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## ISOTOPIC AND GEOCHEMICAL ASSESSMENT OF CONFINED THERMAL AQUIFERS OF SOUTHERN CÓRDOBA PROVINCE, ARGENTINA

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*The study area is located in the Pampean Plain (Córdoba, Argentina), where the groundwater resources of major interest are confined deep aquifers, which are often used due to the poor quality of the shallow unconfined aquifer. The study objective is to present a preliminary hydrogeochemical and isotopic model of the deep aquifers. Hydrogeological and isotopic analyses are used to characterize the deep aquifers. Three deep multilayered aquifer systems were defined taking into account groundwater quality: a semiconfined lower deep system, a confined system with a low degree of confinement and a highly confined system. All have hypothermal and mesothermal sodium sulphate type waters. The isotopic composition of local and western allochthonous streams, and the characteristics of the deepest confined aquifers, suggest deep aquifer recharge is located outside the study area in the perimountain western region.*

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## INTRODUCTION

Groundwater is an essential resource and constitutes the Earth's major fresh water reservoir. Although it is a renewable natural resource, it is possible for it to be significantly depleted over a period of a few years in many hydrological environments. This is especially true where groundwater renewal times in deep aquifers are on the order of thousands of years. Sustainable management of this resource requires a systematic approach to define integrated geohydrological models. It necessitates the use of geological, geomorphological, hydrostratigraphical, chemical and hydrogeological tools. Hydrogeochemistry is used to characterize the chemical composition of aquifers, including their natural variations and any anthropogenic impacts on groundwater. Techniques that use environmental isotopes, such as  $^{18}\text{O}$  and  $^2\text{H}$ , jointly with classic procedures, are a tool of great utility in hydrogeological studies due to well established isotope behaviors within the hydrological cycle.

The study area is located in the Southern Córdoba province, Argentina (Figure 1), in the Pampean Plain, where groundwater resources occur as unconfined shallow and confined deep aquifers. The area covers 1,216 km<sup>2</sup> and the most important town is San Basilio. This region is mainly dedicated to agriculture and cattle production. The climate is mesothermal-subhumid type with an annual mean precipitation of 835 mm and a mean potential evaporation of 822 mm. Groundwater is the main water supply, mainly from the phreatic aquifer. It is generally of poor quality due to the high values in TDS (total dissolved solids), Cl, SO<sub>4</sub>, As, F, NO<sub>3</sub>, or microorganisms. In some areas users take water from confined and semiconfined aquifers and frequently maintain open permanently flowing deep wells that feed artificial ponds where a specific biota is generated after many years. By leaving flowing wells open, the valuable groundwater resource for this zone is being wasted. The objective of this work is to present a preliminary hydrogeochemical and isotopic model of deep aquifers in the studied area, which could be useful to recommend guidelines for a rational management of groundwater, and to prevent continuous waste.

## MATERIALS AND METHODS

A geologic-geomorphologic analysis was made using topographic maps and satellite images on a 1:100,000 scale. Geologic information is scarce but on the basis of outcrops, two deep profiles

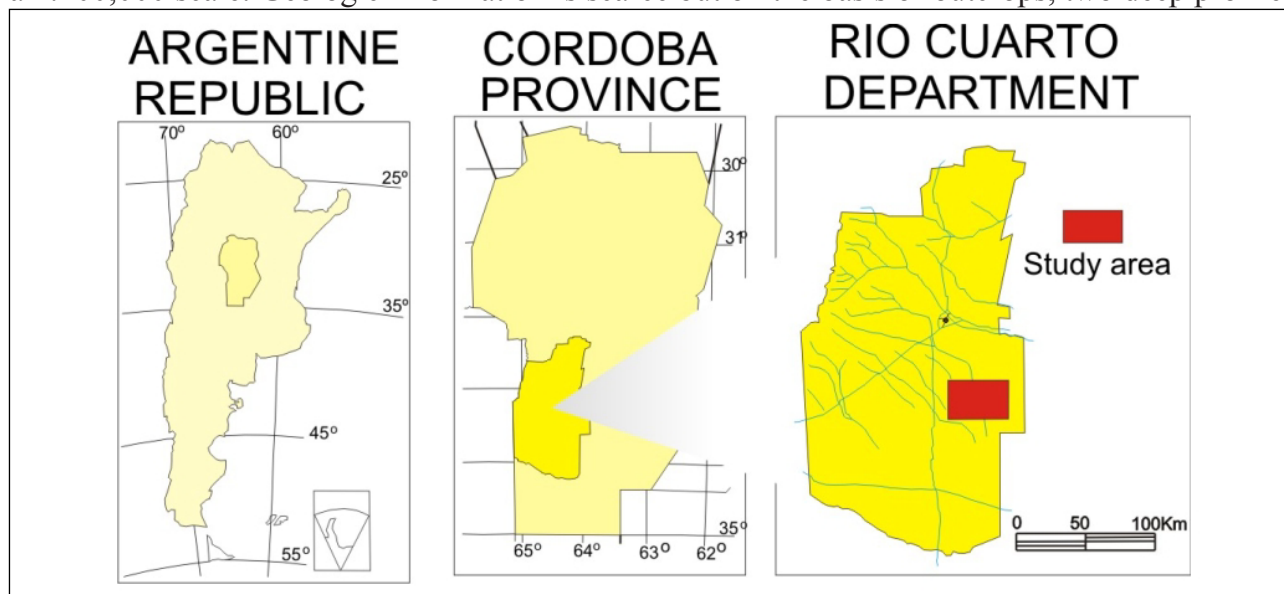


Figure 1. Location map.

of up to 350 m, and information from the Hydraulic Provincial Institute (DIPAS), a preliminary stratigraphic correlation was made to improve the interpretation of the geometry of the water-bearing sediments. A hydrogeological survey, level measurements, hydrogeochemical and isotopic sampling, and data analysis and processing were implemented to meet study objectives. During 2006-2007, samples and measurements were taken from 24 wells (Figure 3) and piezometric levels, temperature, pH, and electrical conductivity (EC) were measured in situ. Major, minor and trace elements ( $\text{CO}_3$ ,  $\text{HCO}_3$ ,  $\text{SO}_4$ , Cl, Na, K, Ca, Mg, F and As) were analyzed by conventional methods at the Geochemistry Laboratory of the National University of Rio Cuarto (UNRC). Isotopic analyses were done at the Geochronology and Isotopic Geology Institute (INGEIS) laboratories. The value of  $^2\text{H}$  in water samples was measured by the Coleman (1982) procedure and, for the measurement of  $^{18}\text{O}$ , the methodology described in Panarello and Parica (1984) was used. Isotope ratios were measured with a multicollector McKinney type mass spectrometer, Finnigan MAT Delta S. The results are expressed as  $\delta$ , defined as  $\delta = (1000R_S - R_P/R_P) \text{‰}$ , where  $\delta$ : isotopic deviation in ‰; S: sample; P: international standard; R: isotopic ratio ( $^2\text{H}/^1\text{H}$ ,  $^{18}\text{O}/^{16}\text{O}$ ). The standard is Vienna Standard Mean Ocean Water (V-SMOW) (Gonfiantini, 1978). The analytical uncertainties were  $\pm 0.1 \text{‰}$  and  $\pm 1.0 \text{‰}$  for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  respectively. The hydrochemical information was analyzed applying univariate and multivariate statistical methods (cluster Q mode) and conventional hydrochemical and isotopic diagrams. The isotope and chemical rainwater composition was evaluated with one collector for monthly composite samples. It was installed in the town of San Basilio. These measurements are supplemented by meteorological information such as mean surface air temperature and amount of precipitation. This information provides the input (rain isotope content) to groundwater as recharge in the area. Although Argentina has a National Collector Network for Isotopes in Precipitation, the existing stations are far from this area and the available time series are short (IAEA, 2002; Dapeña and Panarello, 2005).

## **GEOLOGICAL-GEOMORPHOLOGICAL AND HYDROSTRATIGRAPHIC SETTING**

The zone is characterized by the Tigre Muerto mega fault. This regional structure has a N-S direction and it exceeds the limits of the studied area. It controls, throughout tens of kilometers, the Santa Catalina river, generating a noticeable and particular morphostructural relief that influences its regional hydrological characteristics.

Associated with this structural form are two large environments with the following characteristics:

a) Lower Block (West) - includes the old and modern flood plains of the Corralito and Los Jagüeles streams. It has a smooth undulating to flat plain relief with lengthy topographic slopes and gradients around 0.3 %. The stratigraphic column is composed of aeolian fine-grain size materials (very fine silty-sands) with intercalations of cemented silts and, subordinated and associated with fluvial belts, fine to medium sands and very fine clayey-sands linked to paleofloods. It is characterized by several features of hydro-halomorphic processes, vast flooded areas and permanent lagoons caused by phreatic ponding at many places.

b) Upper Block (East) - shows a large asymmetric regional hill, dipping to the south, with smooth wavy flanks. It is the western flank of shorter slopes and greater gradient (1 %) than to the east. The outcropping sediments are mainly very fine silty sands of aeolian origin. The upper part of this block acts as a water divide for both surface water and groundwater. The joint interpretation

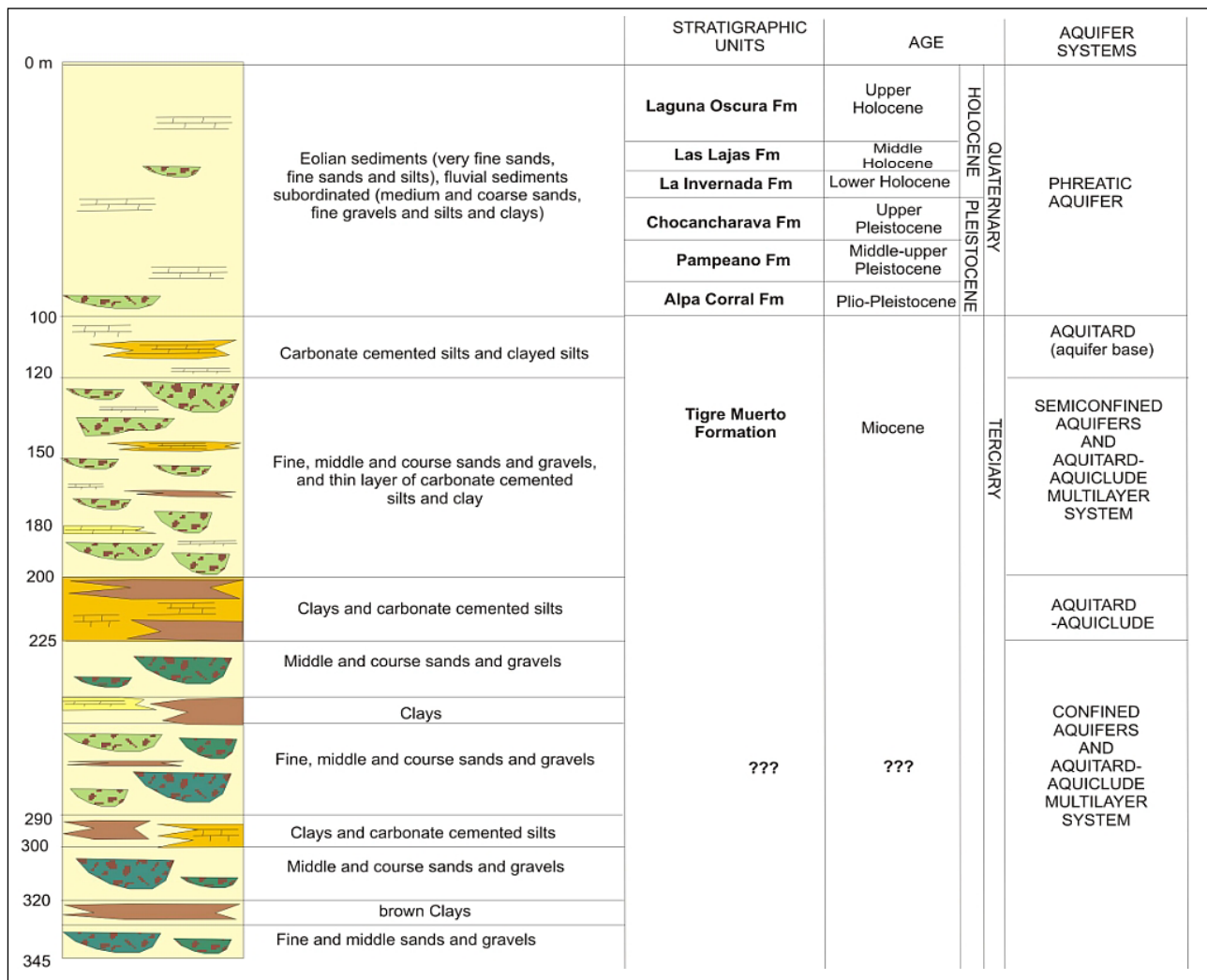


Figure 2. Stratigraphic column.

of lithologic profiles and geologic schemes provided a preliminary hydrostratigraphic column for the zone (Figure 2) and permitted a reconstruction of the geologic history of the area. The deep wells that were sampled are located in the Lower Block. The deepest materials were assigned to Upper Tertiary age (Miocene) (Blarasin et al., 2000).

This hydrogeological model assumes the presence of several multilayer artesian aquifer systems. They are located in sedimentary lenses associated with the paleofluvial Tertiary system, with variable areal development and thicknesses. These lenses are mainly composed of gravels and sands and they are covered by variable fine grain size sediments (cemented silts, clayey silts and clays) which are also associated with different stages of the old fluvial system. All these sediments and their variable depths and thicknesses produced different grades of confinement. In this complex system, three deep multilayer aquifer systems were defined taking into account depths, degree of confinement and groundwater quality. The deepest ones (ca. 225 m-320 m) have more confinement and produce artesian and semi-artesian wells. They constitute a sequence of coarse materials with intercalations of clay levels, and they are identified with the abbreviations SCA and SCB. The aquifer system of shallow depth (ca. 120 m-200 m), consists of fine and coarse sandy and gravel materials intercalated with thin layers of fine sediments. It produces artesian type wells, except C22 (semi-artesian) and is designated SAS. Figure 3 shows the distribution of the deep aquifer system and the location of the sampled wells.

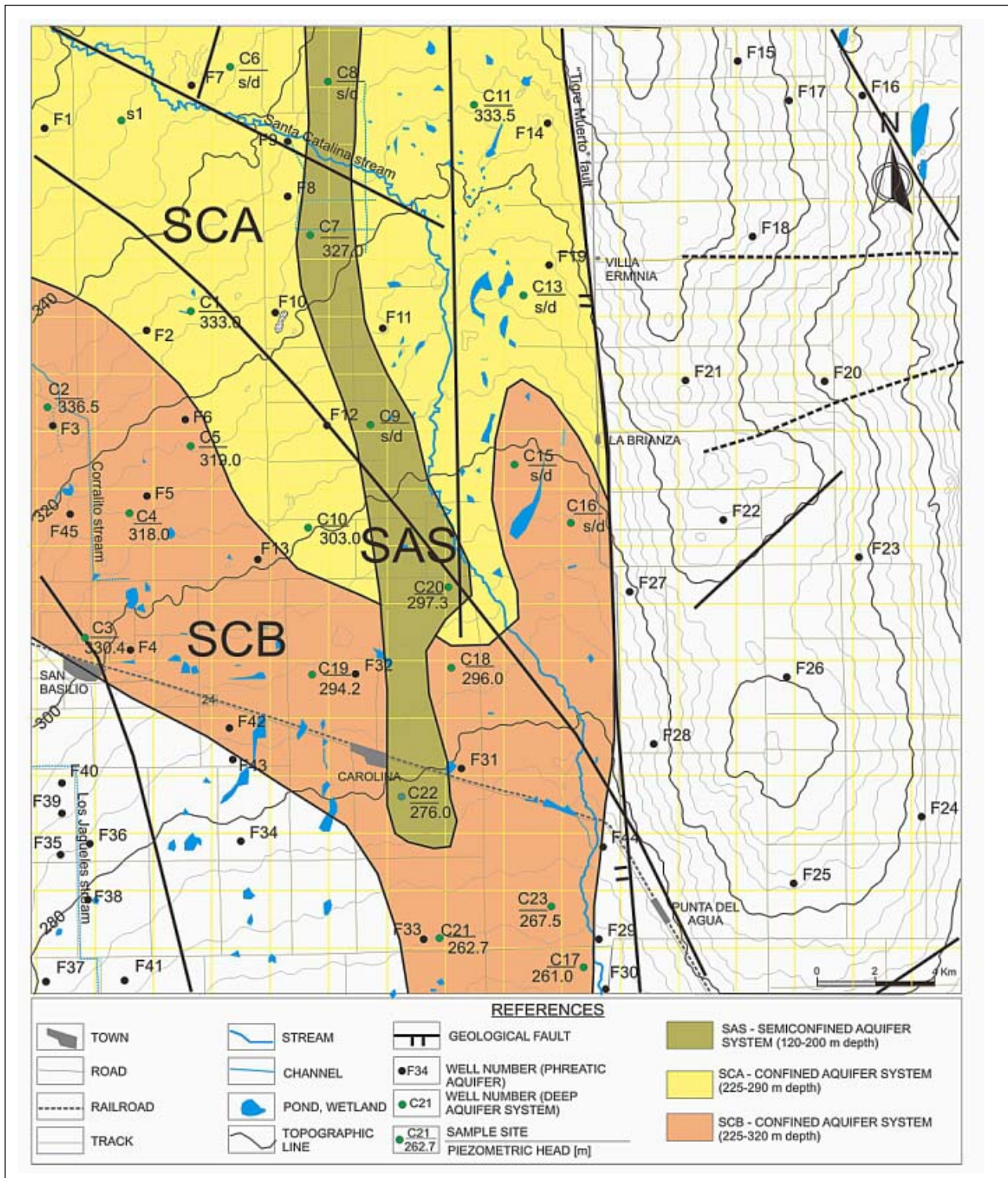


Figure 3. Distribution of aquifer systems and location of sample points.

## HYDROCHEMISTRY AND ISOTOPE COMPOSITION

### Results and preliminary conclusions

Physicochemical and isotopic analysis jointly with univariate and multivariate statistical tests (cluster test) made on the variables  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{As}$ ,  $\text{F}^-$ ,  $^{18}\text{O}$ ,  $^2\text{H}$ , depth and temperature allowed the design of a hydrogeological model and definition of three hydrogeological environments with different water qualities (Table 1). These environments can be associated with

Table 1. Main characteristics of deep aquifers.

	Depth [m]	Hydraulic behaviour	Well number and type	EC [ $\mu\text{S}/\text{cm}$ ]	Water Temperature [ $^{\circ}\text{C}$ ]	Temperature excess [ $^{\circ}\text{C}$ ]	Temperature classification
SAS	120 – 200	Semiconfined	C7, C9, C8, C20 (artesian), C22, (semiartesian.)	1960-2510	25-30.9	5.5-9.4	Hypothermal
SCA	225 – 290	Confined (Low grade)	C11, C1, C13, C10, C6 (artesian)	1786-3050	29-35.3	4.2-10	Hypothermal
SCB	225 – 320	Confined (High grade)	C18, C19, C15, C23, C3, C16, C5, C2, C4 (artesian) C17, C21 (semiartesian.)	944-1850	33.8-35.8	7.7-9.9	Hypothermal to Mesothermal

the three systems defined previously (SAS= semiconfined lower deep system, SCA = confined system with lower degree of confinement and SCB = confined system with a higher degree of confinement).

A box plot diagram shows the electric conductivity (EC) differences between the levels of the deep aquifer systems and the phreatic aquifer, where samples of the lower block are identified with AFH (Figure 4).

Although all the aquifer systems have fresh water, the SAS and SCA present the highest salinity ( $\text{EC} > 1.800 \mu\text{S}/\text{cm}$ ), while the SCB system has the lowest salinity ( $\text{EC} < 1.800$ ). The Schoeller diagram shows no geochemical differences in deep groundwater systems, where all are of the sodium sulfate type (Figure 5). This characteristic suggests a long residence time for groundwater. As and F were measured in all aquifers but, in general the values are less than  $10 \mu\text{g}/\text{l}$  and  $1.3 \text{ mg}/\text{l}$  respectively (thresholds of Argentina Law). The highest values (median ca.  $2 \mu\text{g}/\text{l}$  for As and  $1.1 \text{ mg}/\text{l}$  for F) are associated with the semiconfined system, SAS.

In relation to isotopic results, Figure 6 exhibits a conventional scatter plot  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  of all samples and the global meteoric water line,  $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10 \text{‰}$  (Craig, 1961). Although the rain isotope record is short, covering about one year of sampling at present, a range of values was

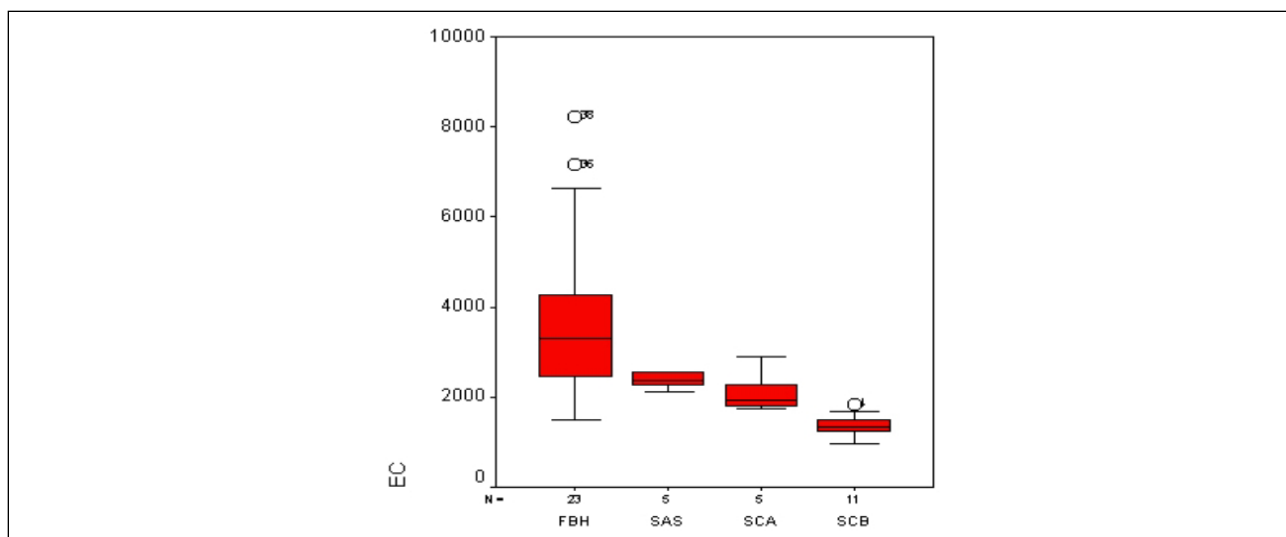


Figure 4. Box plot (EC [ $\mu\text{S}/\text{cm}$ ]).

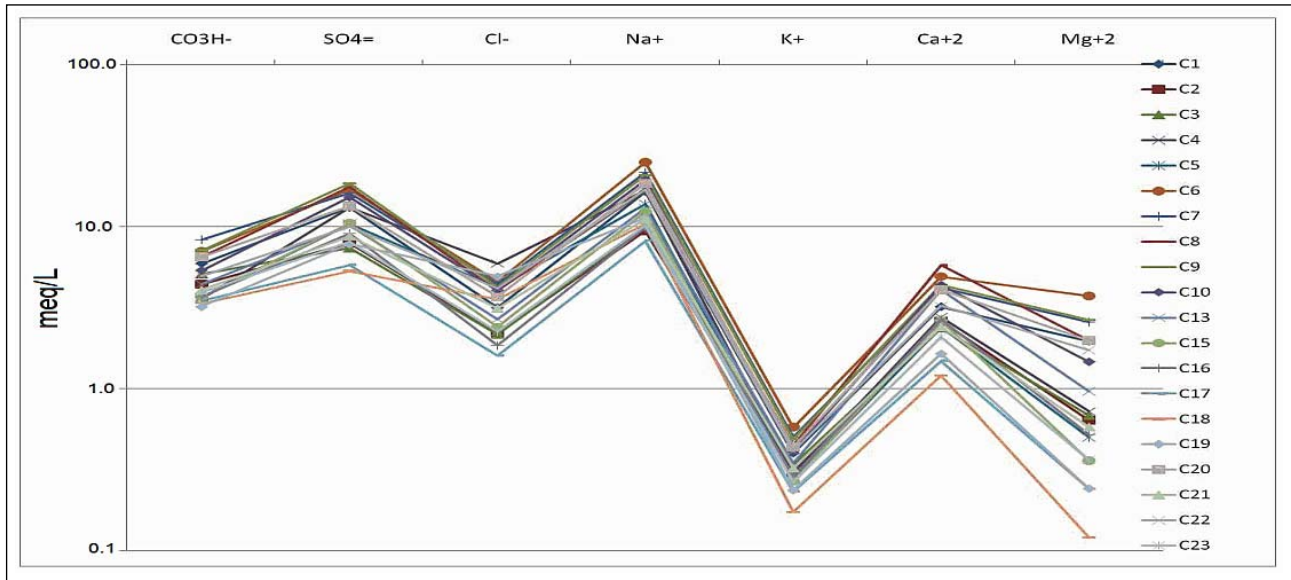


Figure 5. Schoeller diagram.

measured (-11.4 ‰ to -1.7 ‰ for  $\delta^{18}\text{O}$  and -84 ‰ to -7 ‰ for  $\delta^2\text{H}$ ). In the study area, stream isotope composition shows a wide variation, with values between -4.4 ‰ and 1.8 ‰ for  $\delta^{18}\text{O}$  and -25 ‰ to 10 ‰ and for  $\delta^2\text{H}$ , being the samples on the evaporation line ( $\delta^2\text{H} = 5.5 \delta^{18}\text{O} - 1.6 \text{ ‰}$ ).

The isotope composition related to streams situated in the primountain western region presents values between -6.4 ‰ and -4.0 ‰ for  $\delta^{18}\text{O}$  and -39 ‰ and -23 ‰ for  $\delta^2\text{H}$ .

The deep aquifer and semiconfined lower deep aquifer (systems SCA and SAS respectively) show an isotope composition similar to phreatic ( $\delta^{18}\text{O}$  between -5.4 ‰ and -4.6 ‰ and  $\delta^2\text{H}$  between -32 ‰ and -25 ‰), in particular those located in the Lower Block (F1, F2, F3, F4, F5, F6, F7, F10 and F12) but piezometric level relationships indicate that phreatic water cannot recharge deep aquifers locally. The existence of a connection between both systems (phreatic system

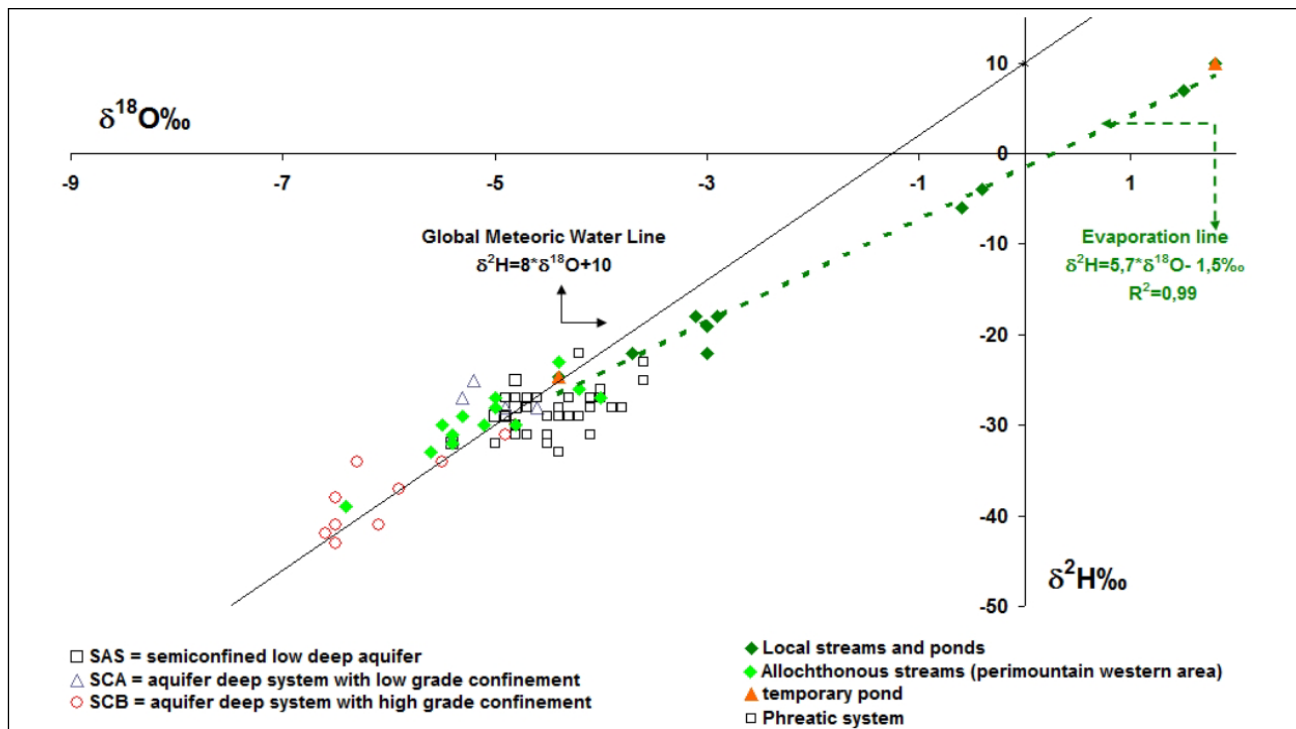


Figure 6.  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  of samples and the global meteoric water line.

recharging the confined systems) would be outside the study area to the west. In addition, the phreatic system has been receiving water coming from wells of the deep confined aquifers, in some cases permanently open flowing wells during many years. On the other hand, the deep aquifer SCB shows a more depleted isotope composition than the other systems, with values around -6.6 ‰ for  $\delta^{18}\text{O}$  and -43 ‰ for  $\delta^2\text{H}$ . The most depleted values of the SCB system are probably due to several causes such as the existence a local preferential depleted recharge, an allochthonous recharge, or the existence of a zone of older waters recharged in a colder period. Nevertheless, the isotopic composition of perimountain allochthonous streams shows that these water bodies would be the source of recharge to confined deeper aquifers, as can be seen in Figure 6. More samples and tritium and  $^{14}\text{C}$  analyses are needed to prove this hypothesis. Cluster analysis between observations (Q mode) shows two large groups. One is associated with the SAS and SCA systems and another is related to the SCB system with fresh and depleted waters (Figure 7). Sample C6 presents a different behavior and new data are needed to build a satisfactory explanation.

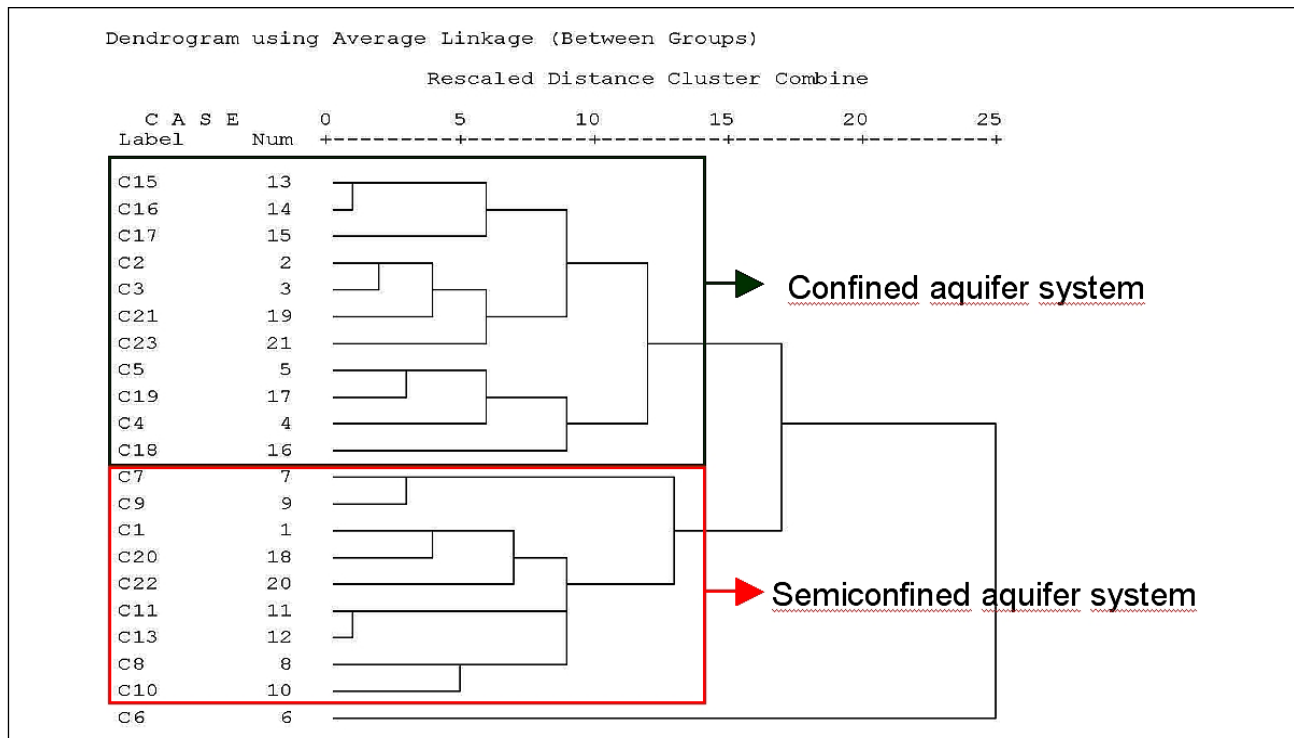


Figure 7. Dendrogram cluster analysis Q mode.



Figure 8. Artesian thermal wells permanently opened.



The deep water systems present different grades of thermalism, from hypothermal to mesothermal (Table 1, Figure 8), with temperatures up to 5 °C and 10 °C above the expected values (considering a normal geothermal gradient of 1°C/33 m).

## CONCLUSIONS

The lack of adequate hydrostratigraphic information and some uncertainties about depth and artesian levels made correlations among aquifers difficult. The preliminary hydrogeological model assumes the presence of several multilayer artesian aquifer systems, which are located in lenses associated with the paleofluvial Tertiary system (with variable grain size materials, depth, lateral development and thickness). Although isotopic and geochemical data are still scarce, the initial results, together with depth and grade of confinement, were very useful in the evaluation of the extent of these systems. Three deep multilayer aquifers are identified: a semiconfined lower system, a confined system with low degree of confinement and a highly confined system. The aquifers in the study area, especially confined systems, are recharged in the perimountain western region, according to isotopic results for surface streams in that area. A longer record for the isotope composition of rainwater and periodic groundwater sampling are needed to refine the hypotheses presented here regarding recharge mechanisms and groundwater residence times.

## ACKNOWLEDGMENTS

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