



Hydrogeochemical features and groundwater renewal rate estimates from deep aquifers in the Pampean plain, Córdoba province, Argentina

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ABSTRACT

In the Córdoba Province (Argentina), people use groundwater from confined aquifers systems (CAS) for different activities (irrigation, livestock, etc.). Therefore, comprehensive studies for a more sustainable use of these resources are necessary. The aim of this study is to assess the geochemistry, the water flow dynamic and the renewal rates of groundwater in the CAS of the Pampean plain of Córdoba. The CAS evaluated in this study are composed of two multilayered subsystems (A1 CAS and A2 CAS) of variable extent formed by thin (3–8 m) sand-pebble lenses. The subsystems are associated with Neogene fluvial palaeosystems. These layers are situated at different depths (120–400 m) and are interbedded with thick clay strata, which generate different confinement grades. Groundwater is fresh and of good quality ($EC < 2.000 \mu S/cm$) because the geochemical processes that allow the transference of ions into solution are diminished by the grain size (sand and gravel) and the aquifer sediment mineralogy (quartz prevailing). A2 CAS has the best water and higher hydraulic conductivity resulting from coarser textures. The main geochemical processes that influence CAS groundwater composition are silicate weathering, carbonate dissolution, cation exchange and atmospheric input. The interpretations made from geochemistry, isotopes (2H , ^{18}O , 3H and ^{14}C) and hydraulic results, demonstrate that these systems are recharged in the piedmont areas and have groundwater ages from hundreds to thousands of years, that is, groundwater recharged during the Holocene. Even though the CAS are currently used for irrigation, no significant decreases are observed in groundwater levels. This situation would indicate that these systems are not yet being over-exploited.

1. Introduction

Groundwater studies require integral and holistic research using many different tools (geological, geomorphological, geochemical, stratigraphic, isotopic, etc.). Using them, various evidence can be obtained that contributes to a better understanding of a regional hydrogeological behaviour, an important and vital basis for groundwater management. The resolution of a large number of different groundwater problems (contamination, overexploitation in irrigation areas, among others) requires improvement in the understanding of the geochemistry, water flow dynamic and renewal times of groundwater. The use of stable and radioactive isotopes are of great interest for the development of hydrogeological models, allowing to identify water origin, water mixing, contamination processes and water residence time in aquifers (Clark, 2015).

According to Llamas and Martínez-Santos (2005) and the Global Water Partnership-GWP (Foster, 2013), irrigated agriculture worldwide is the largest user of groundwater resources, which has generated an important dependence on groundwater in agro-economies. However, the GWP also states that in many arid and drought areas, especially in the last 20–30 years, the unrestricted use of groundwater is causing serious aquifer depletion and environmental degradation. In addition, farming practices have a great influence on groundwater recharge and quality due to deforestation, irrigation modes and pollution from nutrients and pesticides. Within this context, the GWP recommends integrated studies that consider the hydrogeological settings and local agro-economic realities, so as to promote sustainable management of land and water. Taking into account that groundwater cannot be renewed artificially on a large scale, the study and sustainable management of this resource is vital.

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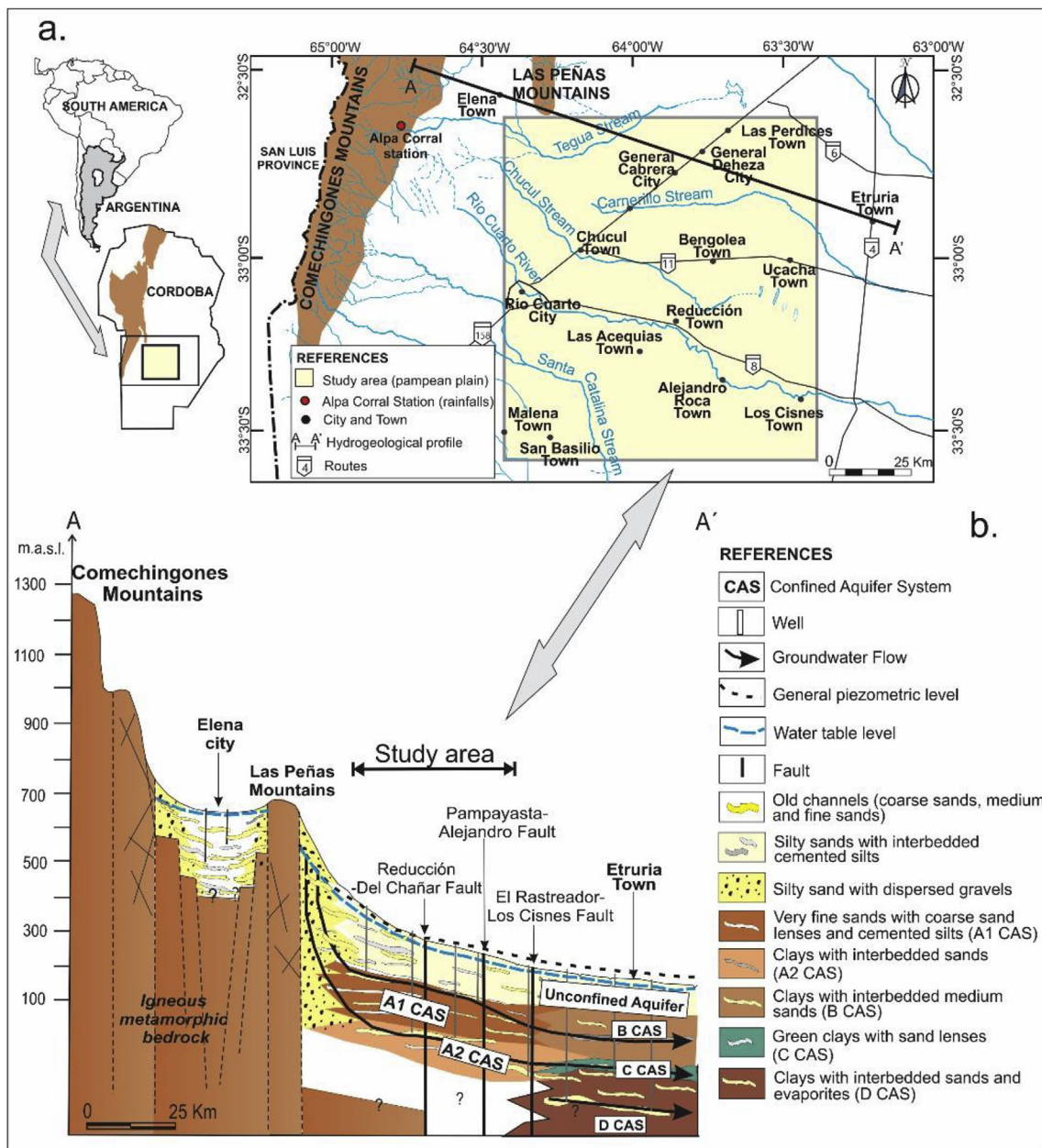


Fig. 1. a. Location of study area. b. Hydrogeological section A-A' in the northern part of the study area (modified from Blarasin et al., 2014).

Table 1
Hydraulic parameters of the different aquifer systems (Maldonado et al., 2016).

Aquifer System	Unconfined Aquifer	A1 CAS	A2 CAS
Hydraulic Conductivity K (m/d)	10 ⁻³ -1	5-30	5-10
Specific Porosity ρ (%)	10-15	25	20
Hydraulic Gradient i (%)	0.10-0.20	0.35	0.30
Velocity V (m/d)	< 0.1	0.07-0.42	0.08-0.15

In the South of Córdoba province in Argentina, groundwater resources support almost all human activities, with irrigation practices as the largest water user for crops such as soybean, wheat and corn. An analysis made by Barrionuevo and Feler (2014) about irrigation systems in Córdoba province, show a remarkable increase in center pivot irrigation systems (from 2 to 1393) and irrigated areas (from 251 ha to 102,393 ha) during the 1994–2014 period. Many pivot systems use

groundwater extracted from the confined aquifers, which exhibit the best chemical quality and best water yields in this region (Blarasin et al., 2014). These circumstances may generate use conflicts considering not only the Córdoba Water Law (N° 5589) gives priority to the use of water for human consumption, but also that groundwater from confined aquifers has long residence times and minimal possibility of annual recharge and water renewal from precipitation (Maldonado et al., 2016). In addition, these aquifers are mapped as discontinuous lenses and therefore may be prone to overexploitation.

The main socio-economic interest in Córdoba province is focussed on confined aquifer systems (CAS) located in the piedmont of the Pampean Mountains, particularly those named “A CAS” by Blarasin et al. (2014). This situation is based on the fact that large volumes of groundwater from each well (in the order of 100 m³/h up to 400 m³/h) are being extracted from these aquifer layers to be used with central pivot irrigation systems. In spite of the expansion of the irrigation area, there is not yet enough regional evidence in relation to significant water level declines. However, some local piezometric level decreases were

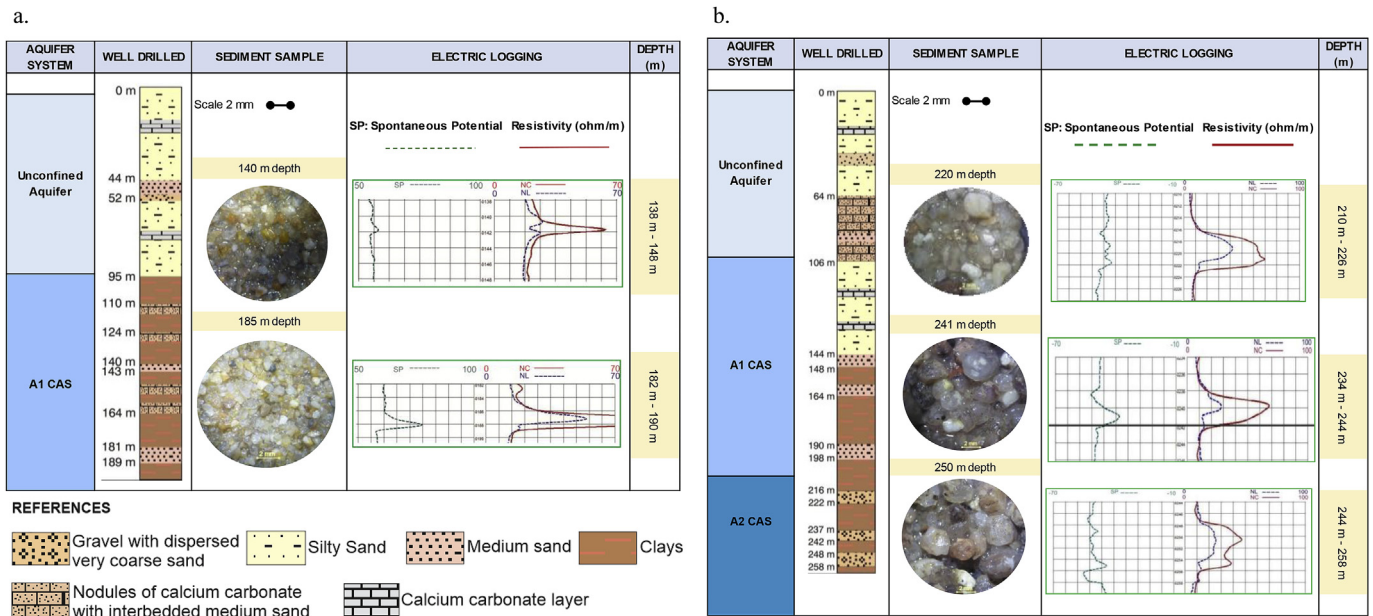


Fig. 2. a) Lithological column from a well drilled in Las Acequias town (A1 CAS), photograph of sediments (141 m and 185 m depth) taken with binocular loupe and sections of electric logging at different depth. b) Lithological column from a well drilled in General Cabrera town (A2 CAS), photograph of sediments (220 m, 241 m and 250 m depth) taken with binocular loupe and sections of electric logging at different depths (Maldonado, 2014).

observed (1–4 m) in wells located near the pivot systems (Blarasin et al., 2014). In a study related to the most important irrigation area in Córdoba province, Carignano and Bettiol (2014) demonstrated that groundwater levels have decreased only locally, especially in the North of Córdoba province. In the area where the best aquifers appear, near the major fluvial systems, the groundwater levels increased after a high precipitation period (2013–2014), although other regional areas were not surveyed.

Consequently, additional comprehensive studies are necessary to plan for more sustainable use considering groundwater quality, water flow dynamics and renewal times in the different aquifer systems. The current study area was selected because it shows different groundwater uses (human consumption, livestock, irrigation and industry) and, as stated earlier, more comprehensive information is needed. In this framework, the aim of this study is to assess the geochemistry, the water flow dynamic and the renewal rates of groundwater from deep aquifers in the Pampean plain of Córdoba Province. This may be an important basis to improve the understanding of the entire system and to provide guidelines for water resources planning and management in a sustainable way.

2. Description of study area

2.1. Location and climate

The research area covers 9975 km² and is located in the south-east of Córdoba province, Argentina (Fig. 1a). It is an extended plain area with great geomorphological, stratigraphic, hydrodynamic and geochemical peculiarities (Blarasin et al., 2014) located about 50–140 km east of the Comechingones Mountains (Pampean Mountain System). The small urban areas located in the studied region are surrounded by large rural areas dedicated to farming activities. Río Cuarto is the most important city (Fig. 1a) with a population of 157,010 inhabitants according to the 2010 INDEC (National Institute of Statistics and Population) survey.

The climate in the region is subhumid characterized by a mean temperature of 16.5 °C and average annual precipitation of 800 mm (1911–2016). Eighty percent (80%) of the precipitation is concentrated during the spring-summer period between September and February.

The sequential soil water balance using monthly time steps shows water excesses during the wettest periods, on the order of 20% of the precipitation. Approximately half of the water excesses produce recharge to the regional unconfined aquifer (Blarasin et al., 2016).

2.2. Geology and hydrogeology

The study area is situated in the middle of the Pampean plain (Fig. 1a). The regional tectonic setting shows an arrangement of fault blocks gradually descending eastwards, which has influenced the sedimentation processes that gave origin to the different aquifers layers (Blarasin et al., 2014). The system selected for this study is the sedimentary confined aquifer system of continental origin denominated “A CAS” by Blarasin et al. (2014) (Fig. 1b), which is being used frequently without management policies. The B, C and D confined aquifer systems (Blarasin et al., 2014), located to the east of the El Rastreador Los Cisnes regional fault (Fig. 1b) were not studied in this work.

The unconfined aquifer consists of fine Quaternary sediments with a thickness of 80–100 m. The water table in this unit exhibits variable depth, from almost outcropping to 20 m below land surface. The groundwater flow direction is NW to SE, with hydraulic gradients and flow velocity on the order of 0.2% and 0.1 m/d, respectively (Table 1). Even though this aquifer is the most widely used because of the low costs for groundwater extraction it was not considered for this investigation since it has very low yields and bad quality in most areas (Blarasin et al., 2014). The unconfined aquifer base, formed by silty-clay sediments, has an average thickness of 20 m (Fig. 1b) and overlies the A CAS.

The A CAS (Fig. 1b) lies between 100 and 400 m deep and it extends from the western limit of the area (Las Peñas and Comechingones mountains) to the El Rastreador-Los Cisnes regional fault. It includes numerous sand-gravel layers (3–8 m thick) that are interbedded with thick silt-clay deposits (Fig. 2). The sand-gravel layers are interpreted as fluvial deposits from the Neogene period and are predominantly composed of quartz and feldspar grains (Maldonado et al., 2016). The layers with coarser texture are located mainly at the South of the studied area, interpreted as major fluvial system deposits (Fig. 2). The A CAS was divided into two subsystems (A1 CAS and A2 CAS), primarily related to aquifer layer depth, a feature that influences the hydraulic behaviour

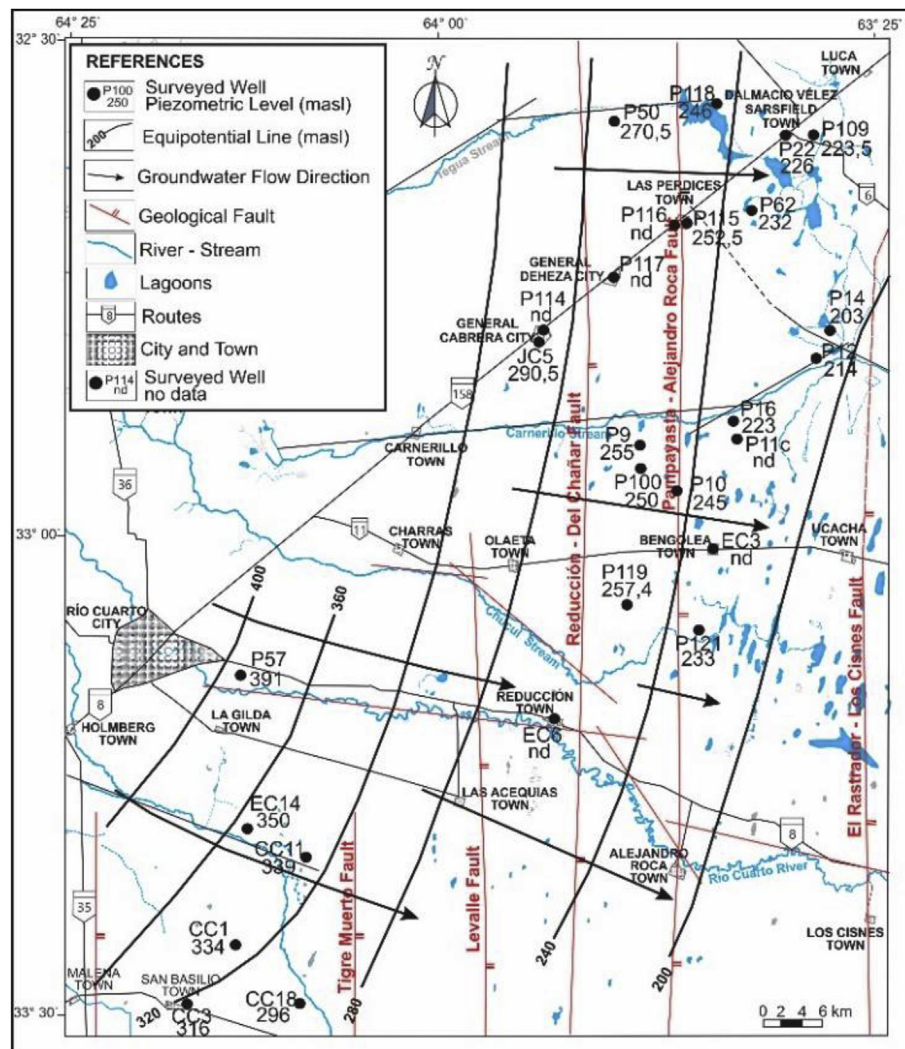


Fig. 3. Equipotential map of the A2 system.

(Blarasin et al., 2014).

A1 CAS is the shallowest confined system, and is mainly found between 100 m and 230 m depth (Fig. 2a). It shows less confinement grade according to the depth and the overlying semipermeable materials. Wells that extract groundwater from this system show piezometric levels between -22 m and -3.5 m below ground level.

A2 CAS underlies A1 CAS. It extends from 230 m to 330 m depth (Fig. 2b) and has the most permeable layers of the A CAS. The wells that extract 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 higher confinement grade that is a result of the depth of aquifer layers and the presence of thick clay interlayered deposits.

Both systems have the same West to East groundwater flow direction with a primary recharge zone located in the piedmont area of Comechingones Mountains (Maldonado et al., 2016). The systems have similar hydraulic gradients, but water velocity differs as a result of different textural characteristics. As an example, the potentiometric map of A2 CAS is shown in Fig. 3. The hydraulic conductivity (K), specific porosity (ρ), hydraulic gradient (i) and groundwater flow velocity (V) of both aquifer subsystems are shown in Table 1.

3. Methodology

In order to achieve the objectives, standard hydrogeological study

methods were used. Water level depths were measured with a Solinst probe while manometers were used for artesian wells. After that, hydraulic heads were calculated and piezometric maps were elaborated. Field parameters, such as pH, Electrical Conductivity (EC), temperature (T) and Dissolved Oxygen (DO) were measured in situ, by means of a Hanna multiparameter probe. Twenty-six groundwater samples were collected from confined aquifers and eight from the unconfined aquifer. Moreover, ten samples from streams and springs from the mountain and piedmont area were collected, in order to corroborate, mainly through the isotope data, the hypothesis that the potential recharge zones for deep aquifer systems are located in these areas. All samples were conditioned, properly cooled and sent to the laboratory to carry out chemical and stable isotope analyses. The local meteoric line for the 2007–2014 rainfall cycle in Río Cuarto city (Cabrera et al., 2017), was updated following the International Atomic Energy Agency guidelines (IAEA/GNIP, 2014). In addition, monthly precipitation data for the period 2015–2017 from the Alpa Corral station, located in the Comechingones Mountains are available (Fig. 1a).

For chemical analysis of the major ions (CO_3^{2-} , HCO_3^- , SO_4^{2-} , Cl^- , Mg^{2+} , Ca^{2+} , Na^+ , K^+) the samples were sent to the laboratory of the Geology Department of the National University of Río Cuarto. The water samples were analysed using Standard Methods (WPCF, A. A. 2005). The geochemical classifications were made using Custodio and Llamas classification (1983). Saturation indexes were calculated for different mineral phases identified in the aquifer systems using the

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

	Sample	Latitude	Longitude	Depth Well (m)	pH	EC ($\mu\text{S}/\text{cm}$)	HCO_3^- (mg/L)	SO_4^{-2} (mg/L)	Cl^- (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	
A1	P6	32°48'57"S	63°51'55"W	213	8.0	2040	355.0	726.8	165.7	449.9	17.3	47.2	20.0	ND	ND	
	P11b	32°55'52"S	63°38'11"W	200	7.6	1560	300.0	341.7	114.3	273.0	12.5	48.0	14.6	-5.0	-26	
	P19b	32°48'59"S	63°39'42"W	120	7.5	1088	210.0	280.9	85.7	169.9	10.9	73.6	11.2	-5.4	-27	
	P120	32°55'27"S	63°50'49"W	235	7.6	1013	447.5	134.9	34.3	216.4	8.8	30.4	8.3	-5.3	-26	
	EC7	33°21'41"S	63°43'48"W	190	7.8	823	322.5	171.9	34.3	176.9	9.7	35.2	7.8	-4.9	-24	
	CH1	33°13'30"S	64°28'47"W	172	7.7	832	292.5	80.3	45.7	121.3	10.4	49.6	11.2	-5.2	-27	
	CM	33°29'25"S	64°26'17"W	220	7.7	1672	365.0	453.6	128.6	317.5	13.9	44.0	24.9	ND	ND	
	A2	P9	32°55'09"S	63°45'43"W	269	7.2	880	375.0	69.8	37.1	181.0	8.1	29.6	5.4	-5.2	-26
		P10	32°58'16"S	63°43'00"W	275	7.2	611	277.5	67.1	22.9	118.63	7.3	28.8	4.4	-5.0	-25
		P11c	32°55'36"S	63°38'09"W	300	7.5	1185	252.5	292.9	74.3	173.9	11.7	64.8	11.2	-5.0	-26
P12		32°50'07"S	63°32'18"W	280	7.3	1111	202.5	233.9	100.0	182.0	11.0	51.2	8.3	-5.8	-34	
P14		32°48'17"S	63°31'16"W	301	7.1	1695	195.0	381.0	245.7	281.1	15.8	88.0	13.7	-6.3	-37	
P16		32°53'47"S	63°38'30"W	273	7.8	830	270.0	83.5	45.7	134.5	9.1	33.6	4.9	-5.7	-29	
P57		33°08'5.3"S	64°14'53"W	230	7.0	270	125.0	10.2	8.6	38.4	3.8	12.8	3.4	-5.1	-26	
P100		32°56'48"S	63°44'53"W	320	7.4	659	287.5	79.8	25.7	130.4	7.0	25.6	5.9	-5.1	-26	
P114		32°48'57"S	63°52'40"W	300	7.8	1032	272.5	260.7	42.9	161.8	10.3	57.6	8.3	-5.5	-27	
P115		32°42'07"S	63°42'25"W	260	7.9	817	187.5	228.7	45.7	129.4	8.9	41.6	4.9	-5.5	-28	
P116		32°41'57"S	63°42'13"W	330	7.9	1174	210.0	261.9	118.6	208.3	10.5	48.8	8.3	-5.7	-32	
P119		33°05'02"S	63°47'27"W	250	7.3	599	292.5	56.7	14.3	102.1	7.9	34.4	5.9	-5.5	-27	
P121		33°06'06"S	63°41'15"W	260	7.3	614	285.0	54.0	14.3	108.2	8.1	35.2	4.9	-5.2	-25	
EC3		33°01'31"S	63°40'37"W	310	6.8	646	260.0	54.0	25.7	117.3	8.2	33.6	5.4	-5.3	-26	
EC6		33°12'00"S	63°51'47"W	263	7.3	571	235.0	33.4	20.0	84.9	8.4	33.6	7.6	-5.1	-25	
CC1		33°22'42"S	64°16'24"W	280	7.9	1920	370.0	625.2	112.9	382.2	15.9	64.0	23.9	-5.4	-31	
CC3		33°29'00"S	64°20'12"W	280	7.8	1325	317.5	350.0	77.1	232.0	13.5	47.2	8.3	-5.5	-34	
CC11		33°19'00"S	64°10'12"W	280	7.8	1815	302.5	582.0	97.4	315.6	15.4	82.4	18.5	-5.3	-27	
CC18	33°29'07"S	64°18'12"W	280	8.1	1201	210.0	253.6	127.1	242.7	6.9	24.0	1.4	-6.5	-41		

ND: No Data.

software PHREEQC 2.17 (Parkhurst and Appelo, 1999). To evaluate the conceptual model in relation to the origin of groundwater solutes in the CAS, different molar relationships were calculated and interpreted. The mineralogical analysis was carried out on the very fine sand fraction with a Nikon petrographic microscope of polarized light. The clay fraction was analyzed by x-ray diffractometry (Phillips PANalytical X'PERT-PRO brand).

For the stable isotopes analysis (^2H and ^{18}O) the samples were sent to the Geochronology and Isotopic Geology Institute Laboratory (INGEIS-CONICET-UBA, Argentina). The analyses were performed through laser spectroscopy methods (Lis et al., 2008). The results were reported relative to Vienna Standard Mean Ocean Water (V-SMOW) (Gonfiantini, 1978), using conventional notation: $\delta = 1000 (R_s - R_p) / R_p$ ‰, where δ is the isotopic deviation in ‰, s is the sample, p is the international reference, and R is the isotopic ratio ($^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$). The analytic uncertainties were $\pm 0.3\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1\text{‰}$ for $\delta^2\text{H}$.

In addition, selected wells were sampled for ^3H and ^{14}C analysis, to obtain representative values for groundwater ages in the studied aquifer system. Samples were sent to the Environmental Isotope Laboratory of the University of Waterloo (Canada). The ^3H content was determined by Liquid Scintillation Counting (LSC) after electrolytic enrichment. The detection limit was of 0.8 Tritium Units (T.U). ^{14}C and ^{13}C samples were analysed by an Accelerator Mass Spectrometer (AMS). The results of ^{14}C are expressed as percent of modern carbon (pmC) relative to the National Institute of Standards and Technology (NIST). The standard was ^{14}C SRM-4990C normalized to $\delta^{13}\text{C}$ -25‰. The standard reference for ^{13}C is V-PDB (Craig, 1957) and the uncertainty is $\pm 0.2\text{‰}$. Groundwater ages were estimated using the Tamers (1975) method, which makes a chemical correction of the initial activity (^{14}A) and Pearson-Gonfiantini (Salem et al., 1980) method, which includes both chemical and isotopic corrections of groundwater composition. The radiocarbon ages were compared with hydraulic calculations using the known Darcy equation for laminar flow in porous media.

4. Results

4.1. Hydrogeochemistry

The temperatures of the A CAS, measured through a flow cell in each well, vary in a range between 22 °C and 33 °C. The DO values in the groundwater are between 2 and 4.7 mg/L, which indicate moderate aerobic conditions.

The A CAS has fresh water with EC values that range between 823 $\mu\text{S}/\text{cm}$ to 2040 $\mu\text{S}/\text{cm}$ for A1 and between 270 $\mu\text{S}/\text{cm}$ to 1920 $\mu\text{S}/\text{cm}$ for A2 (Table 2). For both systems the freshest groundwater is located in the western-central area whereas increasing conductivities are observed in the downgradient (Fig. 4a). The groundwater from A1 CAS is sodium bicarbonate and sodium sulfate geochemical type while groundwater from A2 CAS is sodium bicarbonate, sodium bicarbonate-sulfate and sodium sulfate geochemical type (Fig. 4b). The low conductivity in both systems is linked to the coarse texture of the aquifer layers, which results in lower water-sediment interaction time. Moreover, because quartz grains prevail (Fig. 2b) the mineral weathering reactions decrease, lowering the transfer of ions into solution. The lowest conductivity samples are located in the central sector and related to the paleochannels of the Rio Cuarto River alluvial fan system (Carignano et al., 2014). The samples with higher total dissolved solids are linked to the layers with higher percentage of fine grains (Fig. 2a).

The groundwater from A1 CAS as well as those samples from A2 CAS with $\text{EC} > 1000 \mu\text{S}/\text{cm}$ (Fig. 5) are oversaturated with respect to calcite. The remaining samples of the A2 CAS system, generally those fresh waters located in the central sector, are undersaturated or in chemical equilibrium with respect to this mineral.

Fig. 6 shows different molar ratios (Ca^{+2} vs SO_4^{-2} and Cl^- vs Na^+) that allow the identification of potential geochemical processes that can influence the groundwater chemistry. From Fig. 6a and b and taking into account the location of the samples from both A1 CAS and A2 CAS, it may be interpreted that the ions would not be derived from gypsum dissolution (except for a very small group from A2 CAS samples and P57 sample from A1 CAS) or from halite dissolution. That is to say, the presence of these ions in those samples that cannot be explained by the

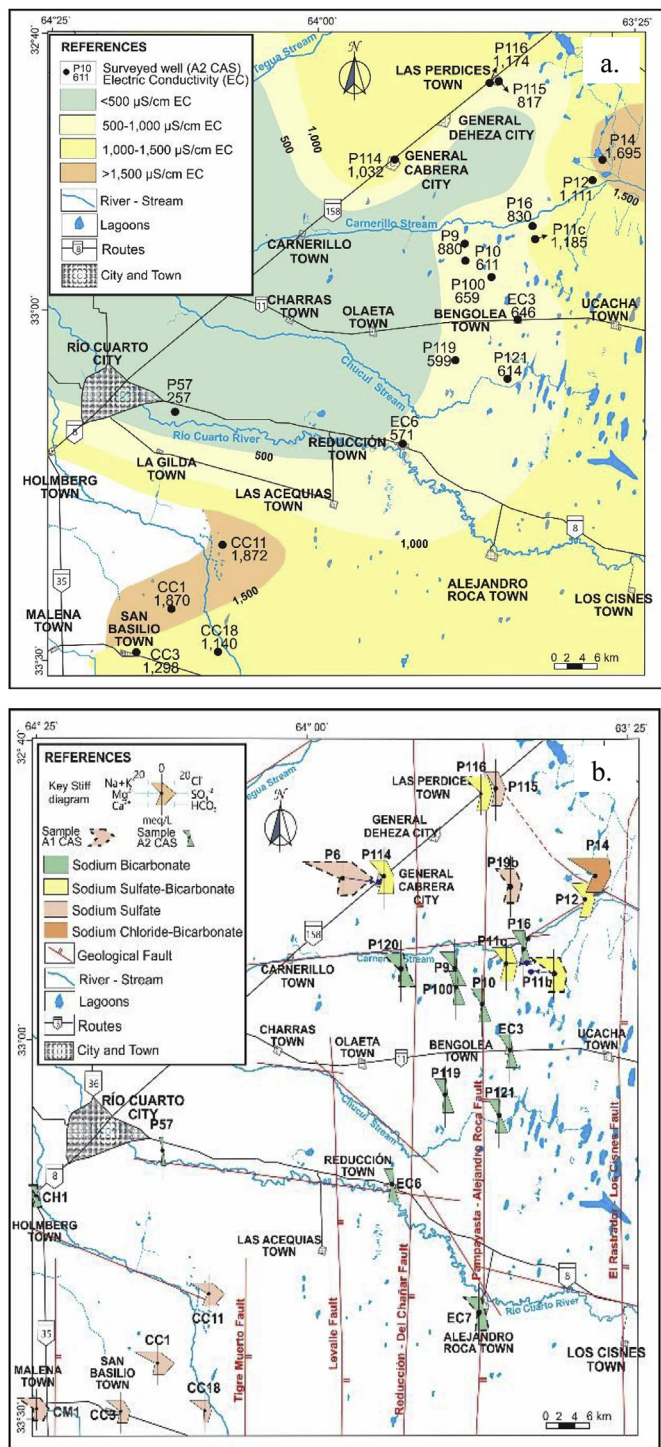


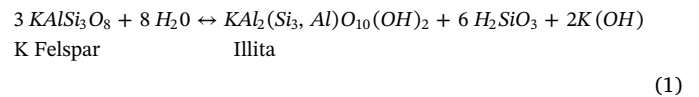
Fig. 4. a) Iso-Electric conductivity of the A2 CAS. b) Stiff diagram of the CAS.

graphics, would indicate that the contribution of Ca^{+2} and Na^{+} derives from other geochemical processes, such as carbonate dissolution, cation exchange or hydrolysis of silicates, while that the presence of SO_4^{-2} and Cl^{-} would derive from the contribution of precipitations in the recharge zone.

The mineralogical analysis carried out in some samples (Fig. 2a and b) for the very fine sand fraction shows that quartz is the dominant mineral. In addition, there is abundant plagioclase (primarily andesine and oligoclase), potassium feldspar (orthoclase and microcline), amphibole (hornblende), biotite, pyroxene, calcite and abundant volcanic glass. In smaller proportion there are iron oxides and opaque minerals.

The mineralogy in the clay fraction indicates a predominance of illite and the presence of some iron oxides (Maldonado, 2014).

Quartz, a highly stable mineral, has a practically inert chemical behaviour so its contribution to dissolved species in water is minimal. On the other hand, the volcanic glass is easily altered and contributes silica and various ions (Na^{+} , K^{+} , Ca^{+}) to the water. Hydrolysis must be considered in the weathering process. Potassium feldspar, while a relatively stable species, undergoes hydrolysis given long periods of time. It can provide ions into the solution and ultimately form illite or kaolinite, depending on the prevailing geochemical conditions, according to the equation:



In Fig. 7a the stability diagram $\log K^{+}/H^{+}$ vs $\log Mg^{+2}/2H^{+}$ (Henderson, 1984), is shown in which it is observed that the samples from A1 and A2 CAS are in equilibrium with the clay fraction corresponding to illite. This mineral is always the identified clay in this temperate subhumid region both in soils and in different aquifer layers (Blarasin et al., 2014).

Other reactions such as the carbonate dissolution and cation exchange are also important and define the chemical water composition. Cation exchange depends on several factors: the nature of the exchanger, the type and concentration of the ions that enter the exchange, and the temperature at which the process occurs (Gomez and Turrero, 1994). According to Appelo and Postma (1993), the illite presents a moderate to low exchange capacity (20–50 meq/100 g). In the regional geochemical processes, some numerical models demonstrate the existence of carbonate dissolution (Fig. 7b) and cation exchange (Cabrera et al., 2009; Matteoda et al., 2011; Blarasin et al., 2014; Bécher Quinodoz and Blarasin, 2015, among others).

4.2. Isotopic analysis for groundwater renewal time assessment

Precipitation isotopic values are aligned with the Río Cuarto local meteoric line (Table 3, Fig. 8), whose equation is $\delta 2H = (8.2 \pm 0.2) \delta 18O + (14.6 \pm 1.2) \%$ obtained via orthogonal regression (Cabrera et al., 2017).

The isotopic results show that the A CAS samples have a meteoric origin considering that the samples are aligned with the local meteoric line (Cabrera et al., 2017) (Table 2, Fig. 8). The isotopic signature of the Alpa Corral precipitation suggests that A CAS is recharged from precipitation in the Comechingones Mountains area, especially A2 CAS, which are more impoverished suggesting that they may have been recharged even in colder times (Maldonado et al., 2016). Thus, the isotopic composition of these aquifers is depleted in relation to local plain rainfall and is similar to those of precipitations in the mountains (Table 3 and Fig. 8), that are impacted by continental and altitude effects (Giuliano Albo et al., 2015; Cabrera et al., 2017). Springs and streams from the mountain area show an isotopic composition that suggests meteoric origin (Table 3 and Fig. 8). They show similar isotopic composition to the mountain precipitation and the CAS. This observation is related to the infiltration of streams in the piedmont, which recharge the groundwater system.

A1 CAS has a lightly enriched isotopic composition because it can be recharged by the unconfined aquifer, which has higher hydraulic head (Table 3 and Fig. 8).

In relation to A1 CAS groundwater age, the hydraulic calculations indicate only allochthonous recharge from the piedmont region with a groundwater age on the order of 600-1500 years. However, as demonstrated by the isotopic values, there is a hydraulic connection with the overlying unconfined aquifer, indicating that water mixing between aquifers can exist. Thus, the groundwater age may be lower than those shown by the hydraulic calculations, but the 3H values are under

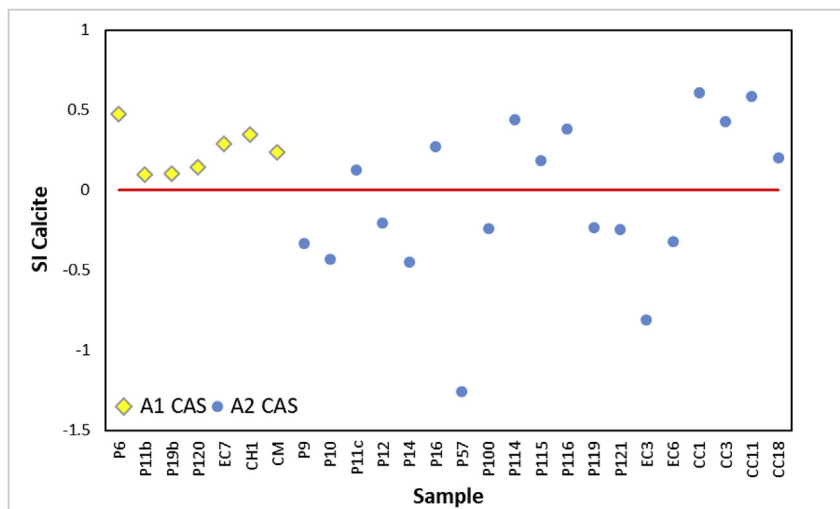


Fig. 5. Saturation Index for calcite phase of the A CAS.

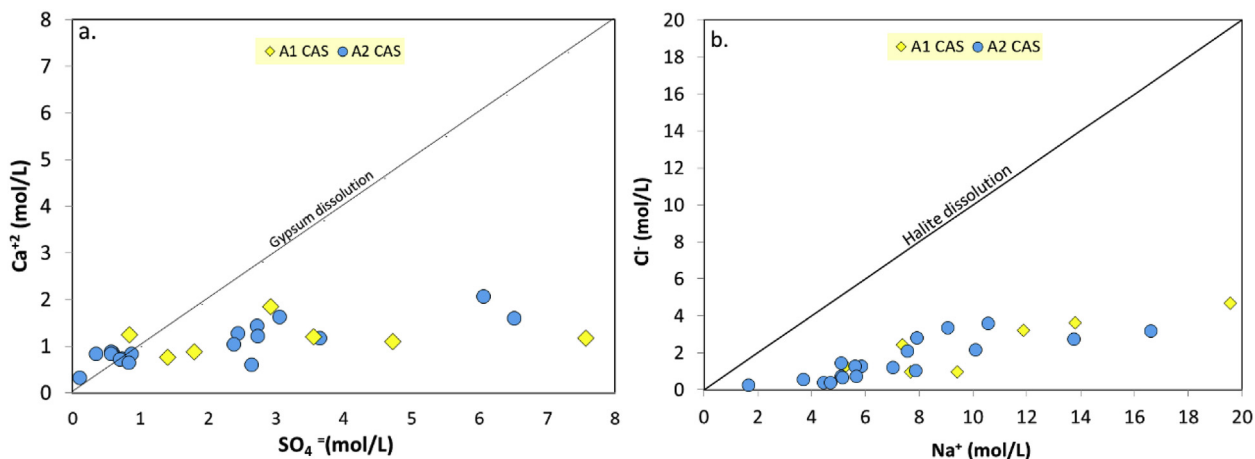


Fig. 6. a) Relationship between Ca^{+2} vs SO_4^{-2} in relation to the gypsum dissolution line and b) Cl^- vs Na^+ related to halite dissolution line.

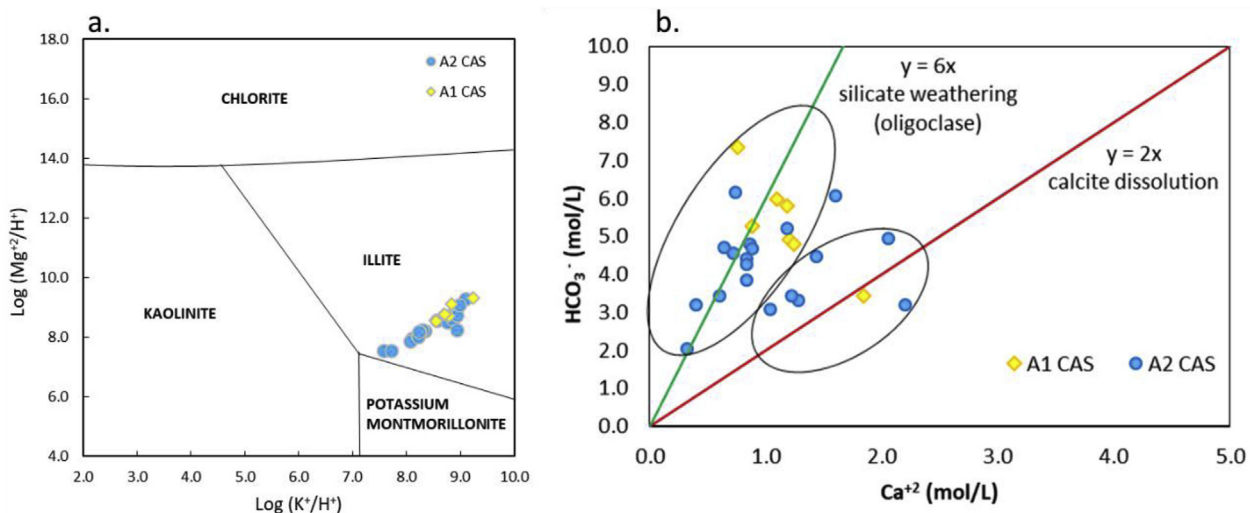


Fig. 7. a. Stability diagram for the system Mg-K-SiO₂-Al₂O₃-H₂O at 25 °C for A CAS samples (taken from Henderson, 1984) b. Geochemical processes that can influence the A CAS groundwater chemical composition.

Table 3
 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ stable isotopic average values for each hydrology system.

Hydrology system	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	d (%)
Río Cuarto Rainfalls (station, period 2007–2014)	-4.8	-22	14
Alpa Corral Rainfalls (station mountain area-period 2015–2017)	-5.5	-30	14
Unconfined aquifer	-4.8	-25	14
Rivers and streams (piedmont western areas)	-5.3	-27	16
A1 CAS	-5.1	-27	14
A2 CAS	-5.5	-29	15

detection limit, also confirming that groundwater is more than 60 years old (Table 4).

The $\delta^{13}\text{C}$ values (-4.42‰ and -3.73‰) in the A1 CAS samples are more enriched than the expected value of present atmospheric CO_2 (-7.5‰). This is because the dissolved carbon of mineral origin is being affected by carbonate dissolution, generating the enrichment of this isotope and diminishing the ^{14}C activity. Using Tamers (1975) and Pearson-Gonfiantini (Salem et al., 1980), the obtained radiocarbon ages were negative. This situation may be explained if other processes not considered in groundwater or in ^{13}C evolution occurred, because it is not possible for the initial activity to be less than the present activity. Also, it could be that the model is overcompensating ^{14}C dissolution (Escuder et al., 2009). Although an absolute age was not obtained, these values indicate that groundwater of A1 CAS is older than the groundwater from the unconfined aquifer, but younger than the underlying A2 CAS.

Concerning A2 CAS groundwater hydraulic ages, the values are on the order of 1500–3100 years. The absence of ^3H (below detection limit) confirms that the groundwater is old. The ages estimated with the cited methods showed similar values, excepting the EC6 sample which indicated older ages with the Tamer method (Table 4). For the A2 aquifer, Pearson-Gonfiantini was the model that better adjusted and ages between 1000 BP and 3600 BP were obtained (Table 4).

The main geochemical process affecting ^{14}C activity in these aquifer systems is carbonate dissolution. Even though the samples are sulfate type, they present moderate to high bicarbonate concentrations (≥ 125 mg/L).

5. Conclusions

Groundwater from the confined continental aquifers of the pampean plain of Cordoba has good quality and shows spatial and depth variations. In both A1 and A2 confined aquifer systems, the best qualities were found at the center of the study area, where the Neogene fluvial paleo systems have the largest impact because they are thicker and more widely distributed. Taking into consideration the grain size (sand-gravels) and the aquifer sediment mineralogy (quartz prevailing), the geochemical processes that allow the transference of ions into solution are diminished and groundwater is fresh. If the aquifer depth is considered, A2 CAS has the freshest water, because of the similar mineralogy but higher hydraulic conductivity (coarser texture).

The main geochemical processes that influence CAS water composition are silicate weathering, carbonate dissolution, cation exchange and atmospheric input.

Regarding the renewability of groundwater in the confined systems, isotopic analysis and the hydraulic and radiocarbon ages demonstrate that these systems are recharged in the piedmont areas and have old water of hundreds to thousands of years, that is, groundwater recharged during the Holocene period. The A2 aquifer system presents the longer renewal times.

The ^{14}C method used to evaluate A1 CAS resulted in a range of 60 to 1000 years, but this was not considered appropriate, because ^{14}C is more accurate in age ranges over 1000 years. In this case another isotope must be used, for example ^{36}Cl or ^{39}Ar , which covers a younger age range.

Even though both the A1 and A2 systems are currently used for irrigation, no significant decreases in groundwater levels are observed. This scenario may indicate that the extraction is being compensated by the present recharge in the piedmont, but more measurements are needed.

Given these results and the long groundwater recharge intervals results it is preferable to use groundwater from A1 CAS and to preserve the A2 CAS groundwater. More field information is required, to improve knowledge of the piezometric levels changes and to calculate the long term available water resources in these systems.

All information generated by these studies is already being provided to the provincial water institutions so that they can establish guidelines for groundwater use management to achieve a sustainable groundwater use.

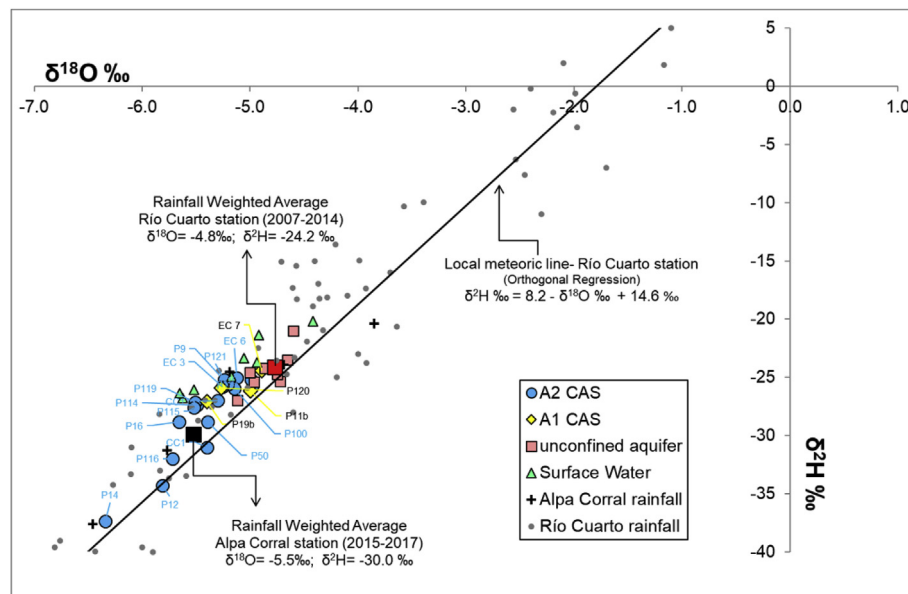


Fig. 8. $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ diagram for rainfalls, surface water and aquifers systems.

Table 4³H, $\delta^{13}\text{C}$ and ¹⁴C results and ¹⁴C ages reported from Canada laboratory and Tamers (1975) and Pearson-Gonfiantini (Salem et al., 1980) models.

Sample	CAS	³ H (TU) (1 σ)	$\delta^{13}\text{C}$ (‰) ($\pm 0.2\text{‰}$)	¹⁴ C (pmC) (1 σ)	¹⁴ C Age (BP)	Tamers (BP)	Pearson-Gonfiantini (BP)
CH1	A1	< 0.8 \pm 0.3	−4.42	68.3 \pm 0.26	3000 \pm 30	−1664 (nc)	−6551 (nc)
CM	A1	< 0.8 \pm 0.3	−3.73	51.9 \pm 0.18	5200 \pm 30	603	−5687 (nc)
EC6	A2	< 0.8 \pm 0.3	−7.27	32.8 \pm 0.13	8900 \pm 33	8900	3600
P115	A2	< 0.8 \pm 0.4	−7.38	45.2 \pm 0.18	6400 \pm 31	1100	1100
P57	A2	< 0.8 \pm 0.3	−7.36	34.1 \pm 0.17	8600 \pm 40	3414	3400

nc: not considered.

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