GEOCHEMICAL AND ISOTOPIC FEATURES OF A CONFINED AQUIFER SYSTEM OF MARINE ORIGIN, PAMPEAN PLAIN OF CÓRDOBA, ARGENTINA

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In Córdoba province (Argentina), people use groundwater from Confined Aquifers Systems (CASs) for different activities. Therefore, it is necessary to carry out comprehensive studies for the planning of a more sustainable use considering that groundwater renewal times can be of several thousands of years. The objective of this research is to evaluate geochemical and isotopic features of groundwater from a confined aquifer system made up by marine sediments in the central Pampean plain (Argentina). This CAS is multilayered and formed by thin (5 m) sand-pebble lenses of variable extension and clay deposits, linked to the Neogene period. These layers are situated at different depths (between 230-300 m) and are represented by fossiliferous sands interbedded with very thick greenish clay sediments. The marine CAS is characterized by fresh-brackish groundwater that evolves from bicarbonate to sulfate sodium type in the flow direction. The interpretations made from ^2H, ^{18}O and ^3H results suggest that groundwater is old. The ^{14}C age for C CAS (10,800 BP) indicates groundwater recharged during Holocene cold periods during the last glaciation.

INTRODUCTION AND OBJECTIVE

Appropriate legal and institutional contexts are vital in order to guarantee that water resources are managed and used sustainably. These include regulations whose implementation ensure a secure balance between water availability and use, and protect the resource against contamination and over-abstraction for the security of forthcoming generations. The science sector is the responsible to produce conceptual and numerical models that explain aquifers behavior, their hydraulic and geochemical characteristics and their relationships with other parts of the hydrological cycle. This information is essential to groundwater use and management.

Most of the groundwater participates in the hydrological cycle although the geochemical features and residence time may vary a lot. Groundwater all around the world is the most abundant liquid fresh water resource, but it is not always available for human consumption, as a result of its natural quality or contamination processes. Furthermore the groundwater residence time may be very long, often of thousands of years, especially in deep aquifers or under arid conditions. Then, the continuous use of these deep old resources without or scarce recharge may be unsustainable (Kazemi et al., 2006).

When a groundwater flow systems is studied, it is necessary to recognize that it has an intrinsic complexity (Turnadge and Smerdon, 2014). A groundwater sample will generally be the result of mixing that can be attributed to processes such as mechanical dispersion, chemical diffusion, and preferential flow, each of which has the potential to complicate environmental tracer interpretation. The use of geochemistry and stable and radioactive isotopes are of great interest for the development of hydrogeological models, to identify water origin and age, water mixing from different origins, water residence time in aquifers, relation between sediment/rock and groundwater, among others.

When confined aquifers are studied, complementary tools to identify old groundwaters are stable isotopes which are used as indicators of recharge during past climates (cool vs. warm, pluvial vs. arid). As was stated by Clark (2015), these do not provide quantitative measurements of subsurface residence time, but do provide useful constraints on age as well as providing important paleoclimate information. About dating, tritium-free groundwaters are considered to be greater than about 50 years old. Beyond about 1,000 years, radiocarbon remains the most useful and routine approach to date old ground waters.

In the South of Cordoba province (Argentina), groundwater resources support all the human activities (human consumption, industry, irrigation, etc.). Consequently, more comprehensive studies are necessary for the planning of a more sustainable use considering geochemistry and groundwater renewal times in the different aquifer systems. The aim of this work is to evaluate groundwater geochemical and isotopic features in a confined aquifer system of marine origin in the central Pampean plain (Argentina). Also, the links between atmospheric, surface and groundwater systems were investigated in order to improve the entire system understanding and to provide guidelines for water resources planning and management.

STUDY AREA

The study area covers 5,950 km^2 and is located between the coordinates 32°30' and 33°30' S and between 63°00' and 63°45' W (Figure 1). The climate is subhumid-tempered characterized by a mean temperature of 16.5 ºC and an average annual precipitation of 850 mm. The selected zone is a plain area that has great geomorphological, stratigraphic, hydrodynamic and geochemical peculiarities (Blarasin and Cabrera, 2005; Degiovanni, 2005; Blarasin et al., 2014). It offers several and different possibilities of groundwater uses for diverse regional human activities which must be planned. The

study area has been selected taking into account that there is scarce information about confined aquifer systems (CASs), especially those made up by marine sediments, and they are being frequently used without management policies.
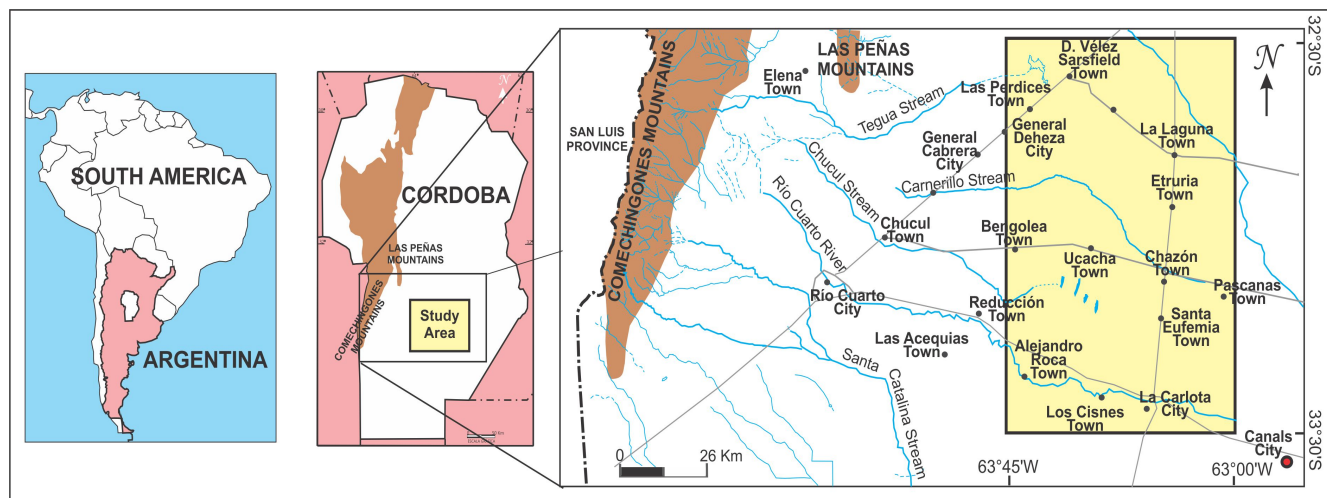

Figure 1. Location of study area.

MATERIALS AND METHODS

Standard geological and hydrogeological methodology was used for data collection. Groundwater levels were measured using water level meters or manometers in the case of artesian wells. After that, hydraulic heads were calculated and piezometric maps were elaborated. Sediments samples were collected during drilling in selected sites to make textural studies. This information was used to analyze the spatial configuration of different aquifer layers, to make correlations and to estimate hydraulic aquifer parameters. Seventeen groundwater samples were collected for chemical and isotope analyses (ten from the unconfined aquifer and seven from the marine confined aquifer layers). The selected samples belong to wells with short screen lengths (less than 10 m) so that they are considered adequate for the interpretation of groundwater behavior at different depths, preventing water mixtures from different aquifers. Also, eight samples from streams and springs from the mountain and perimountain areas were taken, in order to corroborate, mainly through the isotope information, the hypothesis of the CAS' potential recharge zones.

During the 2012-2015 period, 37 monthly composite rainfall samples were collected using a device located in Canals city, near the study area, following the International Atomic Energy Agency guidelines (IAEA/GNIP, 2014). Rain samples were sent to carry out chemical and stable isotopes analyses, to know the input function to the regional hydrological systems.

Field parameters, such as pH, Electrical Conductivity (EC), dissolved oxygen (DO) and temperature (T) were measured in situ. In the laboratory of the Geology Department of the National University of Rio Cuarto the major ions (CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, Mg^{+2}, Ca^{+2}, Na^+, K^+) were determined using Standard Methods (APHA, AWWA, WEF, 2005).

Stable isotopes (^2H and ^{18}O) analyses were performed in the Geochronology and Isotopic Geology Institute Laboratory (INGEIS-CONICET-UBA) by means of a "Off-Axis Integrated Cavity Output Spectroscopy" (OICOS) (Lis et al., 2008), DLT-100 Liquid-Water Isotope Analyzer from LGR inc. Results were expressed in the usual form i.e. δ (‰) defined as:

$$\delta = 1000 \frac{R_S - R_R}{R_R}$$

(1)

where R= isotope ratio ^{2}H/^{1}H or ^{18}O/^{16}O; δ^2H or δ^{18}O, isotopic deviation in ‰, respectively. R_S denotes sample and R_R reference standard. Uncertainties are ±1‰ for δ^2H and ±0.3‰ for δ^{18}O. Reference standard is V-SMOW (Gonfiantini, 1978).

In addition, one sample was taken for ^{3}H and ^{14}C determination to obtain a preliminary idea about groundwater age in the confined system of marine origin. The sample was prepared following the laboratory instructions and sent to the Environmental Isotope Laboratory of the University of Waterloo (Canada). Sample for ^{3}H analysis was collected in 600 mL polyethylene bottle, while that for δ^{13}C and ^{14}C was collected in 150 ml polyethylene bottle. The samples were shipped with ice coolers. The ^{3}H was determined by liquid scintillation counting after electrolytic enrichment. The detection limit was of 0.8 ± 0.3 Tritium Units (T.U). ^{14}C and ^{13}C sample was analyzed by an accelerator mass spectrometer (AMS). ^{14}C results are expressed as percent of modern carbon (pmC) relative to the National Institute of Standards and Technology (NIST). The ^{14}C data was normalized to δ^{13}C (-25 ‰). Reference standard for δ^{13}C is V-PDB (Craig, 1957) and the uncertainty is of ±0.2‰. To correct radiocarbon ages, the Tamers (1975) and Pearson-Gonfiantini (Salem et al., 1980) method were used because it involve chemical and isotope issues.

HYDROGEOLOGY AND GROUNDWATER GEOCHEMISTRY

The study area is situated in the middle of Pampean plain (Figure 1), to the east of Comechingones and Las Peñas Mountains. The regional tectonic scheme, an arrangement of blocks gradually descending eastwards, has influenced the sedimentation processes that gave rise to the different aquifers layers. This geological framework and the Quaternary climatic changes have affected the dynamic and geochemical processes of these groundwater systems.

The unconfined aquifer, with a thickness of almost 80-100 m, consists of fine Quaternary sediments and exhibits shallow groundwater levels. The base of the aquifer, formed by silty-clay sediments, has an average thickness of 20 m (Figure 2). The groundwater flow direction is NW-SE. The aquifer geochemical pattern shows a salinity increase (EC from 1,032 μS/cm to 10,530 μS/cm) along the flow path and the geochemical type change from sodium bicarbonate to sodium sulfate/chloride.

The Confined Aquifer Systems (CASs) present lateral variable extension. They are multilayered and formed by thin (4 m-6 m) sand-pebble lenses linked to Neogene-Pleistocene fluvial palaeosystems or, in the eastern area, related to sand marine and continental layers (Blarasin et al., 2014; Maldonado et al., 2016). These layers are situated at different depths, between 120 m and 400 m and are interlayered with thick aquitard or aquiclude silt-clay strata (40 m-80 m) which generate different confinement grades. Nodules of calcium carbonate can be observed in some layers. Four principal CAS were identified: A, B, C and D (Figure 2). The following are the main characteristics for the confined aquifer systems.

A CAS was divided in two subsystems taking into account depth, geochemical and isotopic features. A1 CAS, the shallowest system, is made up by continental sediments. The most permeable layers may be found especially between 100 m-120 m and 190 m-230 m. It shows the less confinement grade according to the existing upper semipermeable materials. It extends from the western limit of the study area to the El Rastreador- Los Cisnes regional fault (Figure 2). The wells that abstract groundwater from this system show piezometric levels between -22 m and -3.5 m (under ground level). The

groundwater flow is W-E and groundwater velocities are 0.07-0.42 m/d. The groundwater from A1 CAS shows lower salinity than the overlying unconfined aquifer (EC 823 µS/cm to 4,000 µS/cm). A1 CAS has fresh to brackish sodium sulfate and sodium sulfate/bicarbonate water type in the N sector, where fine sediments predominate, and sodium bicarbonate water type in the S sector, where sand-gravel fluvial sediments domain.

A2 CAS underlies A1 CAS and has a similar spatial distribution (Figure 2). It is from continental origin and extends from 230 m - 250 m to 320 m - 330 m depth. The wells that abstract groundwater from this aquifer system are artesian, with piezometric levels that vary from +0.5 m to +15 m (above ground level). This condition is related to the important confinement grade of the more permeable lenses of this system, which are interlayered with thick fluvial clay deposits. The groundwater flow shows W-E direction, with different flow velocities (0.08-0.15 m/d). The A2 CAS has the freshest groundwater of the study area (EC 571 µS/cm to 2,400 µS/cm). Groundwater is sodium bicarbonate, sodium bicarbonate-sulfate and sodium sulfate geochemical type.

B CAS is not used for agricultural and urban activities in the central-south area of Cordoba province, thus, there is scarce information. They were drilled especially in the north-east area of Cordoba, and fluvial fine sands were identified.

D CAS, from continental origin, is recognized in the eastern part of the study area, placed under the C system (Figure 2). It is the deepest system (320 m-400 m) and it shows the highest confinement grade as a result of thick overlying clay deposits and depth. The aquifer layers are characterized by the predominance of continental sand. The wells that abstract water from these layers are artesian, with piezometric levels that vary between +2 m and +25 m. D CAS shows a NW-SE groundwater flow direction, with low flow velocities (0.01-0.02 m/d). The water in this aquifer layer shows EC values up to 3,600 µS/cm and sodium sulfate-bicarbonate, sodium sulfate, sodium sulfate-chloride and sodium chloride-sulfate groundwater types were identified. High salinity values and the abundance of sulfate water type may be linked to the sediments composition which includes fine sands and some gypsum layers (Russo et al., 1979).

The C CAS is the groundwater system about which this paper deals. The deposition of the sediments of this aquifer system is linked to the Neogene period. During the Miocene, a marine transgression occurred in the South-American continent, represented by warm and shallow waters that covered a huge area of Argentina, Uruguay, south of Brazil, south of Bolivia and Paraguay.

In Argentina, the deposits of this marine transgression were called Parana Formation (Yrigoyen, 1969). They were recognized in different provinces of the eastern part of the country in few outcrops. In Córdoba province these marine deposits were recognized under the land surface, between 230 m-300 m depth (Figure 2). The aquifer layers in the C CAS are not so thick, in the order of 5 m (Renz, 1993; Blarasin et al. 2000; Maldonado, 2014) and are represented by fossiliferous sands interbedded with very thick clay greenish sediments (Figure 3b and c). It thickness is higher towards the E-NE direction, outside the studied area. Hydraulic conductivity of the sand layers are in the order of 1-5 m/d and effective porosity is about 10%. The Pampean Mountains elevation at the end of the Miocene, would have contributed to the sea regression.

There are few wells extracting water from these marine layers. All the surveyed wells are artesian, with piezometric levels that vary between +2 m and +11 m. The groundwater flow in this system is NW-SE, standing out the low hydraulic gradients (0.15) and flow velocities (0.02-0.08 m/d) (Figure 3a).

Groundwater extracted from this marine confined aquifer present temperatures between 20.9 °C and 30.4 ºC. In relation to salinity, the C CAS is characterized by EC values between 593 µS/cm and 2,690 µS/cm (Table 1), while the geochemical types are sodium bicarbonate, sodium sulfate, sodium sulfate-bicarbonate and sodium chloride-bicarbonate (Figure 3a). The main control on the groundwater geochemistry is the texture and selection of the deposits (dominant quartz fine sands).

Table 1. Chemical and isotope ($\delta^{18}O$ and δ^2H) composition of confined aquifer system

| Sample	P122	P107	P123	P125	P111	P131	SC5	P54
EC (µS/cm)	662	2,660	593	683	1,497	1,100	2,690	546
HCO_3^- (mg/L)	222.5	292.5	225.0	227.5	230.0	242.5	312.5	195.0
SO_4^{-2} (mg/L)	52.2	870.2	68.9	81.6	166.1	187.0	726.8	37.0
Cl^- (mg/L)	51.4	257.1	37.1	42.9	225.7	100.0	137.1	22.9
Na^+ (mg/L)	117.3	489.4	111.2	121.3	254.8	204.2	424.7	92.0
K^+ (mg/L)	9.4	13.3	8.6	11.4	13.8	11.7	9.8	7.3
Ca^{+2} (mg/L)	34.4	129.6	24.8	30.4	51.2	43.2	48.8	16.0
Mg^{+2}(mg/L)	6.3	6.8	4.9	2.4	13.7	5.4	9.3	2.4
$\delta^{18}O$ (‰)	-5.7	-6.0	-6.1	-6.1	-6.2	-6.3	-6.3	n/d
δ^2H (‰)	-29	-36	-32	-33	-36	-35	-37	n/d
n/d: not determined								
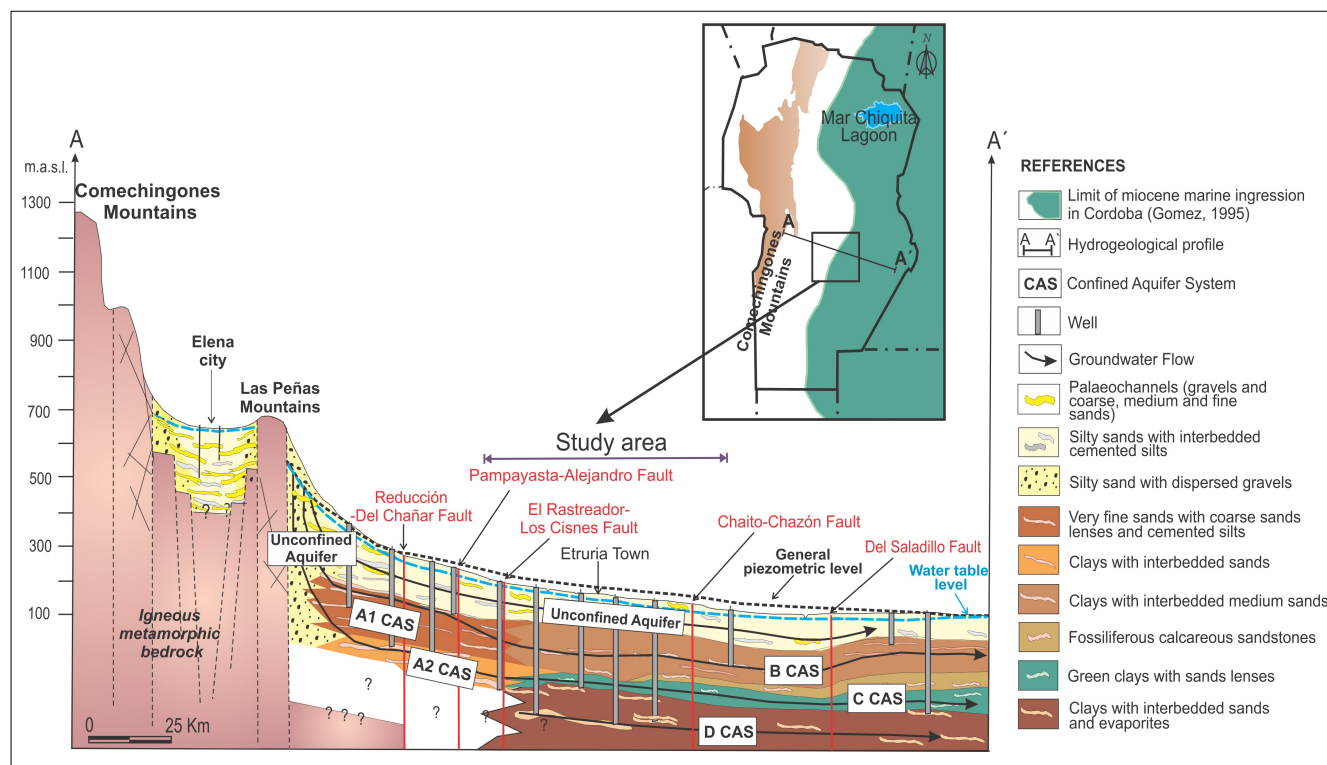
Figure 2. Regional hydrogeological A-A' profile of south of Cordoba province. Argentina (Blarasin et al., 2014).

Following Maldonado (2014) is important to highlight that, from the point of groundwater suitability, groundwater from the C CAS is, in general, apt for irrigation, cattle and sometimes for human consumption.
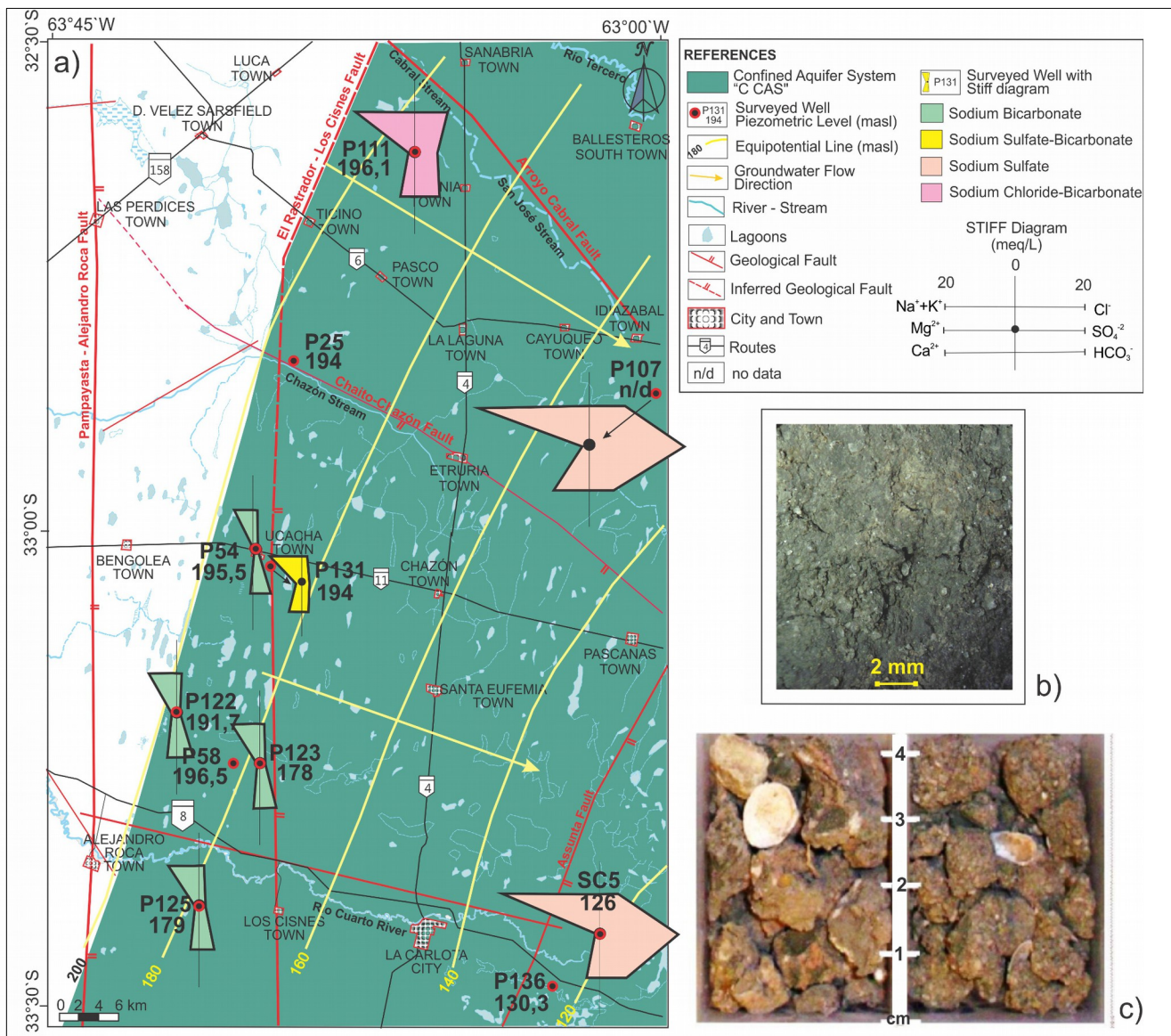

Figure 3. a) Equipotential map and wells with Stiff diagram of the C CAS. b) Greenish clays from the marine Parana Formation (Blarasin et al., 2014). c) Sands with shell fragments from the Parana Formation (Blarasin et al., 2014).

ISOTOPE GEOCHEMISTRY

Stable isotopes (^{2}H and ^{18}O)

Precipitation isotopic values are aligned in a local meteoric line (Table 2, Figure 4), whose equation is $\delta^2H = (8.6 \pm 0.2)\ \delta^{18}O + (17.1 \pm 1.2)$ ‰ obtained with orthogonal regression (IAEA, 1992).

The observed deuterium excess variations ("d" between +11 ‰ and +19 ‰) reveal different air mass origins which probably produce rainfalls from recycled vapor related to the Low Level Jet (LLJ), the El Niño South Oscillation phenomenon (ENSO) and the Inter Tropical Convergence Zone (ITZC) processes (Dapeña et al., 2005; Gonzalez et al., 2009; Cabrera et al., 2013).

The springs and the streams from the mountain area show an isotopic composition that denotes meteoric origin (Table 2, Figure 4). They are more depleted than the eastern plain rainfalls (Canals station (Table 2, Figure 4)). This situation is linked to a regional process in which the rains originated in a wet warm front that comes from the Atlantic Ocean (1,000 km away) suffers continental and altitude effects (Cabrera et al., 2013; Giuliano Albo et al., 2015).

Table 2. $\delta^{18}O$ and δ^2H stable isotopic average values for each hydrology system

Hydrology system	$\delta^{18}O$ (‰)	δ^2H (‰)	d (‰)
Canals Rainfalls (pampean plain station period 2012-2015)	-4.8	-22	16
Unconfined aquifer	-4.8	-25	14
Rivers and streams (piedmont western areas)	-5.2	-24	17
C CAS	-6.1	-34	15

Groundwater from the unconfined aquifer is characterized by an isotopic composition similar to the local rainfalls (Table 2, Figure 4), especially those that fall from September to February, the months during which the major aquifer recharge takes place (Cabrera et al., 2013; Blarasin et al., 2014).
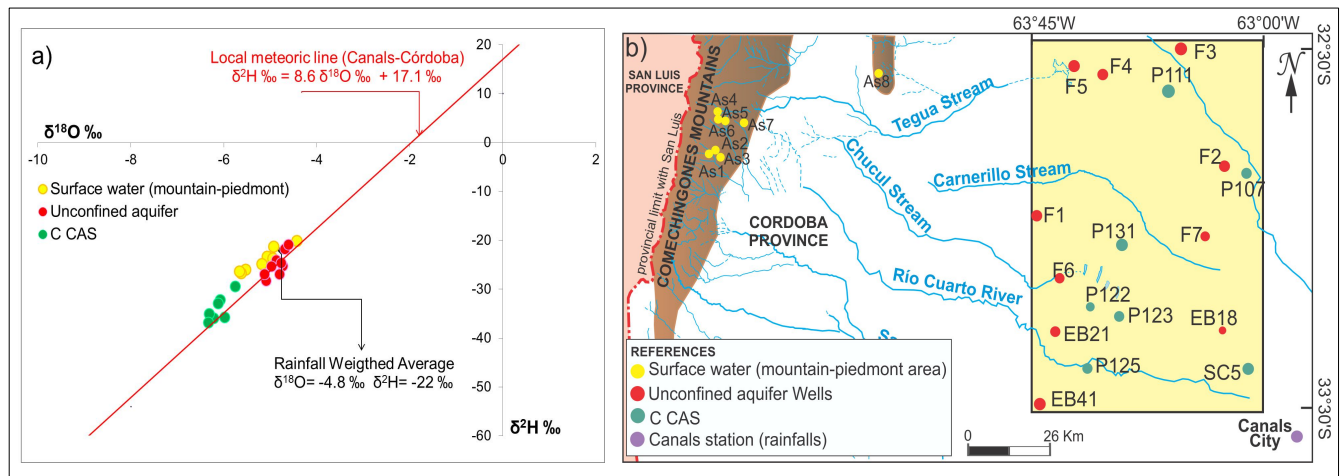

Figure 4. a) δ^2H vs. $\delta^{18}O$ diagram for surface water and aquifers systems. b) Surface and groundwater samples location.

The C CAS (Table 2, Figure 4) groundwater samples are more depleted in ^2H and ^{18}O than the unconfined aquifer, suggesting hydraulically disconnection with this system. Moreover, these deep aquifer layers are more depleted than surface water from mountains and piedmont. This could be due to present recharge in higher areas or past recharge under a colder climate.

Radioactive isotopes (^3H and ^{14}C)

To start with a preliminary estimation of groundwater age of the confined aquifer, ^3H was measured in a selected sample (P131, table 3) in the C CAS, which was compared with ^3H concentration in precipitation, streams and unconfined aquifer, already measured in the south of Cordoba province

(Cabrera et al., 2010). The results can be seen in the Figure 5 and it may be interpreted that the groundwater of this deep aquifer is not directly related to the present hydrological cycle.

When the ^{14}C method is used for groundwater dating, some difficulties arise and ages must be corrected because of two aspects. The first is the difficulty to calculate the initial ^{14}C concentration in the recharge precipitation, due to fossil fuel burning, and the influence of plants and soil. The second is the modification of ^{14}C due to of geochemical reactions in the aquifers (such as the congruent dissolution of carbonate minerals, dissolution of carbonate or the others calcium-containing minerals, the addition of dead carbon from other sources, etc.).
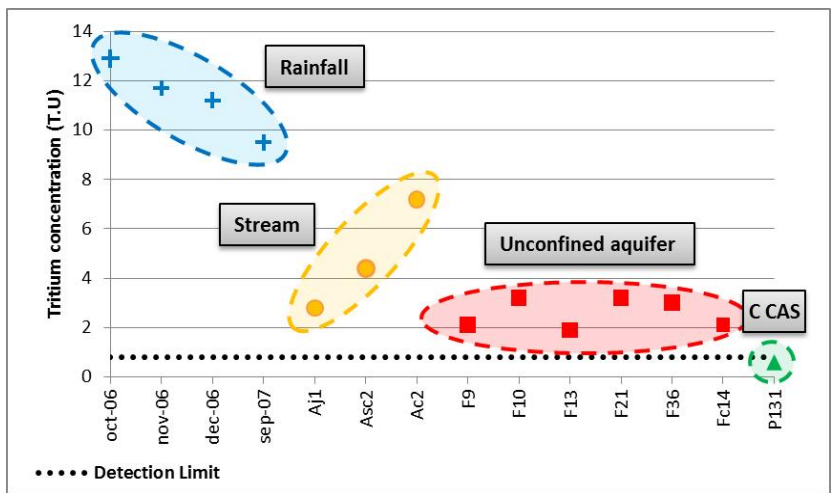

Figure 5. [3]H concentration in different hydrology system (Cabrera et al, 2010; Maldonado et al., 2016)

In the study area the main geochemical process that would affect the ^{14}C activity in the deep aquifers, is the dissolution of carbonates. Although these aquifers have bicarbonate-sulfated waters, they have moderate to high bicarbonate concentration ($\geq$ 195 mg/L). Another process that would modify ^{14}C activity is sulfate reduction, which can be discarded if is taken into account that moderate oxic conditions exist at the studied depth (dissolved oxygen > 2 mg/L) and that groundwater contain moderate to high sulfate values.

As was stated, to deal with these complexities some methods for age corrections were developed by different authors. In this work, ages were estimated using Tamers (1975) and Pearson-Gonfiantini (Salem et al., 1980) models, because both take into account groundwater composition and, in the case of Pearson-Gonfiantini model (equation 3), it includes the isotopic composition.

$$t(years) = 8267 \ln \frac{C_0}{C} \tag{2}$$

$$C_0 = \left[\frac{100 \left(\delta^{13}C_m - \delta^{13}C_m \right)}{\left(\delta^{13}C_{co_2} - \delta^{13}C_c + \varepsilon \right)} x \left(1 + \frac{2\varepsilon}{1000} \right) \right] \tag{3}$$

where:

C = [14]C concentration in the sample

$C_0 = {}^{14}C$ concentration initial

$\delta^{13}C_m$ = content of the carbonate species dissolved in the sample

$\delta^{13}C_C$ = content of the aquifer carbonate

$\delta^{13}C_{CO2}$ = concentration of the soil CO_2 at the time of recharge

ε = fractionation factor between bicarbonate and CO_2

The obtained ages are in the order of 10,000 BP (Table 3), that is, they are old groundwaters. This fact agrees with the location of the aquifer in the central sector of the plain, away from the recharge area, and low groundwater velocities, which favor water aging.

Table 3. ^3H, $\delta^{13}C$ and ^{14}C results and ^{14}C ages reported from Canada laboratory and Tamers (1975) and Pearson-Gonfiantini (Salem et al., 1980) models

Sample	^3H (TU) (1σ)	$\delta^{13}C$ (‰) (±0.2 ‰)	^{14}C (pmC) (1σ)	^{14}C Age (BP) (1σ)	Tamers (BP)	Pearson-Gonfiantini (BP)
P131	<0.8±0.3	-9.09	17.2±0.27	14,150±124	9,100	10,800

CONCLUSIONS

The marine sediments of Cordoba province are characterized by thick greenish clay deposits interlayered with thin sand layers, located at depths in the order of 230-300 m. Although there are few wells extracting water from this aquifer, the sand layers are productive and have fresh-brackish groundwater that evolves from bicarbonate to sulfate sodium type in the flow direction. All the recognized wells showed artesian conditions.

The C CAS groundwater samples are more depleted in ^2H and ^{18}O than the unconfined aquifer, suggesting hydraulically disconnection with this system. Moreover, these deep systems are more depleted than surface water from mountains and piedmont. This could be due to the past recharge under a colder climate.

The interpretations made from stable isotope results and the absence of ^3H, confirm that groundwater is old, not related to the present hydrological cycle. Then it may be interpreted that it would be recharged in a previous geological epoch with colder climatic conditions than the present times. The ^{14}C ages obtained for C CAS indicate waters recharged during Holocene, during the last glaciation. The ages estimated with the mentioned equations showed similar values. Taking into account geochemical features, methanogenesis, sulfate reduction, denitrification or anaerobic oxidation of organic matter would not be taking place into the confined aquifer systems. Therefore, it is assumed that the applied model takes into account dead C from carbonate dissolution as the main cause of decreased ^{14}C activity.

The proposed hydrogeological model demands attention in relation to the present mismanagement of CAS groundwater, especially if we take into account that these first results show long groundwater renewal times, that is, groundwater resources that must be careful used. It is necessary to extract more groundwater samples from this marine origin aquifer and to use other methods to improve the assessment of the internal dynamics of the groundwater system and the quantification of timescales associated with groundwater flow.

ACKNOWLEDGEMENTS

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