



Relationships between geomorphological features and groundwater geochemistry in the upper and middle basin of Las Peñas stream, Pampean Mountains, Córdoba. Argentina

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Abstract

Las Peñas stream basin, located in the Pampean Mountains of Cordoba (Argentina), has specific groundwater features which are of great interest for the local socioeconomic activities. The objective of this work is to define the geomorphological characteristics of the basin and interpret their influence on hydrogeological processes, emphasizing hydrodynamic and hydrogeochemical aspects. Groundwater flow in the unconfined aquifer has developed in both sediments and fractured rocks. The groundwater is fresh with electrical conductivities between 586 $\mu\text{S}/\text{cm}$ and 2000 $\mu\text{S}/\text{cm}$, although there are localized samples in the piedmont of brackish type (up to 3900 $\mu\text{S}/\text{cm}$). Sampled groundwaters are almost entirely of calcium and sodium bicarbonate geochemical type, with local occurrence of mixed type (sodium-calcium bicarbonate and sodium bicarbonate-sulfate) waters. Taking into account geomorphological and lithological features, both groundwater flow and hydrochemical aspects are linked with the main geomorphological environments: a relict paleosurface with a sedimentary cover, a rocky dissected paleosurface with filled valleys and the sedimentary piedmont. It was interpreted that groundwater geochemistry is mainly linked to input from precipitation and weathering of silicates. Dissolution of carbonates and cation exchange processes contribute to the observed groundwater chemistry especially in the relict paleosurface and piedmont.

Keywords Hydrogeology · Geomorphology · Silicate weathering · Groundwater chemistry

Introduction

The United Nations World Report on Water Resources Development (UNESCO 2019) emphatically establishes that improving water resources management and providing access to safe and affordable drinking water and sanitation are essential to eradicate poverty and build peaceful and prosperous societies. In this sense, it is essential to promote strategic and interdisciplinary policies promoting

the investigation of dynamics, quality and availability of groundwater—the most abundant source of fresh liquid water on the planet—and expand current knowledge of these topics. Such work can provide effective and innovative tools for planning and management of water resources, to mitigate environmental problems and to promote sustainable socioeconomic development.

In many areas of the world, the behavior of aquifer systems is strongly influenced by the dominant geological setting and local variations in relief. The study of these variables and their relationship with the occurrence, distribution, movement and quality of groundwater allow to evaluate the hydrogeological potential of a region (del Pilar Alvarez et al. 2010; Blarasin et al. 2013; Adjani and Sejati 2014; Rajaveni et al. 2017; Bécher Quinodóz et al. 2019a, b). In addition, the use of different hydrogeochemical methods that take into consideration molar ionic relationships is a useful tool to interpret rock-water interactions and atmospheric influences to improve the assessment of solutes sources and to infer the main mechanisms that control the geochemistry

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of groundwater (Elango et al. 2003; Subramani et al. 2010; Currell and Cartwright 2011; Yang et al. 2016; Zhang et al. 2020).

Groundwater is fundamental for society and the environment in the province of Córdoba (Argentina). It is the most extensively utilized water resource in large regions of the province, providing water for domestic, industrial, livestock and irrigation and maintains many natural processes, being essential for the support of different aquatic and terrestrial ecosystems (Blarasin et al. 2014). In the south of the province, numerous catchments that are developed both in the mountains and the plains have not yet been studied in detail, despite the need to understand the hydrological and hydrochemical behavior and their relationship with human activities. Within the regional hydrogeological framework (Blarasin et al. 2014), it is necessary to analyze more deeply the hydrological connectivity between mountain, piedmont and plain for the understanding of the factors that control water geochemistry and thus, the quality for different uses.

The Las Peñas stream basin, selected for this study, needs investigation to generate information for local socioeconomic activities and for water and environmental managers. The basin drains the eastern slopes of the Sierra de las Peñas Mountains (located in the Pampean Mountains of Córdoba) and spills into the piedmont and adjacent fluvio-eolian plain (Fig. 1). This mountainous area is undergoing a process of exhumation and maintains pre-Andean erosive surfaces with different degrees of preservation (Carignano et al. 1999, 2014; Degiovanni 2008). The drainage network of Las Peñas stream basin is in the process of re-establishment, mainly in response to the mentioned exhumation.

The objective of this study is to define the geomorphological characteristics of the Las Peñas stream basin and to interpret the relationship with hydrogeological characteristics,

emphasizing hydrodynamic and hydrogeochemical aspects. The main research hypothesis is that different topographic zones with distinctive lithological and morphological characteristics control the groundwater quality.

Materials and methods

The research was carried out in the Las Peñas stream basin (catchment area of approximately 200 km²) located in the northeast of the Rio Cuarto Department, in the province of Córdoba, Argentina (Fig. 2). The study was based on the analysis and compilation of topographic sheets from National Geographic Institute (NGI) at 1:50,000 scale and satellite images (Google Earth, Landsat ETM). Background regional information (e.g., geological, geomorphological, climatic data) of the regional context was previously collected, reported and analyzed (Blarasin et al. 2014; Carignano et al. 2014). The precipitation data were analyzed and interpreted using a local 30-year time series (1990–2020). Evapotranspiration and water excess were calculated with a sequential monthly water balance, using the software PDIWIN (Ravelo and Herrero 1999). The geological and geomorphological study was performed through field observation and description of the relief and outcropping lithological profiles.

The hydrogeological data were obtained by surveying 25 wells which penetrate the upper part (10–50 m) of the unconfined sedimentary aquifer, although some wells penetrate into the upper few meters of the underlying fractured rock system. The surveyed wells are all used for people and cattle water supply and, in general, they have very short screened intervals (1–3 m). The water samples were extracted using installed windmills or very small pumps, purging at least two

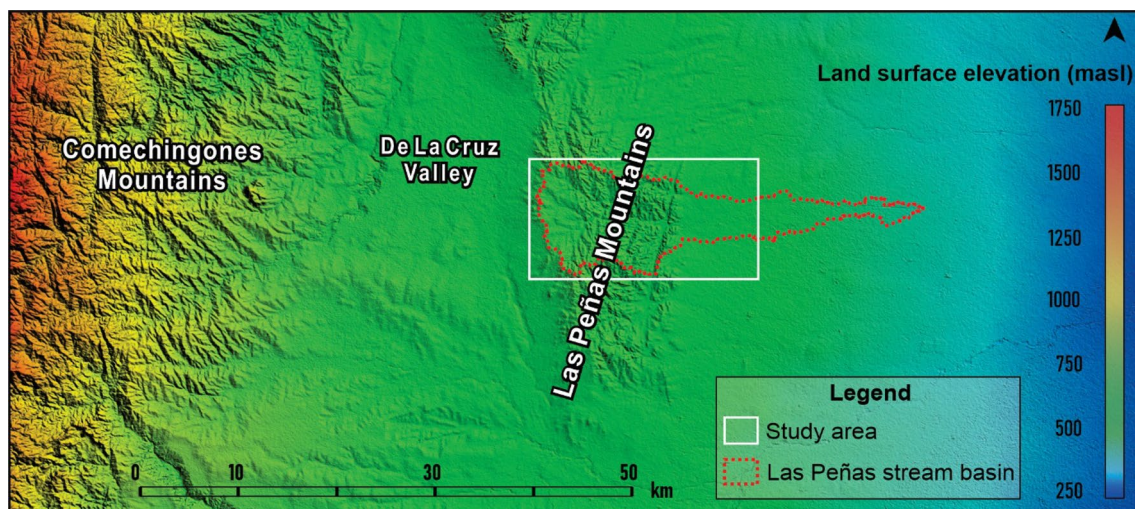
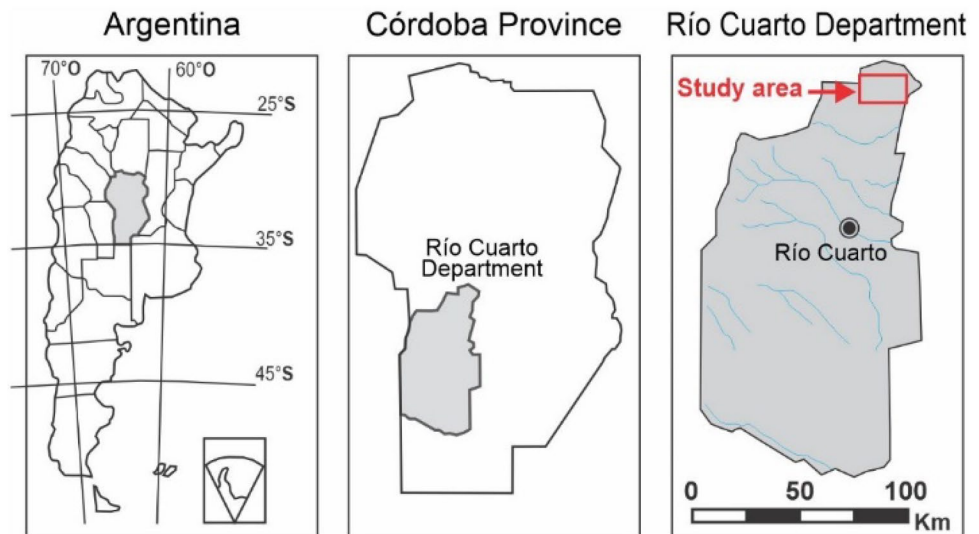


Fig. 1 Regional digital model elevation

Fig. 2 Location of the study area



volumes of water and waiting until the chemical parameters stabilized. Physical–chemical parameters—pH, electrical conductivity (EC) and temperature (T)—were recorded in the field using a multiparameter probe with GPS (Hanna HI 9829). Finally, the samples were appropriately preserved, being filtered through 0.45 μm , acidified with nitric acid until $\text{pH} < 2$ when necessary, packed in high density plastic bottles, refrigerated at 4°C and transported to the laboratory for analysis. Samples were analyzed in the laboratory of the Geology Department of the National University of Río Cuarto using standard analytical procedures reported elsewhere (APHA 2005). The following chemical variables were measured: carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) by titration with HCl (Orion-Thermo selective electrode); sulfate (SO_4^{2-}) by turbidimetry (Macrotonic centrifuge); chloride (Cl^-) by titration with silver nitrate; sodium (Na^+) and potassium (K^+) by flame photometry (Metrolab 315 digital photometer); magnesium (Mg^{2+}) and calcium (Ca^{2+}) by titration with EDTA. The mean Charge Balance Error (CBE) of the analysis, obtained for each sample from Eq. 1, did not exceed 5%. Maps were created and modified using QGIS 2.18 and Corel Draw v.17.

$$\% \text{CBE} = \frac{\sum \text{anions}(\text{meq}) - \sum \text{cations}(\text{meq})}{\sum \text{anions}(\text{meq}) + \sum \text{cations}(\text{meq})} \times 100. \quad (1)$$

Study area description: climatic, geologic and geomorphologic characteristics

The regional climate is of mesothermal sub-humid-dry type, with potential evapotranspiration generally exceeding precipitation. Based on the hydrometeorological data of the study area from 1990 to 2020, precipitation exhibits a very

marked seasonality, with 75% of rainfall from November to March (spring–summer), within an annual average precipitation of 757.4 mm. The soil water balance shows that between 74 and 100% of precipitation is returned to the atmosphere as actual evapotranspiration. Water deficits occur mainly in the autumn–winter months. The results of the monthly water balance show water excesses in more humid years, which can contribute to surface runoff and/or recharge to the unconfined aquifer. The water excesses were found to be variable (between 0 and 132 mm) and mainly occur in spring–summer, conditioned by the temporal distribution of precipitation and topography.

The crystalline bedrock in the mountainous area is constituted of metamorphic rocks corresponding to the Sierra de Las Peñas Metamorphic Complex (Neoproterozoic–Lower Paleozoic), which includes paragneisses, paraamphibolites, marbles, orthogneisses and orthoamphibolites that outcrop mainly in the eastern and western extremes of the mountains (Bonalumi et al. 2005). This complex also contains a plutonic body of batholithic dimensions and granitic composition called Granitoide Las Peñas (Cambrian), which is located in the center of the mega-block and is partially concordant with the metamorphic rocks. It is a biotite porphyric granite, pink to red in color, with moderately marked banding. Pleistocene–Holocene aeolian and alluvial deposits (loessical sediments and fine sandy sequences) outcrop in the valleys and high areas of the mountainous block. The piedmont environment is characterized by thick Neogene–Quaternary clastic sequences of alluvial, colluvial and aeolian origin. In this sector, most of the area is covered with loessical type sediments interlayered at different depths by sands and gravel of paleochannels that came from Las Peñas mountains.

The genesis of the local topographic relief is associated with the interaction between tectonic processes, e.g., the

Andean Orogeny, and exogenous processes, controlled by climatic variations through the Upper Pleistocene and Holocene periods, which partially re-worked the pre-existing land surface and generated the current landscape features (Degiovanni 2008; Carignano et al. 2014). The most distinctive geomorphological characteristics of the area are structurally controlled, related to regional faults and the differential degree of dissection of the mountain block (Fig. 3).

Results and discussion

Geomorphological units

The Sierra de las Peñas Mountain is a mega-block plutonic-metamorphic bedrock that preserves very little and highly modified ancient relief (Mesozoic-Paleogene), coexisting with Neogene-Quaternary geofoms. It exhibits a transverse asymmetric profile, characterized by a steep west-facing escarpment and a gentle structural slope to the East, drained by the Las Peñas stream and its tributaries (Fig. 3). The river carved out a dendritic rectangular drainage network both on rock and sediments, developing broad mountain valleys and rectilinear courses, whose orientation is dominated by the structural controls. In the upper basin, the dominant morphologies are inferred to result from the exhumation of

ancient erosive surfaces, which show different degrees of preservation, against the action of denudation processes that are mainly associated with the dynamics of the river network (Degiovanni 2008; Carignano et al. 2014; Kröhling et al. 2014).

The major identified geomorphological units of the region are (Fig. 4):

1.a Main relict paleosurface with sedimentary cover: The paleosurface is a planation surface developed on crystalline bedrock, generated during extensive denudation cycles (between Late Cretaceous and Paleogene age) and then faulted, tilted and exhumed during the Andean orogeny. This unit is the area that best represents the pre-Andean paleosurfaces, described in other places of the Pampean Mountains of Córdoba by various authors (Carignano et al. 2014; Rabassa et al. 2014; Andreazzini and Degiovanni 2014). The landscape is gently undulating with a low overall slope (1–2%). Almost the whole unit is covered by Quaternary sedimentary sequences (loess and fine colluvial/alluvial deposits) with variable thickness (1–15 m). However, some scattered outcrops of bedrock—appearing as flattened blocks, can be observed. This unit is drained by a dendritic stream network with low dissection and poorly developed hierarchy, with first and second order streams, representing the headwaters of the Las Peñas stream. These are characterized by slightly sinuous channels, of variable width (between

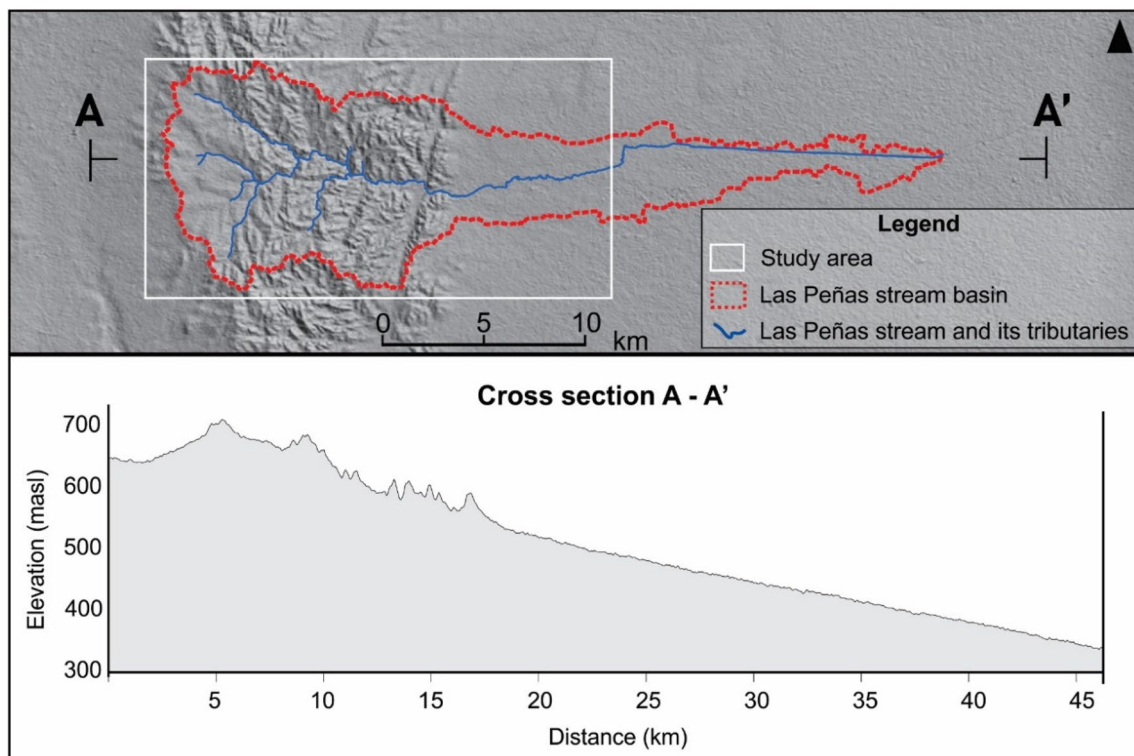


Fig. 3 Cross section of the central part of the Las Peñas basin

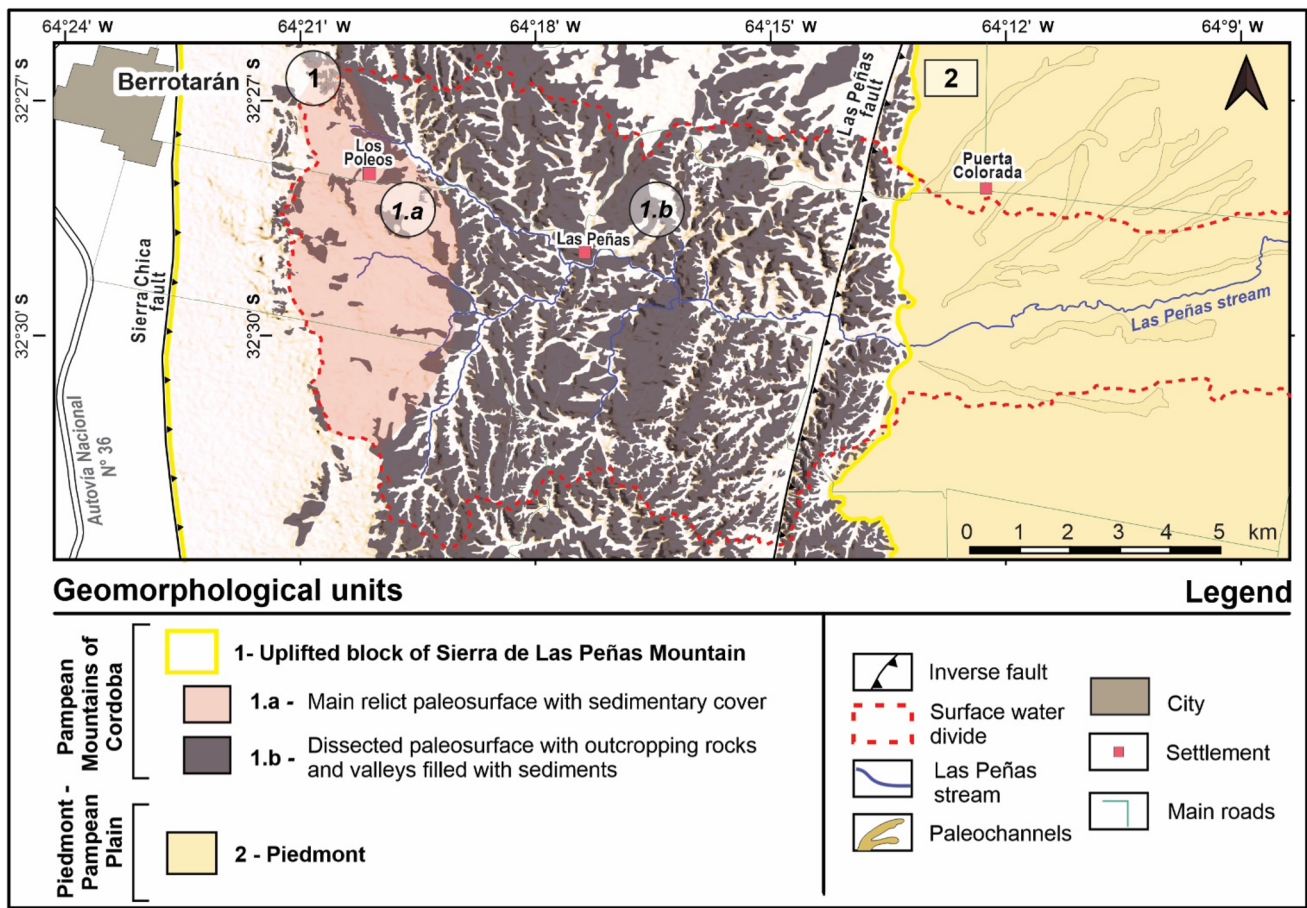


Fig. 4 Map of Geomorphological Units

1 and 6 m) and shallow depth. In some sections, the contact with bedrock can be observed in the stream bed.

1.b Dissected paleosurface with outcropping rocks and valleys filled with sediments: The bedrock consists mainly of biotite-rich garnet gneiss and granite rocks corresponding to the Sierra de Las Peñas Metamorphic Complex (Bonalmi et al. 2005). The regional slope (1.9%) decreases progressively as the block tilts to the east, while local slopes (5%) are more developed than in the previous unit (1.a), due to increased river dissection, reaching up to 30-m depth. The channels of the drainage network, mostly ephemeral, have a rectilinear morphology, strongly controlled by the fractures and anisotropies of the bedrock. The minor valleys have an erosive origin and variable size (from a few tens of meters to kilometers in length). These valleys are filled by Quaternary sediments, mainly fine-grained materials from the remobilization of the loessic (aeolian) sequences, which covered the mountainous areas during dry Quaternary cycles (Carignano et al. 2014; Kröhling et al. 2014). Some local intercalations of coarse-grained sediments are observed. Due to their morphology and position of sedimentary filling, these are considered ancient, at least pre-Quaternary, molded by

river activity in response to the main Andean uplift during the Paleogene period.

2 Piedmont: This zone is located in the eastern sector of the Sierra de las Peñas Mountains. The relief is made up of smooth hills, with heights and slopes that decrease progressively away from the mountains. It is characterized by thick sequences of ancient alluvial fans, re-transported aeolian sediments, and aeolian deposits. The morphological and sedimentological features of these deposits reflect energy changes associated with climatic alternations and neotectonic regional activity (Degiovanni 2008).

Hydrogeological characterization

Most of the sampled wells penetrate the sedimentary unconfined aquifer which was identified in the main relict paleosurface (unit 1.a), the main valleys of unit 1.b, and in the sedimentary environment of the piedmont (unit 2). Six wells in units 1.a and 1.b also partially penetrate only few meters of the fractured bedrock. The unconfined aquifer exhibits varied lithology and thickness within the three units. It is composed of very fine sands with a high percentage of silts

in unit 1.a, consistent with the aeolian origin of the sediments. In the valleys of unit 1.b, there are generally fine deposits of re-transported aeolian sediments, with thin layers of coarse textured sands and gravels of alluvial origin. In the piedmont (unit 2), the aquifer system is made up of clastic materials of aeolian origin (very fine silty sands), re-transported aeolian sediments and some intercalations of sand-gravel deposits, linked to alluvial paleofans from the Sierra de Las Peñas Mountains. In all cases, calcite appear dispersed in the sediments or as nodules and calcrete layers. This implies that the aquifer is heterogeneous in terms of hydraulic conductivity and flow characteristics.

Taking into account the sedimentary sequence outlined above, and based on estimated values from theoretical tables, textural analysis of local sediments and regional pump tests (Custodio and Llamas 1983; Blarasin et al. 2014), there is a marked variability in effective porosity and hydraulic conductivity (*K*), with *K* values predominantly in the range 1–10 m/d. Furthermore, given the highly variable thickness of sedimentary deposits (a few meters in the relict surface and valleys, and several tens of meters in the piedmont) the

sedimentary aquifer shows highly variable transmissivity (*T*), ranging between 4 and 600 m²/d.

The studied area includes a single phreatic aquifer that is recharged mainly by precipitation and local infiltration from the Las Peñas stream in the piedmont. Regional groundwater flow is towards the piedmont and the adjacent eastern plain (outside the study basin), where the major discharge areas, represented by lagoons and wetlands, are located. The groundwater flow direction is predominantly W-E, with local variations, indicating the influence of the topographic surface (Fig. 5 and Fig. 6). The western end of the basin (unit 1.a) shows a convergent radial flow pattern and low hydraulic gradients (1.11–1.61%), with local discharge areas located in the center of the basin, giving base flow to the main mountain streams. The highest hydraulic gradients (2.44–2.57%) are found in the central part of the basin (associated with moderately sloping valleys) and in the proximal eastern piedmont. Hydraulic gradients within unit 2 are in the order of 1–1.5%, as a consequence of the progressive flattening of the topographic relief to the east.

Within this hydrogeological framework, only the major drainage feature—Las Peñas stream—is permanent, as a

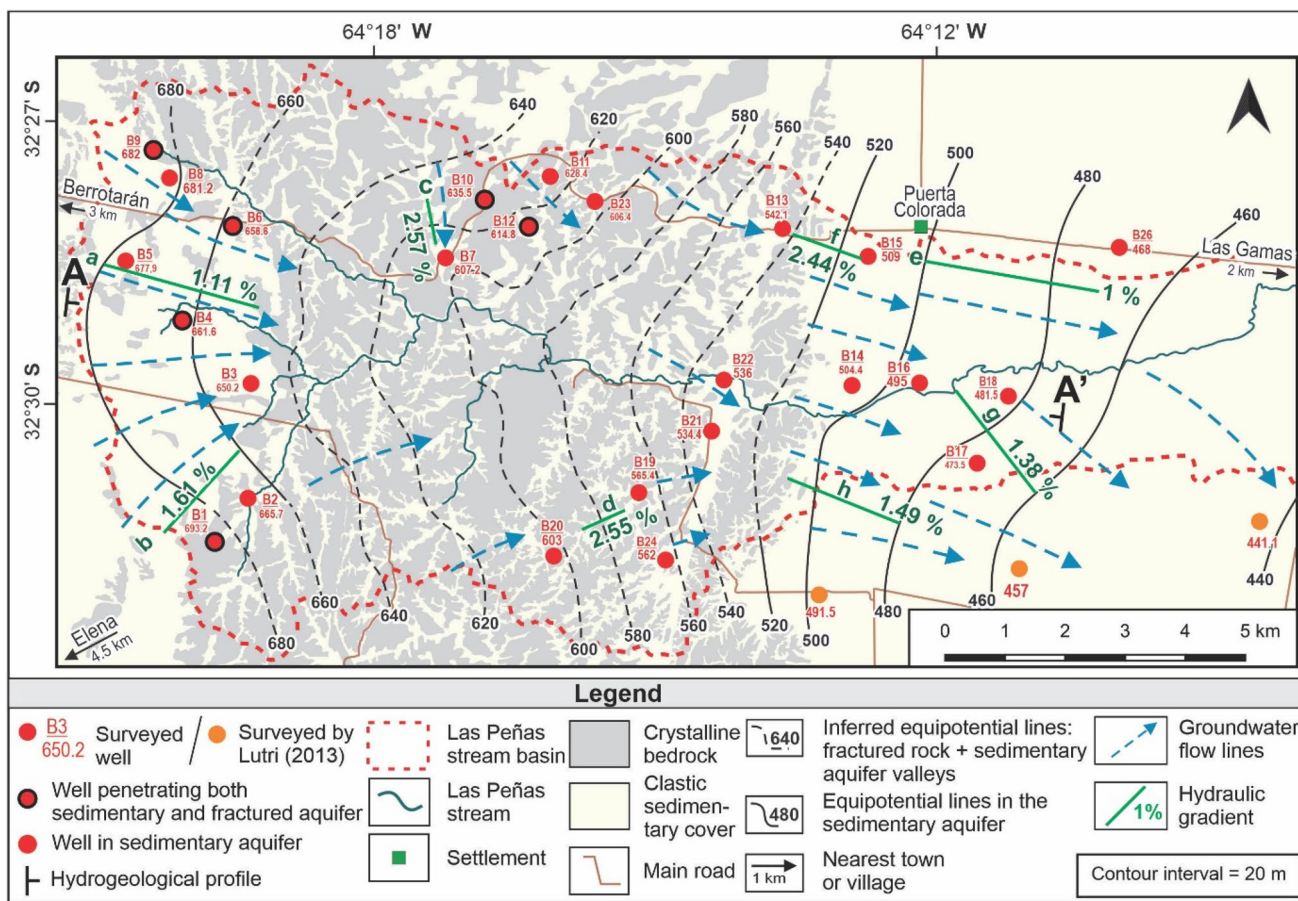


Fig. 5 Potentiometric map of the Las Peñas stream basin

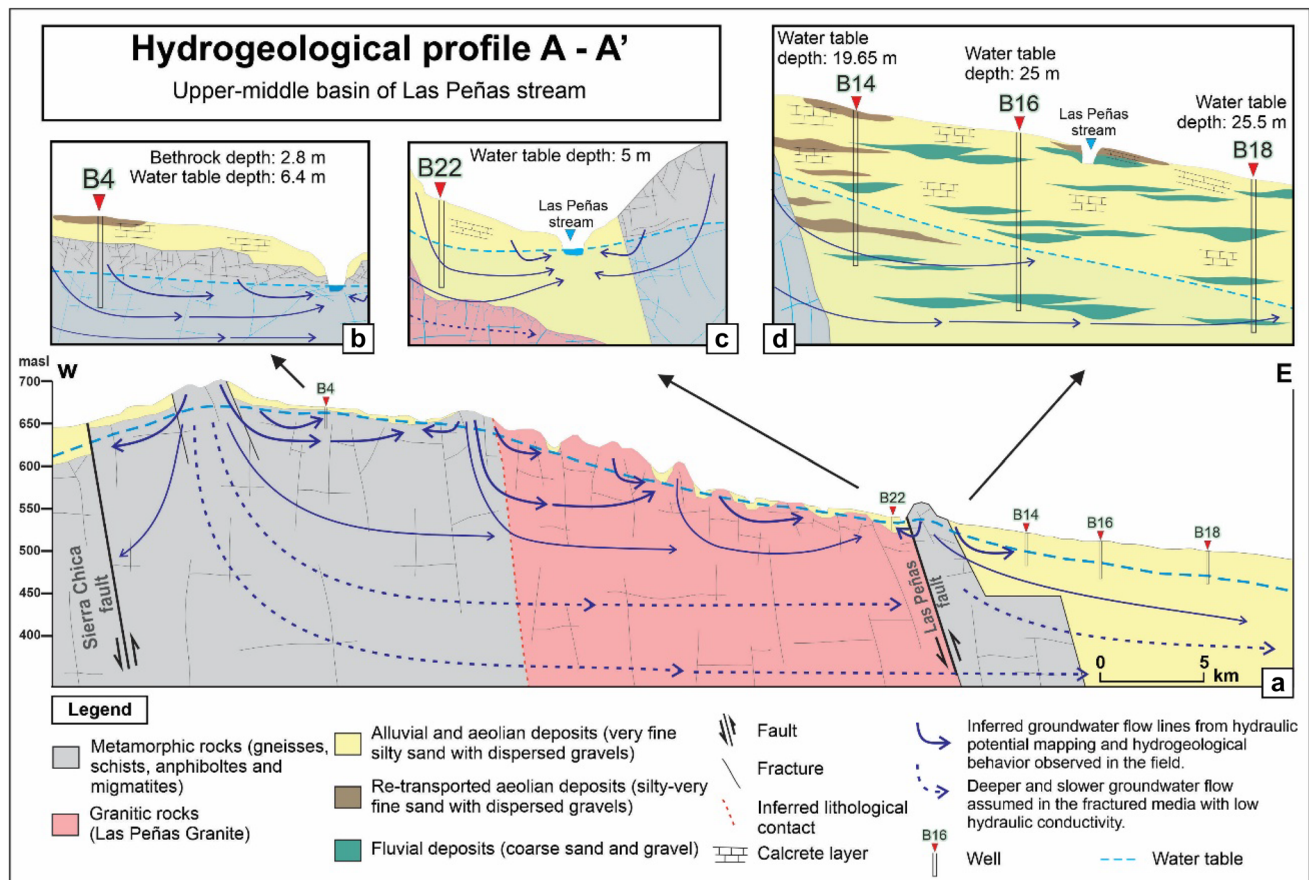


Fig. 6 Schematic hydrogeological profile in the Las Peñas stream basin. **a** Regional cross-section (section AA' showed in Fig. 5). The upper insets correspond to detailed schemes of the geomorphological units: **b** unit 1.a. **c** unit 1.b and **d** unit 2

result of base flow from the aquifer, although the stream water infiltrates contributing to the aquifer (i.e., switches to 'losing' conditions) when it arrives at the piedmont, where the water table is 20–30 m deep (Fig. 6).

Geochemical characterization

Groundwater in the basin is fresh to brackish, with field electrical conductivities between 586 $\mu\text{S}/\text{cm}$ and 3880 $\mu\text{S}/\text{cm}$ (approximately 420–2720 mg/L total dissolved solids (TDS)). Table 1 presents the physico-chemical analysis of groundwater samples while the descriptive statistics for groundwater chemical variables are shown in Table 2. The geochemical type, according to the Piper diagram (Fig. 7), is mainly calcium-bicarbonate and sodium-bicarbonate. The spatial distribution of Stiff diagrams can be observed on Fig. 8.

Main hydrochemical processes

To evaluate the origin of groundwater solutes in the different geomorphological environments, a diverse range of

factors were considered. Taking into account that the mountainous region is a key recharge area (Blarasin et al. 2014), input of chemical elements from rainfall was examined. It is well established that the primary source of chloride in groundwater is atmospheric aerosols in rainfall (aside from rare cases in other geological settings where evaporite minerals occur), and this is also a dominant source of Na in areas of precipitation recharge (Wood 2019; Gaillardet et al. 2019). These solutes may be concentrated significantly by evapotranspiration in recharging groundwater, depending on recharge rate, processes and climate (Cartwright et al. 2007). Numerous hydrological studies, including numerical mixing models, in the southern region of Córdoba consider solutes derived from precipitation as inputs to groundwater and surface water (Blarasin et al. 2014; Cabrera et al. 2009; Bécher Quinodóz and Blarasin 2017).

The chemical analysis of precipitation (Fig. 7) sampled for more than 10 years in this region (Cabrera et al. 2013), indicates that rainfall exhibits relatively low salinity content (average EC in the order of 54 $\mu\text{S}/\text{cm}$), low concentrations of all major ions, calcium-bicarbonate or sulfate geochemical type and slightly acidic pH (~ 6.00). Evaporite minerals such

Table 1 Physicochemical analysis of groundwater (25 samples). Unconfined aquifer of Las Peñas stream basin

No. sample	pH	CE ($\mu\text{S}/\text{cm}$)	SDT (mg/L)	CO_3^{2-} (mg/L)	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)	CBE* %
B1	7.42	652	456	<LOD	431.3	11.8	14.3	26.3	14.2	105.1	1.8	5.9
B2	7.09	586	410	<LOD	367.5	14.9	11.4	28.3	11.1	96.0	5.4	0.6
B3	8.15	1399	979	<LOD	735.0	39.7	34.3	245.7	20.8	45.6	19.5	-1.1
B4	8.25	1363	954	<LOD	666.3	42.5	25.7	295.2	19.0	18.4	13.7	-5.5
B5	7.97	2340	1638	<LOD	1502	43.3	28.6	515.7	20.8	29.6	23.2	-0.2
B6	8.02	879	615	<LOD	535.0	25.6	14.3	139.0	20.8	43.6	20.2	-2.5
B7	7.70	663	464	<LOD	427.5	14.6	25.7	36.4	10.5	98.4	11.2	1.6
B8	7.73	1556	1089	<LOD	655.0	25.6	51.4	235.6	20.8	66.0	37.3	-6.6
B9	7.45	662	463	<LOD	410.0	42.5	17.1	42.5	18.0	81.6	20.5	-0.2
B10	7.52	784	549	<LOD	522.5	25.6	20.0	29.3	11.1	108.8	10.7	9.4
B11	7.36	696	487	<LOD	447.5	47.6	20.0	42.5	10.5	86.4	19.0	4.7
B12	7.42	751	526	<LOD	441.3	26.4	22.9	28.3	20.7	101.6	10.7	6.8
B13	7.42	953	667	<LOD	525.0	33.0	34.3	100.1	20.4	88.0	24.4	-5.2
B14	7.85	1375	963	<LOD	437.5	238.7	17.1	139.5	17.6	148.8	9.3	-4.4
B15	7.48	812	568	<LOD	451.3	17.3	25.7	59.7	14.5	95.2	5.9	3.4
B16	7.40	784	549	<LOD	375.0	11.0	37.1	89.5	13.3	72.0	11.7	-0.9
B17	7.47	1247	873	<LOD	330.0	220.9	51.4	97.1	19.9	135.2	6.8	-0.4
B18	7.55	827	579	<LOD	412.5	18.9	41.4	81.9	13.6	104.8	10.7	-9.9
B19	7.22	1023	716	<LOD	551.3	41.7	51.4	58.6	9.1	145.6	0.5	8.6
B20	7.22	823	576	<LOD	470.0	21.2	25.7	29.3	4.1	125.6	1.0	8.0
B21	7.45	1041	729	<LOD	540.0	74.4	40.0	77.9	10.8	119.2	7.3	8.7
B23	8.12	623	436	<LOD	387.5	16.9	14.3	26.3	8.1	91.2	2.9	6.4
B24	7.57	928	650	<LOD	490.0	26.0	28.6	35.4	7.9	106.4	21.5	6.6
B25	7.72	2620	1834	<LOD	311.3	973.3	80.0	386.8	20.5	147.2	22.0	2.6
B26	7.94	3880	2716	<LOD	340.0	1569.1	82.9	737.1	20.5	180.8	13.7	-2.0
Limit of Detection LOD (mg/L)	-	-	-	1.2	1.3	0.4	1.4	1	0.2	0.4	0.2	

*Charge balance error

as halite and gypsum have not been identified in outcropping sediments or reported in drilling in this basin, indicating that those minerals are unlikely to influence major ion concentrations in groundwater. As can be seen in Fig. 9, the proportions of SO_4^{2-} , Ca^{2+} , Cl^- and Na^+ are not indicative of the dissolution of these minerals.

In addition to the contribution of solutes derived from precipitation, ionic ratios were further investigated for indications of water–rock interaction processes. The ratios of $\text{Na} + (\text{Na} + \text{Ca})$ and $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ as a function of TDS, plotted in the Gibbs diagram (Gibbs 1970), indicates the dominance of rock-weathering in the study area (Fig. 9). Higher total cation/Cl ratios (Fig. 10a) also indicate mineral weathering is a major origin of solutes in groundwater. Points located below the 1:1 line of $(\text{Ca} + \text{Mg})$ vs. $(\text{HCO}_3 + \text{SO}_4)$ diagram (Fig. 10b) indicate that silicate weathering is a considerable source of calcium (consistent with high Ca/Cl ratios—Fig. 10c), especially in the dissected paleosurface zone (unit 1.b) (Elango et al 2003; Currell and

Cartwright 2011). Figure 10.c also shows that the areas where sedimentary deposits predominate (unit 1.a and unit 2) show a preponderance of cation exchange processes. Values of the Na/Cl ratio greater than 1 (Fig. 10d) confirm halite is not a source of sodium. Rather, this ion is likely derived from cation exchange (in unit 1.a) and silicate weathering (in unit 1.b).

The slight shift outside the rock-weathering/evaporation dominance domain towards TDS values around 1000 mg/L is linked to the fact that the samples are mainly extracted from the sedimentary aquifer where other mentioned processes appear, for example adsorption–desorption and ion exchange. This has been observed and verified in the region's sedimentary aeolian aquifers using numerical modeling (Bécher Quinodóz et al. 2019a, b).

The rocks and sediments present in the different geomorphological units are mainly composed of quartz, plagioclase, K-Feldspar, biotite, muscovite, amphiboles and garnet. It is also common to find volcanic glass (contained in loess),

Table 2 Descriptive statistics for groundwater hydrochemical parameters from the unconfined aquifer, Las Peñas stream basin

Parameter	Unit	Amount of samples	Min	Max	Mean	Median	Standard deviation
pH	–	25	7.1	8.3	7.6	7.5	0.3
CE	μS/cm	25	586	3880	1,171	879	759
CO ₃ ⁻²	mmol/L	25	–	–	–	–	–
	mg/L	25	<LOD	<LOD	–	–	–
HCO ₃ ⁻	mmol/L	25	5.10	24.6	8.37	7.33	3.80
	mg/L	25	311	1,503	511	448	232
SO ₄ ⁻²	mmol/L	25	0.11	16.3	1.51	0.27	3.69
	mg/L	25	11.01	1,569	145	26.4	354
Cl ⁻	mmol/L	25	0.32	2.34	0.92	0.73	0.53
	mg/L	25	11.43	82.9	32.6	25.7	18.9
Na ⁺	mmol/L	25	1.14	32.1	6.24	3.39	7.67
	mg/L	25	26.3	737	143	77.9	176
K ⁺	mmol/L	25	0.10	0.53	0.39	0.37	0.13
	mg/L	25	4.1	20.8	15.2	14.5	5.23
Ca ⁺²	mmol/L	25	0.46	4.51	2.44	2.46	0.97
	mg/L	25	18.4	181	97.6	98.4	38.7
Mg ⁺²	mmol/L	25	0.02	1.54	0.54	0.46	0.37
	mg/L	25	0.49	37.3	13.2	11.2	8.91

clay minerals and calcite. Table 3 shows the mineralogical composition of six samples from the fluvio-eolian sediments (53–63 μm fraction) located in the southwest of the study area (Matteoda 2012). To analyze in more detail the water–rock interactions processes, the following minerals were primarily considered: feldspars (plagioclase, oligoclase, andesine) and calcite (Kim 2002; Destéfanis et al. 2019), due to their reactivity. It is known that the alteration

of plagioclase and other feldspars, which constitute almost half of the minerals in earth’s crust (Gout et al. 1997; Char-don et al. 2006) provides solutes to groundwater, from rocks, mineral clasts and lithic fragments. Given the abundance in the terrestrial crust of intermediate forms (25–45% anortite) (anortite-albite) and taking into account the lithological and mineralogical characteristics of Sierra de Las Peñas Moun-tains (Demichelis 1986; Bonalumi et al. 2005) oligoclase (10–30% anortite—90–70% albite) and andesine (30–50% anortite- 70–50% albite) were primarily considered to evalu-ate the provenance of dissolved ions. The hydrolysis of these minerals generates alkalinity, in addition to Na⁺ and Ca⁺² in solution.

Based on the molar ratios of HCO₃⁻ vs Ca⁺² (Fig. 11a), significant differences are observed in the samples coming from the three different geomorphological environments. Groundwater samples from the central dissected rocky paleosurface sector (unit 1.b) plot distinctively near the theoretical dissolution line of andesine (y = 3.38x). Some of these samples correspond to wells that partially inter-sect the fractured rock aquifer. Samples corresponding to the main relict paleosurface with sedimentary cover (unit 1.a) approach the theoretical dissolution line of oligoclase, indicating calcium derived from this mineral. These wells are located in the eolian/colluvial/alluvial sediments (while four partially penetrate the bedrock).

The presence of calcium carbonate is also evident at field in different parts of the basin. The contribution of calcium and bicarbonate from calcite dissolution is con-sistent with saturation indices that explain oversaturation

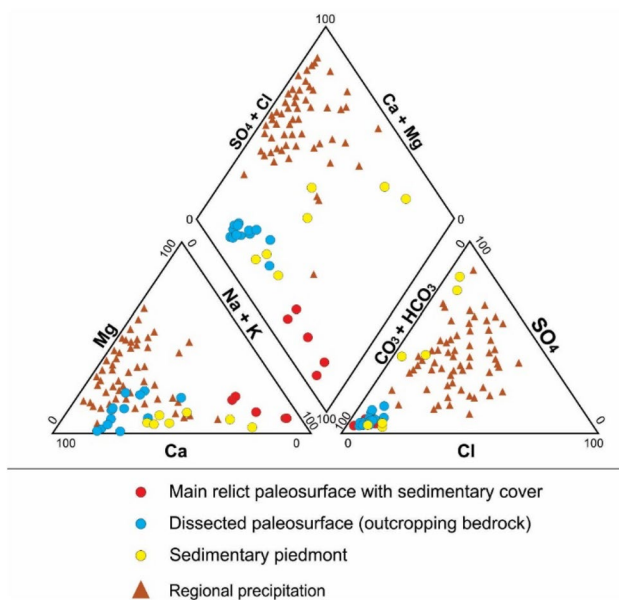


Fig. 7 Piper diagram for chemical characteristics of regional precipi-tation and groundwater samples of the Las Peñas stream basin

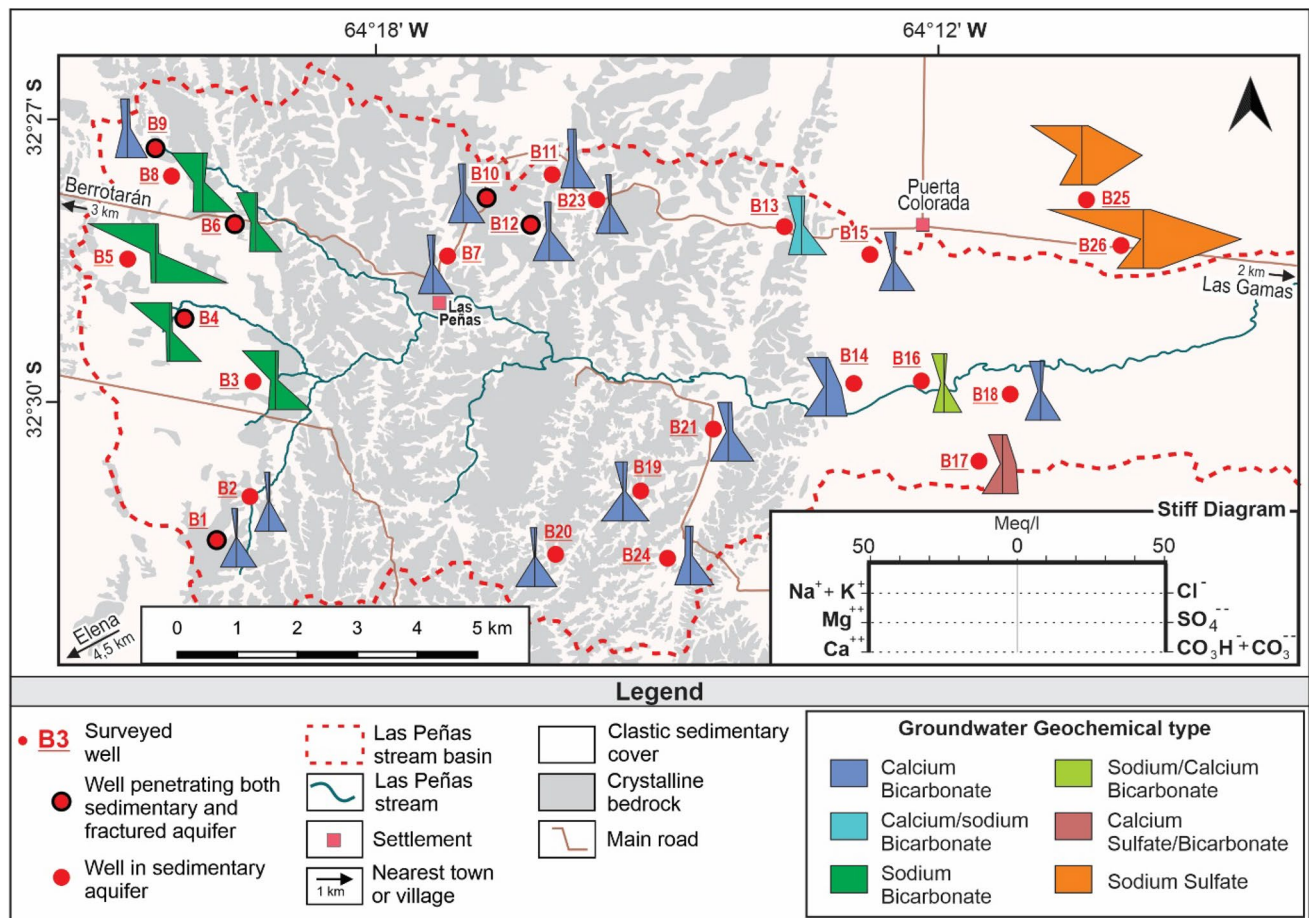


Fig. 8 Geochemical classification of groundwater samples and their distribution in the study area

(between 0.17 and 1.23), exhibiting almost all samples' indexes above 0.5. Groundwater samples from the central rocky sector and piedmont have molar relationships close to the theoretical dissolution line of calcite (Fig. 11a), although ratios show that the presence of calcium cannot be exclusively explained by this. If the relationships between Ca^{+2} and Na^{+} are compared (Fig. 11c), it is observed that samples belonging to the rocky area and piedmont associate with the theoretical dissolution line of andesine. On the other hand, samples of unit 1.a show a weak approximation to the oligoclase dissolution line.

As previously described, some contribution of sodium and bicarbonate from the rocky central area (unit 1.b) could be explained by andesine hydrolysis. However, examining $\text{HCO}_3^-/\text{Na}^{+}$ molar ratios (Fig. 11b), it can be seen that the general trend of all samples has a slope of $y=0.19x$, which differs markedly from the stoichiometric dissolution line of plagioclase. Although some samples of the relict paleosurface and piedmont approach the theoretical dissolution line of oligoclase, the calculated molar

ratios are not consistent with this as the main source of these solutes.

Deviation from the calcite and other mineral dissolution trends on Fig. 11 suggests a combination of other processes. An approximation of the influence of cation exchange process can be derived using the chloro-alkaline indices (CAI—1 and CAI—2), proposed by Schoeller (1965) (Eqs. 2 and 3). If the value of these indices is positive, this indicates Na^{+} or K^{+} from water is replaced by Ca^{+2} from the sediments (direct ion exchange). In contrast, when the indices are negative, Mg^{+2} or Ca^{+2} in solution is exchanged with Na^{+} from sediments (reverse ion exchange). In this case, CAI—1 values range between -27.4 and -0.9 while CAI—2 varies from -0.9 to -0.1 , indicating a dominance of reverse ion exchange. Due to the interaction of the water and clay minerals (being illite the dominant in this region, Matteoda 2012), this process likely explains the excess sodium in groundwater, especially in the samples from the main relict paleosurface.

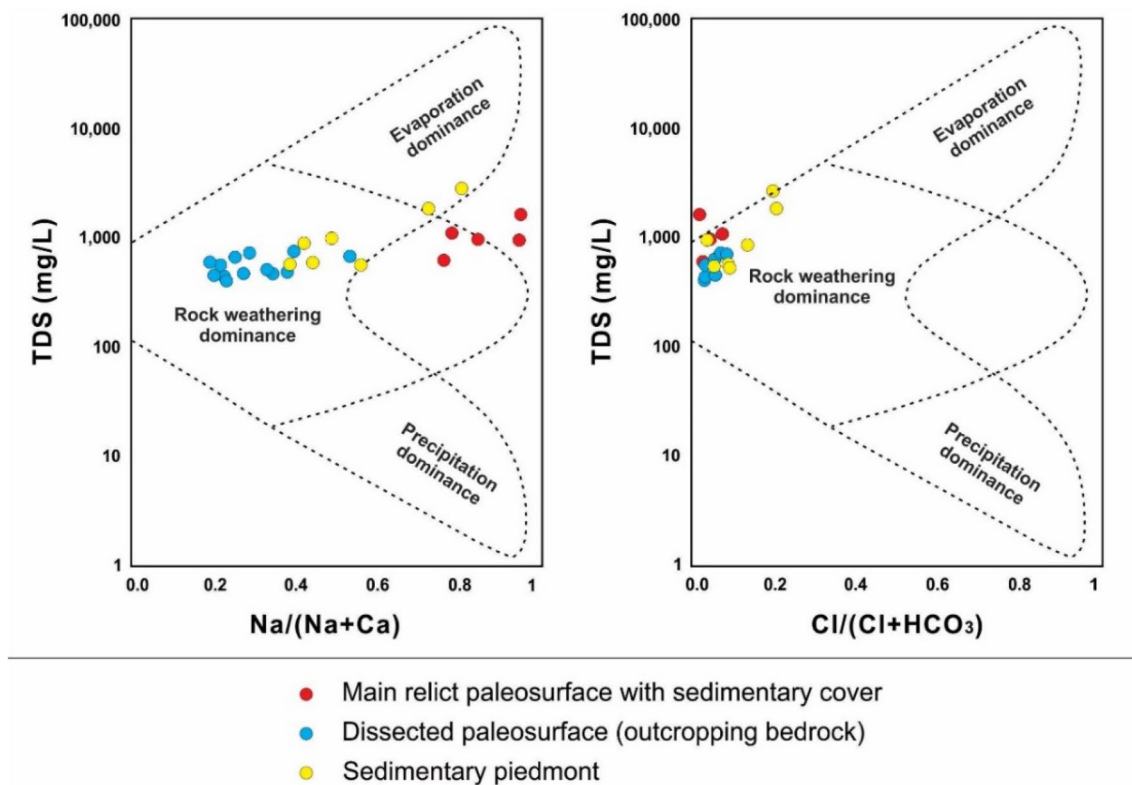


Fig. 9 Gibbs diagram of groundwater samples from Las Peñas stream basin

$$CAI - 1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \tag{2}$$

$$CAI - 2 = \frac{Cl^- - (Na^+ + K^+)}{HCO_3^- + SO_4^{2-} + CO_3^{2-} + NO_3^-} \tag{3}$$

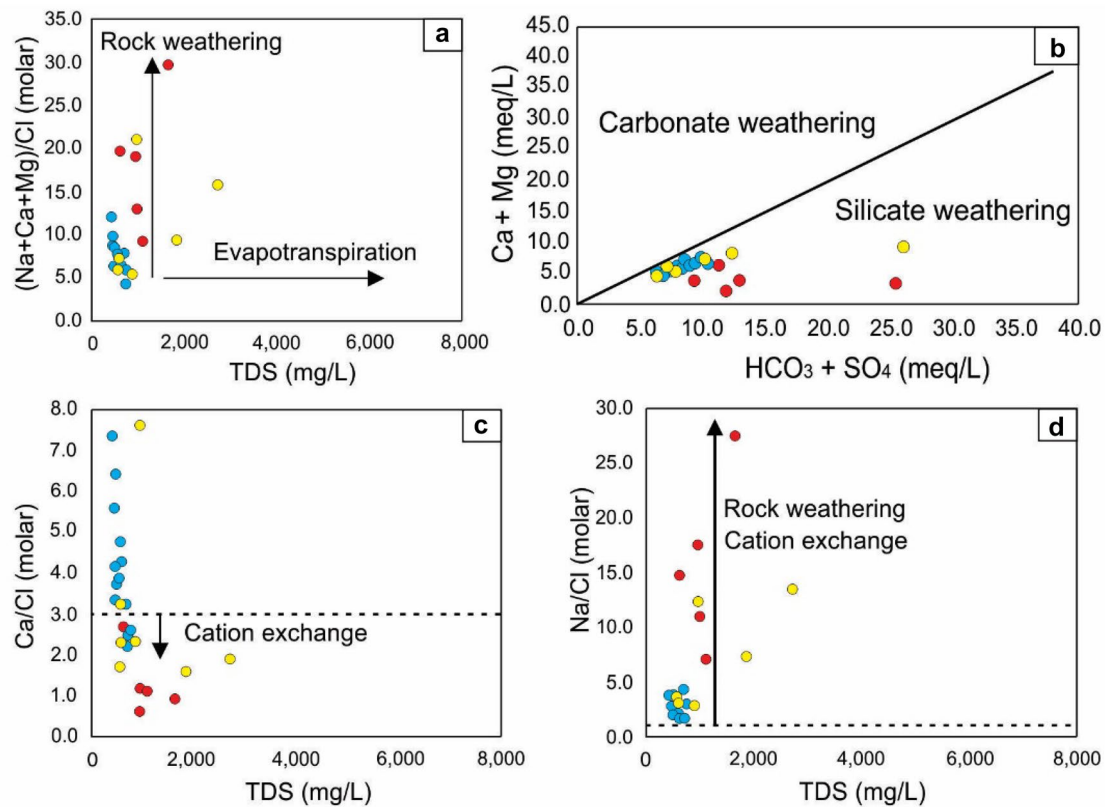
The hydrolysis of volcanic glass that appears in regional sediments is also known to provide ions in groundwater (Nicolli et al. 1989) while the incorporation of Mg^{+2} may be partially explained by the alteration of ferromagnesian minerals, e.g., biotite and hornblende. This can also be linked to atmospheric solutes, ion exchange and dissolution of carbonates. K^+ can also be derived from hydrolysis of rocks and ion exchange (Custodio and Llamas 1983).

Hydrogeochemical conceptual model

The study area, due to its topographic position and hydrogeological characteristics, is an important recharge zone for the unconfined groundwater systems of the region. Part of the rainwater infiltrates into the ground and is transmitted through local and regional fractures in the high areas towards the sedimentary aquifers of the valleys and the

eastern piedmont. The atmospheric input plays an important role in the contribution of different solutes to groundwater, and has a certain influence to the geochemical signature of these waters.

Based on the described processes, the hydrochemistry of groundwater is strongly controlled by the main geomorphological and lithological characteristics of each unit. The water chemistry of unit 1.a is mainly caused by the intense weathering processes due to the relatively high specific surface area of the sedimentary particles in aeolian sediments (loess and fine colluvial/alluvial deposits) and low water velocities (estimated between 0.09 and 0.13 m/day). In unit 1.b, the rock-water contact is affected by the higher velocities (~0.6 m/day) which reduces the possibility of enrichment of the groundwater with solutes from the weathering of rocks and minerals of the plutonic-metamorphic bedrock. Finally, in unit 2, the sedimentary heterogeneities (very fine and silty sand units and intercalations with sand-gravel deposits) and the geomorphological configuration of the piedmont are the main factors that controls the hydrodynamic of the groundwater system and, consequently, the water geochemistry. Therefore, hydrochemical reactions are favored by relatively low flow velocities and longer water residence time, especially in those sectors characterized by low hydraulic



- Main relict paleosurface with sedimentary cover
- Dissected paleosurface (outcropping bedrock)
- Sedimentary piedmont

Fig. 10 a Total Cations / Cl ratios vs. TDS. b (Ca + Mg) vs. (HCO₃ + SO₄) c a/Cl ratios vs. TDS d Na/Cl ratios vs. TDS in groundwater

Table 3 Primary mineral composition of fluvio-eolian sediments (53–63 μm fraction) of the study area, analyzed in Matteoda (2012)

No Sample	Qtz	Plag	K-fs	Bt	Cpx	Opx	Amph	Opaque minerals	Volcanic glass	Other minerals (Ap, Cal, Grt, etc.)
	%	%	%	%	%	%	%	%	%	%
M1	7.1	5.3	1.5	1	1.8	–	1.2	1.9	78.6	1.6
M3	9.5	5.4	3.0	1.3	5	0.1	4.0	8.2	63.3	0.2
M4	12.4	3.1	1.8	14	2.3	0.2	9.8	4.1	48.6	3.6
M6	7.7	9.8	4.5	1.5	4.1	0.1	3.4	6.0	62.6	0.4
M2	8.8	4.6	1.0	1.8	2.0	–	3.2	4.4	73.1	1.1
M5 SC3	6.7	5.2	2.6	0.8	1.9	0.1	3.7	2.5	75.9	0.6

gradients and thick layers of aeolian sediments. Figure 12 summarizes the main hydrogeological characteristics of the geomorphological units and the dominant hydrogeochemical processes.

Conclusions

Regarding the origin of the dissolved solutes in groundwater of Las Peñas stream basin, the relationships between Na⁺, Ca²⁺, SO₄²⁻ and Cl⁻ ions are controlled

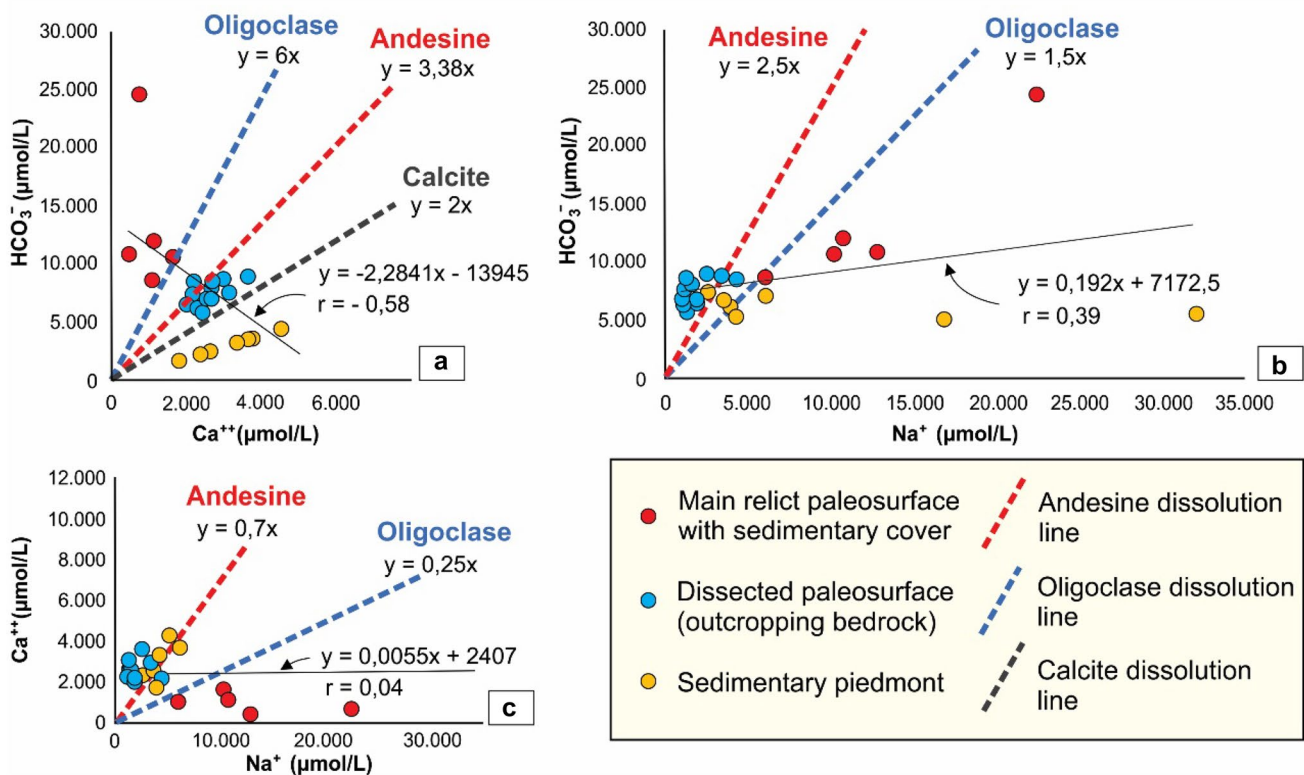


Fig. 11 Molar ratios of groundwater samples. Las Peñas stream basin

by atmospheric deposition and mineral dissolution. The analysis of molar relationships between major ions indicates the groundwater geochemistry is mainly linked to mineral weathering and (reverse) ion exchange. Although there are numerous minerals in the local igneous-metamorphic rocks that could provide chemical elements to groundwater, ionic ratios indicate solutes in groundwater derive from andesine weathering, especially in the central sector of the area (rocky sector), while contributions from oligoclase are minor. Ca^{+2} is also partially associated with calcite dissolution. The release of Na^+ , Mg^{+2} and K^+ to solution also comes from (reverse) cation exchange in fine sediments.

According to these results, it is interpreted that there is a clear geomorphological/lithological control on the groundwater dynamics and geochemistry of the basin. The central sector of the mountains, a dissected rocky paleosurface with valleys filled with sediments, is interpreted to be an important recharge area of the groundwater system. The chemical characteristics of groundwater here suggest recent infiltration of rainwater and relatively short circulation times through rocks and sediments, which reduces the possibility of enrichment of groundwater with solutes from rock and

mineral weathering. Considering that rainwater is dominated by sulfate ions, the bicarbonate dominance of groundwater in this sector is explained by alkalinity generated by hydrolysis of silicates. On the other hand, in the main relict paleosurface, upstream of the central sector of outcropping rocks, the existing sedimentary cover controls the occurrence of more saline groundwater. This is caused by more intense weathering processes due to the relatively high specific surface area of the sedimentary particles in aeolian sediments and low groundwater velocities which increase water–sediment interaction. The sodium geochemical type is interpreted to relate to rapid ion exchange processes favoring the retention of Ca^{+2} on sediments and release of Na^+ to solution.

From the central rocky area and towards the piedmont, the transit of groundwater flow through the eastern valleys and through the piedmont is associated with an increase in dissolved solutes and also a change in the geochemical type, due to the increase of water–mineral interaction. Taking into account that calcite saturation indices indicate super-saturation, it is assumed that carbonates partially precipitate and the sulfate and chloride content increases in solution as the water circulates towards the adjacent plain. In the piedmont, the increase in groundwater salinity may also be linked to the fact that the water acquires more solutes as it passes through the greater thickness of the unsaturated zone. Also, the increase of ions derived from probable contamination

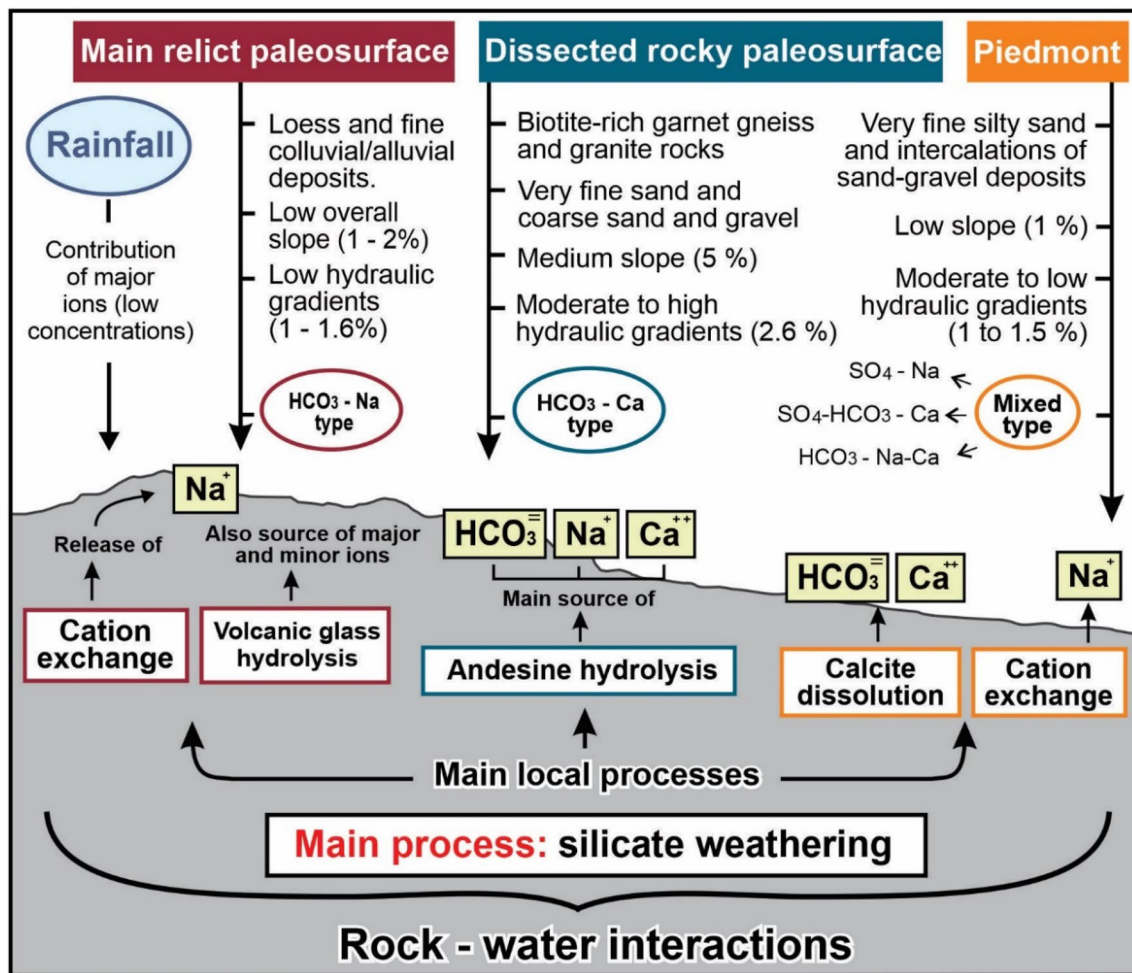


Fig. 12 Summary of the main processes that control the flow and the hydrochemistry of the groundwater on the geomorphological units in Las Peñas stream basin

processes and organic matter supply must be studied in the future.

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Authors contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by SP, MB, SD, VL, CE, FBQ, DG and AC. The first draft of the manuscript was written by SP, MB and MC and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability All data as well as software application claims and comply with field standards.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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