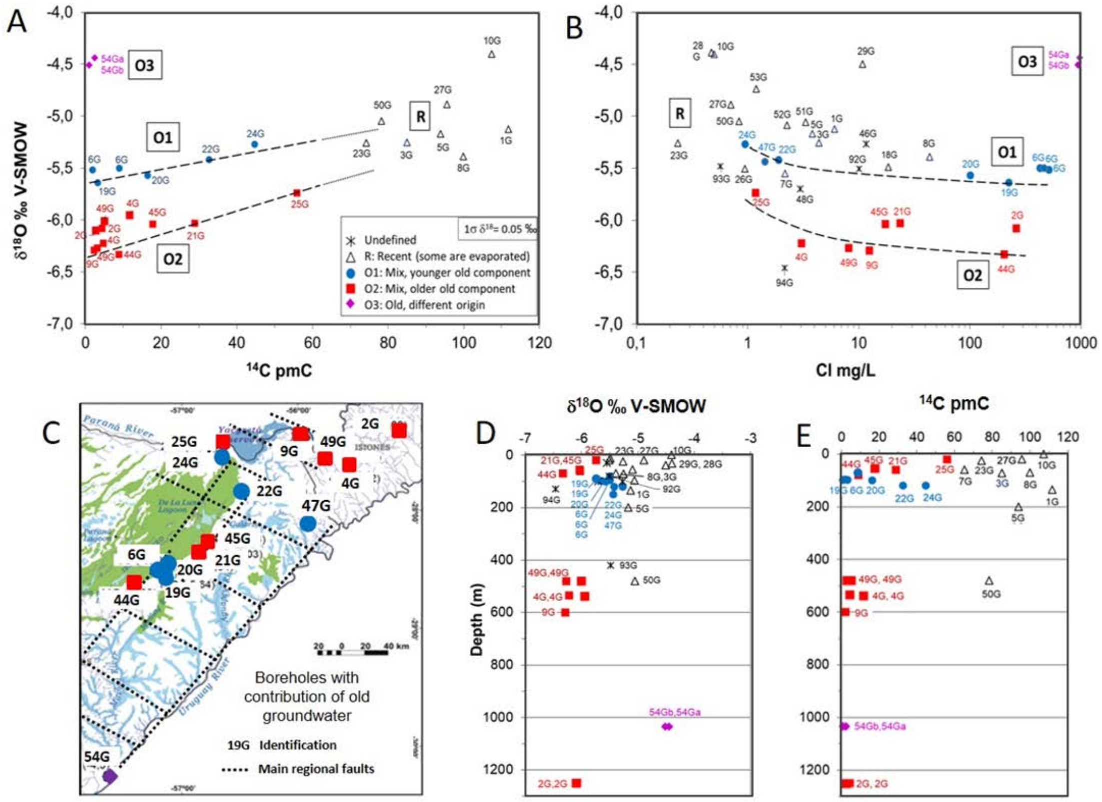

Figure 7. A) $\delta^{18}O$ vs radiocarbon activities, illustrating the existence of mixing trends. [R] Present-day recharged groundwater; [O1] Mixing trend between groundwater different than SAG waters and recent groundwater; [O2] Mixing trend between assumed SAG waters and recent groundwater; [O3] Monte Caseros deep borehole, representing Pre-SAG groundwater. B) $\delta^{18}O$ vs chloride, also illustrating the mixing trends. C) Spatial distribution of studied samples along the mixing trends identified. D) Distribution of $\delta^{18}O$ with depth and identification of the water groups. E) Distribution of ^{14}C with depth and identification of the water groups.

Since the residence time of most SAG (and Pre-SAG) groundwaters is beyond the dating range of radiocarbon, the isotopic contents of dissolved noble gases (helium-4 and radio-krypton) were determined in five representative boreholes with varying depths (90 – 1,250 m) located nearby regional faults (points 2G, 9G, 19G, 49G and 54G in Figure 5). The high ^4He concentration found in the deep boreholes sampled (up to 1.98×10^{-5} cm^3 STP/g), more than two orders of magnitude higher than the typical values found in shallow groundwaters, pointed out to residence times of SAG and Pre-SAG groundwaters well beyond the radiocarbon age limit, in agreement with the values found by Aggarwal et al. [22] in the northern sector of SAG in Brazil. More precise Mean Residence Times (MRT) of groundwaters derived from the $^{81}Kr/Kr$ ratios (Table 1s) ranged from about 140 ± 30 ka (49G) up to about 770 ± 130 ka (54G), providing unequivocal evidence of the presence of different flow-paths with contrasting ages as well as intricate mixing patterns controlled by local hydrogeological settings (water groups O1, O2, O3 in Figure 7). For instance, apparent ages estimated for assumed SAG groundwater samples ($\delta^{18}O \approx -6.4$ ‰; trend O2 in Figure 7) ranged from 142 ± 31 ka (49G, 480 m deep), 235 ± 29 ka (9G, 537 m deep) up to 387 ± 46 ka (2G, 1,250 m deep), in agreement with the results obtained in previous studies in the SAG [20,21]. The MRT estimation obtained for samples 19G (108 ± 19 ka) and 54G (770 ± 130 ka) supported the hypothesis of groundwater contribution to the mixtures from Post-SAG and Pre-SAG systems, respectively, as sustained by hydrochemical and $\delta^{18}O$ data shown in Figure 7. Although groundwater MRT derived from these isotopic noble gas tracers were based on different principles (accumulation rate in the case of ^{4}He, and radioactive decay in the case of ^{81}Kr), both isotopes provided consistent information on the time scales of various deep groundwater flow paths in the area.

3.3.3 Groundwater modeled ages

Numerical simulations were run on steady state conditions [14]. The finite element mesh covered 383,698 km^2, containing 16,611 2D elements (average size 19 km^2), and 7,611 nodes. The model consisted of two layers: the upper layer represented post-basaltic sediments, and the lower layer represented the SAG formations. Both layers were connected by 1,888 one dimensional-1D finite elements representing basalts of the Serra Geral Formation.

The calibration was satisfactory, hydrogeological parameters were coherent with background data, and groundwater levels were fitted within a mean relative absolute error of 8 %. Simulated potentiometric surfaces (or piezometric levels) reproduced adequately well-measured water levels, as well as piezometric gradients between layers that would verify the hypothesis of potential upward groundwater flows if a physical connection between layers exists (Figure 8.A).

A second four-layer model was implemented aimed at simulating groundwater age for synthetic cases that represent different connectivity conditions between layers. Figure 8.B corresponds to a synthetic W-E profile near the Iberá Lagoon. The profile was composed of four layers which, from top to bottom, correspond to the following geological and hydrogeological conditions: Layer 1: post-basaltic sediments-aquifer; Layer 2: basalts-aquitard; Layer 3: SAG sandstones-aquifer, Layer 4: Pre-SAG sediments-aquifer. The aquitard was simulated for two conditions: A) homogeneous with low vertical hydraulic conductivity; B) heterogeneous with two different vertical hydraulic conductivities, with a more conductive zone at the center of the layer that could facilitate the occurrence of preferential flows. The vertical geometry of the profile maintained the real proportion between the thickness of the various formations, and the hydrogeological parameters were coherent with previous estimations for each layer.

MRT of the incoming groundwater flows were derived from the radio-krypton results. It was assumed that the shallow aquifer receives uniformly distributed recharge, and the piezometric head was prescribed at each layer boundary to simulate lateral flows from/towards adjacent zones. At the center, a prescribed piezometric head simulated groundwater outflows through the EIW. Figure 8.C shows the vertical distribution of the simulated groundwater age as well as age data for Layer 1 and Layer 4. For a homogeneous aquitard, groundwater is stratified. Despite a favorable vertical hydraulic gradient, deep, old groundwaters were precluded from reaching the upper layers. Groundwater in Layer 1 presented MRT typical of recent recharge, while in Layer 4, i.e., Pre-SAG sediments, groundwater MRT is around 1 M yr. When the aquitard was simulated as heterogeneous, groundwater mixing occurred, and groundwater MRT tended to uniformize vertically, controlled by the presence of older, deep waters. Therefore, in the surroundings of the EIW, groundwater MRT in modern sediments may result unusually old for this type of formations because of the hydraulic connections with underlying, old groundwaters through more permeable geologic formations or fault systems. These results were entirely consistent with the information provided by piezometric levels, and the environmental isotopes combined with hydrochemistry, as shown by age data included in Figure 8.C.

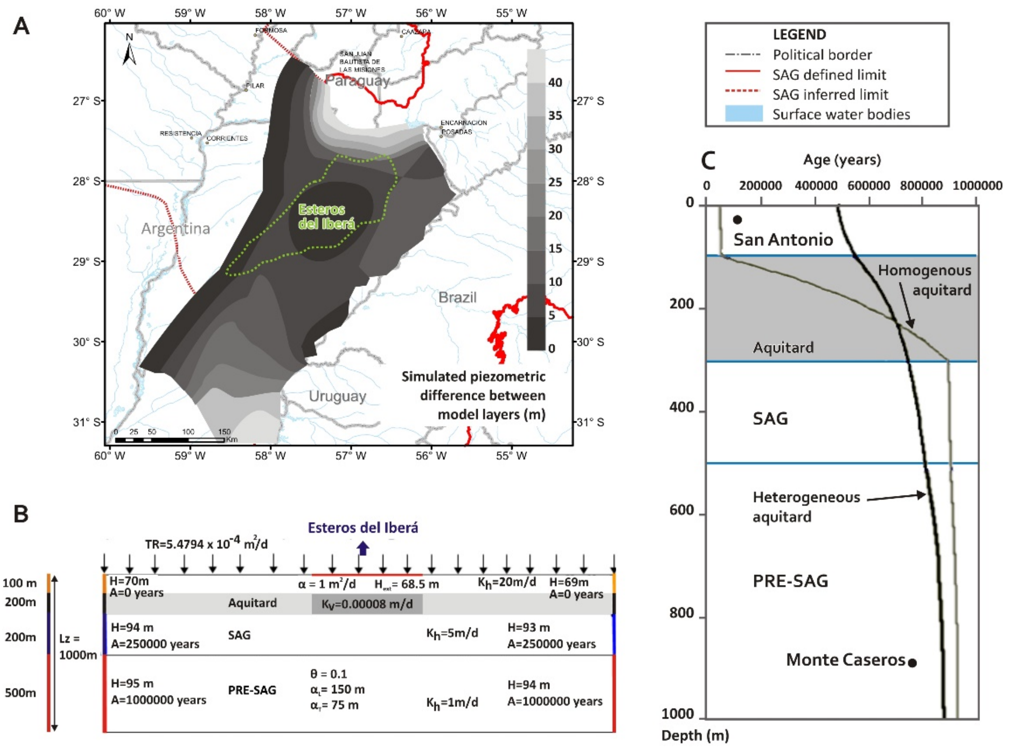

Figure 8. A) Simulated piezometric difference between the water table aquifer and the SAG in the area with the probable upward flow [14]. B) Synthetic model used for the estimation of MRT in a multilayer aquifer with an intermediate aquitard and preferential flow in the central zone. It represents a W-E section across the Iberá Lagoon in its central part and includes the Pre-SAG formations (layers thickness not to scale). C) Vertical distribution of simulated groundwater MRT in the central part of the section shown in B, where preferential upward flow exists due to geological heterogeneities, and in the rest of the section, where the aquitard is homogeneous.

4. Conclusions

The SAG, the largest transboundary aquifer in Latin America, is being increasingly exploited for freshwater supply and numerous industrial and agricultural uses. Therefore, a thorough understanding of the flow patterns is essential for the sound management of this valuable resource under future climate change scenarios and expected increasing water demand.

The findings of this work have contributed to build a robust conceptual model of SAG on its southern sector, corroborated by the hydrochemical, environmental isotopes and groundwater age-modelling results.

The conceptual model development process also provided new insights on different aspects of the regional geology, and on the geometry and configuration of the different aquifers with depth. The SW boundary of the SAG was redefined, and the stratigraphic column of Corrientes Province was defined more precisely, correlating the stratigraphic units with those previously known for the entire SAG.

Groundwater flow patterns in the area are complex due to the influence of local and regional geologic structures favoring upward flows. Hydrodynamic conditions for deep groundwater discharge exist in the area (which includes the Mercedes High, a zone formerly considered as recharge area). The EIW constitute a region candidate for regional groundwater discharge.

Different chemical facies with uneven spatial distribution and lack of correlation between particular hydrochemical facies and depth were identified. Most studied groundwaters represent mixtures of waters from different depths and geological formations. The evidence of saline groundwater in shallow wells located on the Eastern boundary of the EIW supported the hypothesis of regional discharge of deep groundwater near the Iberá Lagoon.

Stable isotopes combined with hydrochemistry showed the existence of different mixing trends involving recent groundwater and two old components, one corresponding to SAG groundwaters and a second corresponding mostly to Pre-SAG groundwater. The regional distribution of both groups of mixed waters is controlled by geological and hydrogeological features: deep faults; shallow depth of SAG due to tectonic elevation; variations in thickness, and upward gradients.

Consistent information on time scales of groundwater flow in the area was provided by the isotopic contents of dissolved noble gases (helium-4 and $^{81}Kr/Kr$ ratio), which allowed estimation of MRT ranging from 142 ± 31 ka up to about 770 ± 130 ka, providing unequivocal evidence of the presence of different flow-paths with contrasting ages as well as complex mixing patterns controlled by local geological and hydrogeological settings. Groundwater age modelling supported the existence of upward flows through thin layers and fractures, and thus the existence of mixed waters with old components in shallow aquifer layers.

Finally, the revised conceptual hydrogeological model for the southern portion of SAG consists in a multilayer system, with hydraulic interconnections between layers in selected zones and at different depths; deep, regional discharge near the EIW and along stretches of the Paraná and Uruguay rivers, and zones of regional and local recharge.

One of the main contributions of this revised model is the significant role of the vertical component of groundwater flow across all the studied area, enabled by the geological structure. This produced intricate mixing patterns and the presence of groundwater with contrasting ages at shallow depths, which made difficult to understand the groundwater flow pattern with traditional tools and conceptual approaches. The robustness of the proposed hydrogeological conceptual model relies on the consistency of the results provided by the many and different tools used to build it.

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