



Geochemical processes that explain arsenic in groundwater in a basin developed in the Pampean Mountains and piedmont, Córdoba, Argentina

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Abstract

Las Peñas stream basin, developed in the Pampean Mountains of Córdoba (Argentina), has hydrogeological characteristics of high interest for local human activities. The objective of this study is to interpret the influence of the geomorphological and lithological features of the basin, their control on the main hydrodynamic and hydrochemical processes and the factors that constrain the occurrence of arsenic (As) in groundwater. The unconfined aquifer develops in fractured rocks and sediments of diverse origin and provenance. Hydraulic gradients and groundwater geochemistry are conditioned by lithology and relief. The groundwater is mainly fresh (electrical conductivities between 586 and 2000 $\mu\text{S}/\text{cm}$), although there are brackish-type samples (up to 3900 $\mu\text{S}/\text{cm}$) located in the piedmont. The groundwater showed calcium and sodium bicarbonate geochemical types, with the local occurrence of mixed types (sodium-calcium bicarbonate and sodium bicarbonate-sulfate). The dominant geomorphological and lithological aspects condition the chemical composition of groundwater while controlling the distribution and concentration of As in solution. The highest As values were found in gently undulating reliefs where loess sediments prevail, especially in the main relict paleosurface area located in the upper basin. Taking this into account, it is assumed that the abundant volcanic glass—which is known as an arsenic bearer—in the regional sediments, is the possible source of this chemical element as a result of hydrolysis. Also, desorption processes in Fe and Mn oxy-hydroxides present in the loess sediments are related to the passage of As ions to the solution. As it is known, not only the source but a specific geochemical environment to allow the transference of chemical elements from minerals to groundwater is needed. In this way, the results, including a multivariate statistical analysis, demonstrate that the highest As values in groundwater, well correlated with high fluoride (F) contents, are related to an alkaline environment of sodium bicarbonate groundwater with high pH values.

Keywords Hydrogeology · Geomorphology · Groundwater geochemistry · Trace elements

Introduction

Groundwater participates in numerous geological processes and supports partially or exclusively a wide array of species and their habitats (Aldous and Gannett 2021). Also, it plays a vital role as a source of domestic, industrial and agricultural water supply in many urban and rural regions around the world. As a consequence of the accelerated population growth and the constantly increasing of water demand, it is essential to promote strategic policies linked to the investigation of the dynamics, quality and availability of groundwater, which represents the most abundant fresh liquid water in the planet.

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In this sense, an important aspect focused on the use of groundwater resources consists of more comprehensive studies of their geochemistry, emphasizing the presence of dissolved minor and trace elements, e.g., arsenic (As) and fluoride (F) that, due to their prolonged ingestion through drinking water, could be harmful to the health. In fact, the presence of high levels of arsenic in groundwater is a severe problem in many parts of the world, such as Argentina, China, India, Bangladesh, Mexico, among others countries (Smedley et al. 2002; Chakraborti 2011; Kumar et al. 2020; Bundschuh et al. 2022).

Groundwater is the most extensively utilized water resource in the province of Córdoba, providing water for different activities (domestic, industrial, livestock, irrigation, animal drinking, etc.) and maintaining many natural geological processes (Blarasin et al. 2014). The presence of As and F has been widely reported in this province especially in shallow aquifers, representing the only available resource for drinking water during the whole year for most of the rural population (Blarasin et al. 2014; Litter et al. 2019). The spatial distribution of the mentioned chemical elements is strongly linked to the main regional hydrogeological units, with maximum concentrations in plain sectors and discharge areas located in the south, southeast, and east of the province (Blarasin et al. 2014).

Because of their evident incidence in the human health, As and F are one of the most studied chemical elements in groundwater. It is known that prolonged drinking of water with high concentrations of As ($> 10 \mu\text{g/L}$) can cause skin lesions and cancerous and non-cancerous systemic alterations (Biaggini et al. 1993), leading to chronic arsenic poisoning. Arsenic health problems have been documented in

different sectors of the province and also in other areas of the Pampean Plain (Goyenechea 1917; Ayerza 1918; Hopenhayn-Rich et al. 1996; Bates et al. 2004; Steinmaus et al. 2010).

As described in numerous investigations carried out in the Chaco-Pampean plain (Smedley et al. 2000; Bhattacharya et al. 2006; Blarasin et al. 2009; Alarcón-Herrera et al. 2013; García et al. 2014; Bécher Quinodóz et al. 2019; AullónAlcaine et al. 2020; among others), the source of dissolved As in water—as a result of natural hydrogeological processes—would be linked to the presence of minerals, volcanic glass and lithic fragments contained especially in the typical regional loess. Nicolli et al. (1989) showed that, under high pH conditions, arsenic can be released into solution by hydrolysis of volcanic glass, while Smedley et al. (2000) expose that also certain geochemical conditions (alkalinity and high pH) and low flow groundwater velocity promote the desorption of As ions from Fe and Al oxides and oxy-hydroxides.

Although groundwater studies have been made usually in the sedimentary aquifers located in the Pampean Plain, investigations in upper basins developed mostly in mountainous areas have not yet been made in detail. In the regional hydrogeological framework, it is necessary to analyze the geochemistry of these basins which function mainly as rainwater catchment areas for later distribution of water towards lower areas. Las Peñas stream basin, selected for this research, is located in the NE of the Río Cuarto Department (province of Córdoba, Argentina, Fig. 1a). It drains an area of about 170 km^2 and includes a part of the eastern slopes of the Sierra de las Peñas Mountains (Pampean Mountains

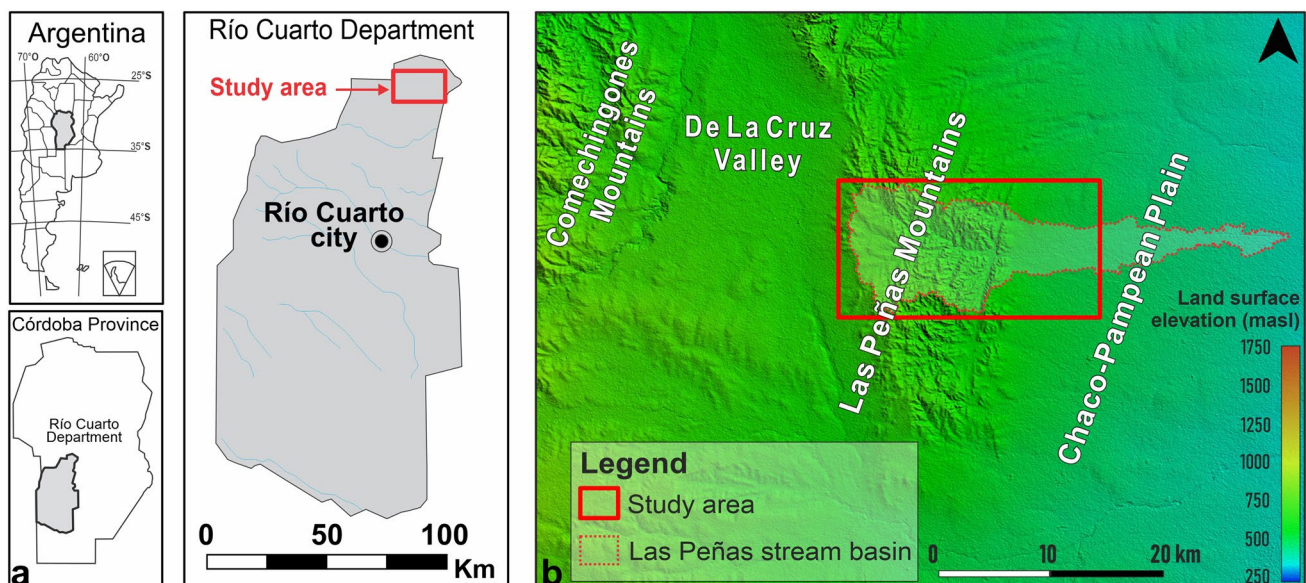


Fig. 1 a Location of the study area (province of Córdoba, Argentina). b Geologic context of the study region

of Córdoba) and the piedmont area, which belongs to the Argentinian Chaco-Pampean plain (Fig. 1b).

The objective of this study is to show the geological-geomorphological characteristics of the upper-middle basin of the Las Peñas stream and to interpret the relationship with hydrogeochemical features, emphasizing the presence and origin of dissolved arsenic in groundwater. The most relevant hypothesis, defined for this study, is that different geomorphological units with distinctive lithological and morphological characteristics control the groundwater chemical composition and, consequently, the concentration of arsenic in solution.

Materials and methods

The study was based on the analysis and compilation of topographic sheets from the National Geographic Institute (NGI) at a 1:50,000 scale, satellite images (Google Earth and Bing) and the Digital Elevation Model (SRTM, 30×30 m). Background regional information (geological, geomorphological, climatic, etc.) of the study area was collected and analyzed (Blarasin et al. 2014; Carignano et al. 2014). The precipitation data were analyzed and interpreted using a local 30-year series (1990–2020). The hydrogeological information was obtained surveying local landowner wells, which penetrate the upper part (10–50 m) of the unconfined sedimentary aquifer, although some wells enter few meters in the fractured rock system. The groundwater samples were obtained in 25 wells in which field parameters like pH, electrical conductivity (EC), dissolved Oxygen (DO), redox potential (ORP) and temperature (T) were measured using a multiparametric portable probe with an incorporated GPS (Hanna HI 9829). The samples were collected in 1 L plastic bottles and were analyzed in the laboratory of the National University of Rio Cuarto using standard analytical procedures (APHA, 2005), within a period of the 24 h since collection. The following parameters were analyzed: Na^+ , K^+ , HCO_3^- , Cl^- , Mg^{2+} , Ca^{2+} , SO_4^{2-} , As, and F^- . The mean percentage error of the chemical analysis was under 10%. Arsenic (total) was measured using the Merck As kit at field and a UV–visible Spectrophotometer (Hach) at the laboratory. The whole analysis linking chemical variables was made using descriptive statistical techniques (multivariate analysis) by means of the software package SPSS11.5 for windows (SPSS 2012). Accordingly, to explain relationships between all chemical variables a principal component analysis (PCA) was made for data reduction and for deciphering patterns within the data set.

Climatic, geological and geomorphological characterization

The research was carried out in the upper-middle basin of the Las Peñas stream, covering a study area limited by 32° 25' 27" and 32° 33' 21" Latitude S and 64° 21' 43" and 64° 08' 20" Longitude W.

The regional climate is of mesothermal, sub-humid type with little to no water excesses in the average hydrological balance, however, water excesses were measured in humid periods. The distribution of the precipitations exhibits a very marked seasonality, with a concentration of 75% from November to March (spring–summer), with an annual average precipitation of 757.4 mm.

The outcropping rocks of Sierra de las Peñas Mountains are from Neoproterozoic to Lower Paleozoic ages. The lithologies include paragneisses, para-amphibolites, impure marbles, orthogneisses, and ortho-amphibolites (Bonalumi et al. 2005). In addition to the metamorphic complex, there is a large igneous granitic body (Las Peñas granite) whose age is assigned to the Lower Cambrian. The biotitic gneiss is the lithological type that shows the greatest areal distribution. It is composed of quartz, plagioclase, muscovite, and biotite, with sectors of plentiful garnet grains. There are abundant ortho-amphibolites and migmatic rocks, small outcrops of meta-quartzites, pegmatites, and a few marble banks. Las Peñas granite has a mylonite texture and the mineral associations include quartz, orthoclase, plagioclase, biotite, muscovite, magnetite, perthite, and quartz. Geochemically, the granite has a calco-alkaline composition with a potassium tendency (Bonalumi et al. 2005).

The mineral composition of the Argentinean loess has been described in different studies (Teruggi 1957; Etchichury and Tófaló 2004). In the regional eolian sediments, local researchers (Becker 1987; Matteoda 2012; Blarasin et al. 2014) established that the very fine sand and silty dominant fractions present a weight percentage of light minerals in the order of 98% (as a maximum) and heavy minerals in the order of 2%. The light minerals are volcanic glass (up to 55%), potassium feldspar and plagioclase (*An* 25–40) (20%), mineral volcanic aggregates (14%), quartz (3%) and alterites (5%), while heavy minerals are constituted by opaque minerals like oxides (0.4%) amphiboles (0.7%), pyroxenes (0.2%), biotites (0.05%), alterites (0.4%) and minor contents of apatite, garnet and others. In the clay fraction illite predominates. In the area of Las Peñas Mountains, Matteoda (2012) identified three types of volcanic glass: VG1: colorless, with bubbles, dacitic-rhyolitic type; VG2: brownish, with palagonite alterations, basaltic and andesitic type and VG3: very altered, with Fe, basaltic type.

From the geomorphological point of view, the genesis of the local relief is associated with the interaction between tectonic processes related to the Andean Orogeny and different

exogenous processes, controlled by climatic variations of the Upper Pleistocene and Holocene, which partially modeled the pre-existing surface and the current landscape features (Degiovanni 2008; Carignano et al. 2014). Therefore, the most highlighting geomorphological characteristics of the area are the structural control related to regional faults and the differential dissection degree of the mountain block. The Sierra de las Peñas Mountain is a megablock of plutonic-metamorphic bedrock that still preserves very little modified ancient reliefs (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, strongly dissected by the Las Peñas drainage network, which preserves relicts of erosion paleosurfaces in the summit areas. The river developed a dendritic rectangular drainage network on basement rocks and mountain valleys filled with quaternary sediments where water courses are currently being reinstalled. The drainage network orientation is dominated by the structural control. In the upper basin, the dominant morphologies reflect the different degree of preservation of the ancient surfaces, which were dissected by fluvial action (Degiovanni

2008; Carignano et al. 2014; Kröhling and Carignano 2014). The main distinguished geomorphological units defined by Pramparo et al. (2022) are exhibited in Fig. 2:

1a Main relict paleosurface with sedimentary cover: the landscape is gently undulating with a low overall slope (1–2%). Almost all the unit is covered by quaternary sequences (loess and colluvial/alluvial deposits) with a variable thickness (1–15 m). However, some scattered outcrops of bedrock flattened blocks can be observed. This unit is drained by a dendritic network with low dissection and little hierarchy, with courses of orders 1 and 2, representing the headwaters of the Las Peñas stream. They are characterized by being slightly sinuous channels of variable width (1–6 m) and low depth. In some sectors, the contact with the bedrock can be observed. This sector is the one that best represents the pre-Andean paleosurfaces described by various authors in other places of the Pampean Mountains of Córdoba (Carignano et al. 2014; Rabassa et al. 2014; Andreazzini and Degiovanni 2014).

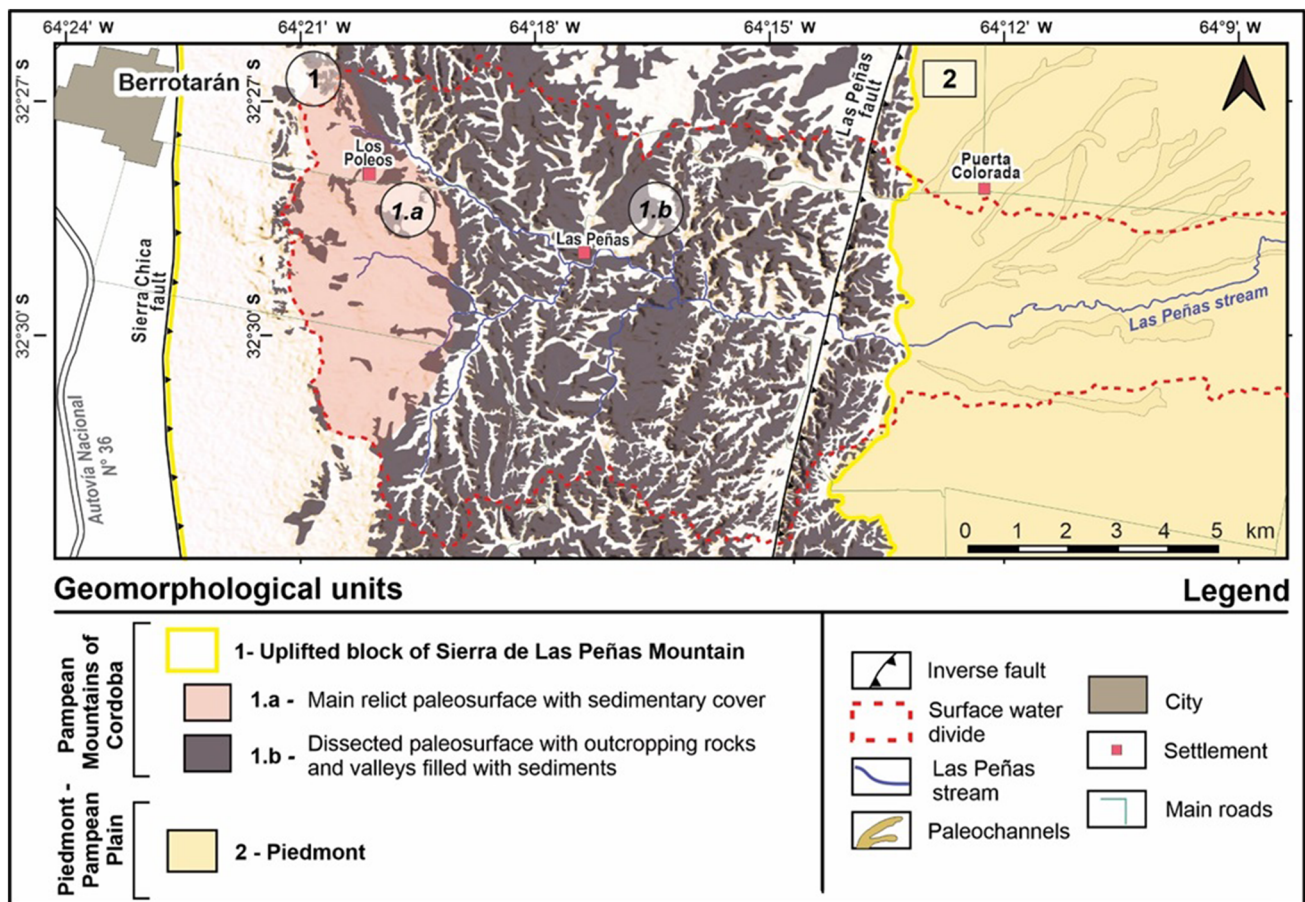


Fig. 2 Map of Geomorphological Units in Sierra de Las Peñas Mountains (Pramparo et al. 2022)

- 1b 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 Las Peñas Metamorphic-Igneous Complex (Bonalmi et al. 2005). The general slope decreases progressively as the block tilts to the East, while the local slopes are greater than in the previous unit, due to increased river incision (reaching up to 30 m). The channels of the drainage network have a rectilinear design, strongly controlled by the bedrock fracture system. The minor valleys have an erosive origin and a variable size (from a few tens of meters to kilometer lengths). They are filled by quaternary sediments, mainly fine materials from the remobilization of the loess sequences, which covered the mountainous areas during the dry Quaternary cycles. Some intercalations of coarse local sediments may be observed.
2. Piedmont: it is located in the eastern sector of the Sierra de las Peñas Mountain. The relief is made up of smooth hills, with heights and slopes that decrease further away from the mountains. It is characterized by thick sequences of ancient alluvial fans, re-transported eolian sediments and eolian deposits. The morphological and sedimentological features of these deposits reflect energetic changes associated with climatic alternations and neotectonic regional activity (Degiovanni 2008).

Hydrogeological and hydrodynamic characterization

Most of the sampled wells penetrate the sedimentary unconfined aquifer which was identified in the main relict paleosurface (Unit 1.a), in the main valleys of Unit 1.b and in the sedimentary environment of the piedmont (Unit 2). However, 6 wells located in units 1.a and 1.b partially penetrate the sediments and a few meters in the fractured bedrock. The studied unconfined aquifer exhibits varied lithologies. It is composed of very fine sands with a high percentage of silts in unit 1.a, considering the eolian origin of the sediments. In the valleys of Unit 1.b. there are generally fine deposits of re-transported eolian sediments, with thin layers of coarse texture (sands and gravels) of alluvial/colluvial origin. In the piedmont environment (Unit 2), the aquifer system is made up of clastic materials of eolian origin (very fine-silty sands), re-transported eolian sediments and some intercalations of sand-gravel deposits, linked to alluvial paleofans from the Sierra de Las Peñas Mountains. In all cases carbonate salts appear dispersed in the sediments or as nodules and calcrete layers. The mentioned lithological features imply that the aquifer is obviously heterogeneous (Pramparo et al. 2022). Taking into account the described sediments, there is an important diversity of specific porosity and consequently

of hydraulic conductivity (K) which values are in the order of 1–10 m/day. Furthermore, given the very variable thickness of sedimentary deposits (a few meters in the relict paleosurface and valleys and several tens of meters in the piedmont) the aquifer shows also a highly variable spatial transmissivity (T), between 4 and 600 m²/day. The groundwater flow direction is predominantly W-E and the hydraulic gradients are in the order of 1.1–2.5% (Fig. 3, Pramparo et al. 2022). In this hydrogeological framework it must be mentioned that only the collector stream is permanent as a result of the water supply from the aquifer, although the stream water infiltrates when it arrives to the piedmont, where the water table is 20–30 m deep (Fig. 3, Pramparo et al. 2022).

Results and discussion

Groundwater geochemistry

The groundwater in the basin is fresh to brackish, with electrical conductivities between 586 and 3880 $\mu\text{S}/\text{cm}$. The main statistical values of groundwater chemical variables are showed in Table 1. The geochemical type corresponds mainly to bicarbonate calcium (Unit 1.b) and bicarbonate sodium (Unit 1.a) or mixed types (Unit 2) whose spatial distribution can be observed in Fig. 4. Regarding the origin of the dissolved chemical compounds and given the unlikely existence of gypsum and halite in local sediments and rocks and the null relationship of Na^+ , Ca^{2+} , SO_4^{2-} and Cl^- ions with the dissolution lines of these minerals (Pramparo et al. 2022), it is estimated that these chemical elements are partially supplied by rainfalls. Taking into account chemical information about regional precipitations (Cabrera et al. 2013), the rainfalls can also contribute part of the rest of the majority ions (Mg^{2+} , K^+ , HCO_3^-).

Alkalinity in most natural waters is mostly derived from the equilibrium with atmospheric and soil CO_2 and also from the hydrolysis of carbonate and silicate minerals. In fact, the analysis of different molar relationships of major ions made by Pramparo et al. (2022) showed that groundwater geochemistry is mainly linked to the weathering processes of silicates which can produce HCO_3^- ions. Although numerous minerals in the local igneous-metamorphic rocks can provide chemical elements and compounds to groundwater, the evaluation made by Pramparo et al. (2022) comparing molar relationships between cations and anions showed that the ions were related to andesine weathering, especially in the central rocky sector. On this basis, it was estimated that a part of the HCO_3^- , Na^+ and Ca^{2+} concentration would be explained by the effect of the hydrolysis of this mineral.

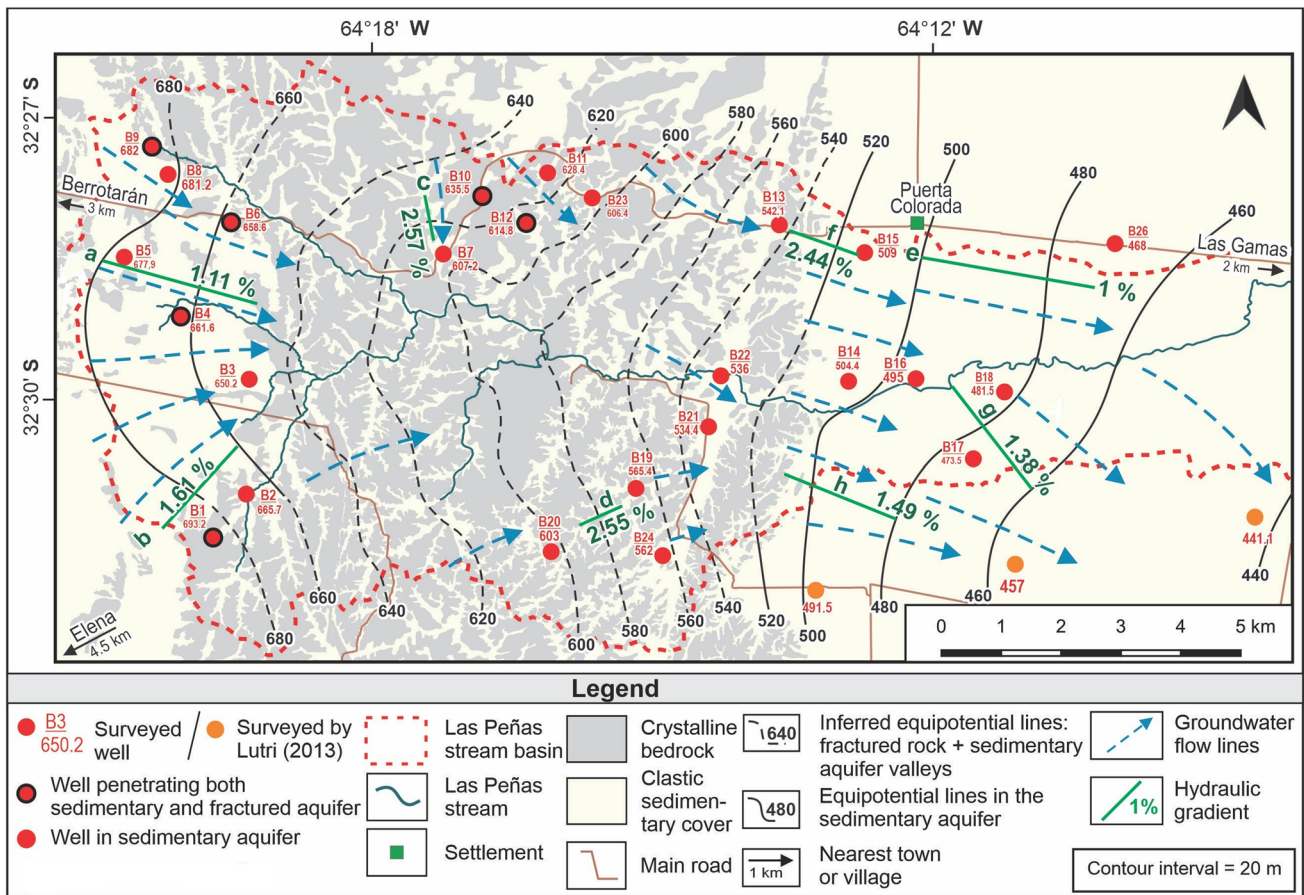


Fig. 3 Equipotential map of the unconfined aquifer in Las Peñas stream basin (Pramparo et al. 2022)

Table 1 Descriptive statistics for groundwater hydrochemical parameters. 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	mg/L	25	<LOD	<LOD	-	-	-
HCO ₃ ⁻	mg/L	25	311	1503	511	448	232
SO ₄ ⁻²	mg/L	25	11.01	1569	145	26.4	354
Cl ⁻	mg/L	25	11.43	82.9	32.6	25.7	18.9
Na ⁺	mg/L	25	26.3	737	143	77.9	176
K ⁺	mg/L	25	4.1	20.8	15.2	14.5	5.23
Ca ²⁺	mg/L	25	18.4	181	97.6	98.4	38.7
Mg ²⁺	mg/L	25	0.49	37.3	13.2	11.2	8.91
F	mg/L	25	0.2	3.9	1.0	0.6	1.0
As	μg/L	25	<LOD	110	20.7	7.0	30.3

The contribution of Ca²⁺ would also be partially associated with calcite dissolution. The release of Na⁺, Mg²⁺ and K⁺ to the solution would not only be linked to the precipitation input or weathering of silicates but would also come from cation exchange processes in fine sediments as indicated by

numerous regional antecedents (Blarasin et al. 2014; Bécher Quinodóz et al. 2019; Pramparo et al. 2022). Considering that the precipitations have sulfate ions dominance (Cabrera et al. 2013) the groundwater bicarbonate type in the central

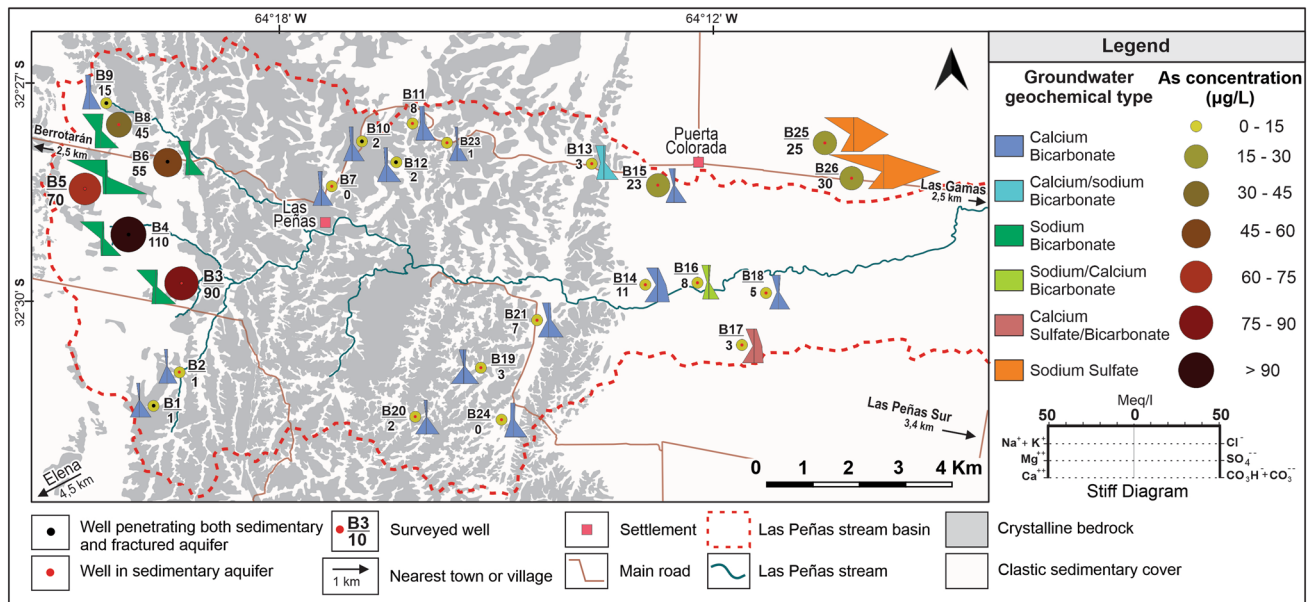


Fig. 4 Geochemical classification of groundwater samples and distribution of As concentration in the study area

rocky sector of the basin may be explained by the alkalinity generated by soil CO₂ and the hydrolysis of silicates.

Arsenic in groundwater

The arsenic values measured in groundwater vary throughout the study area from < Limit of Detection (LOD) to 110 µg/L (Table 1), being the highest contents located in the upper basin and the piedmont, as can be seen in Fig. 4. From the total samples, 40% (B3, B4, B5, B6, B8, B9, B14, B15, B25, and B26) were above the maximum permissible limits (10 µg/L) established by the World Health Organization (WHO 2017) and the Argentine drinking water standards (CAA 2019).

The highest As concentrations (45–110 µg/L) were found in Unit 1.a, where the sedimentary cover is mainly loess and the hydraulic gradients vary between 1 and 1.5%. The greater specific surface of the sedimentary grains and the lower flow velocity, favor not only the water salinization process but also promote the release of minor and trace elements, like As and F. On the other hand, the lowest As levels (0–8 µg/L) were measured in Unit 1.b, linked to fractured rock and sedimentary aquifer (mainly sand and gravel) present in the mountainous valleys. Thus, the low As concentration is the result of the highest hydraulic gradients (2.44–2.57%) that decrease the contact time between groundwater and sediments or rocks in the identified local flows and the absence of bedrock minerals that may supply As to groundwater. Finally, in Unit 2, the samples showed As values in the range of 3–30 µg/L. The highest levels would be associated with intermediate flows in sedimentary bodies

with a higher proportion of fine sediments (loess and re-transported loess), where the aforementioned As enrichment processes can occur.

In relation to As sources, some authors (Nicolli et al. 1989, 2012) have established that the chemical composition of volcanic glass in the Argentinean loess is typically rhyolitic, with SiO₂ ranging between 72.2 and 78.6% and variable values of trace elements. Arsenic contents in volcanic glass range between 5 and 8 mg/kg while fluoride varies between 109 and 1020 mg/kg (Bundschuh et al. 2004; Blanco et al. 2006; García et al. 2007; Nicolli et al. 2012). Thus, volcanic glass and/or volcanic lithic fragments within the loess have been proposed as the source of some minor and trace elements (e.g. As and F)—released by mineral weathering processes—which are favored under moderate to high pH conditions (Nicolli et al. 1989; Smedley et al. 1998). In an alternative and complementary explanation, As, F and other trace elements could be desorbed from the surface of Al-, Fe- and Mn-oxyhydroxides (coating lithic fragments) at high pH conditions resulting from weathering (Smedley et al. 1998; Nicolli et al. 2012). Smedley et al. (2002) established that Fe minerals that retain As (magnetite, ilmenite, biotite, goethite, and hematite) may be a source of this element.

A study of adsorption/desorption processes was carried out in this research group by Michelli et al. (2022) with different types of sediments (Fig. 5) from sites located 8 km south of the study area, in the same mountainous system (Sierra de Las Peñas Mountains). The batch tests included sediments of eolian (very fine silty sands) and colluvial (coarse gravels and sands) origin, which were put



Fig. 5 Sediments used in batch tests to evaluate the release of As and F (Michelli 2020)

in contact with two different types of solutions (Solution 1: EC = < 1 μS/cm, pH = 6.15, HCO₃⁻ = 0 mg/L; Solution 2: EC = 31 μS/cm, pH = 8.45, HCO₃⁻ = 25 mg/L). A total of 24 batch experiments were conducted, each consisting of 75 g of sediment sample and 150 ml of solution. The concentrations of As and F were measured 1, 7, and 14 days after starting the experiment. The experimental results (Tables 2, 3) indicate that the highest releases of As and F occur in the loess sediments. In the case of arsenic, the release was also more important in those with dissolved bicarbonates and while the pH was increasing along contact time.

Table 2 Results of batch tests conducted to measure the release of As and F from eolian sediments (Michelli et al. 2022)

Test no	1	2	3	4	5	6	7	8	9	10	11	12
Sediment type	Very fine silty sand											
Solution	1						2					
pH	6.5–7.5			7.5–8.5			6.5–7.5			7.5–8.5		
Time (days)	1	7	14	1	7	14	1	7	14	1	7	14
Sd (As) (μg/kg)	3.0	15	10	1.5	7.0	12	3.0	17.3	15	8.0	13	18
Sd (F) (mg/kg)	0.68	0.8	0.7	0.8	0.92	0.72	0.64	0.8	0.6	0.6	0.6	0.68

Table 3 Results of batch tests conducted to measure the release of As and F from colluvial sediments (Michelli et al. 2022)

Test no	13	14	15	16	17	18	19	20	21	22	23	24
Sediment type	Coarse gravel with sand											
Solution	1						2					
pH	6.5–7.5			7.5–8.5			6.5–7.5			7.5–8.5		
Time (days)	1	7	14	1	7	14	1	7	14	1	7	14
Sd (As) (μg/kg)	2.0	3.0	7.0	1.5	2.0	6.0	2.0	2.0	7.0	1.5	3.0	4.0
Sd (F) (mg/kg)	0	0	0	0	0	0	0	0	0	0	0	0

Sd ratio of the quantity that has been leached out (mg metal per L of the solution) to the amount of material (kg of sediment)

Table 4 As and F Pearson correlation

	As	F
As		
Pearson correlation		0.921**
Sig. (2-tailed)		0.000
N	25	25
F		
Pearson correlation	0.921**	
Sig. (2-tailed)	0.000	
N	25	25

**Significant at 0.01 level

In addition to the mineral sources, it is known that the release of arsenic into groundwater is dependent on chemical and physical processes that take place between the groundwater and the geological environment. As was explained for the above-mentioned experiment, arsenic-rich groundwaters are often associated with high pH conditions where sodium bicarbonate dominates. Taking into account that OH⁻ and HCO₃⁻ ions can compete on adsorption sites, this situation can promote desorption of As from Fe/Mn oxyhydroxides present in the loess sediments (Anawar et al. 2004; Blarasin et al. 2011, 2014; Nicolli et al. 2012; Bécher Quinodóz et al. 2019). The more basic water (pH between 7.97 and 8.25) and high HCO₃⁻ concentration (ranging from 410 to 1502 mg/L), evidenced in Unit 1.a, are favorable conditions for As dissolution and mobilization. Taking into consideration that the dissolved oxygen in the studied aquifer is high (2.3–9.6 mg/L) and the Eh values range between 50 and

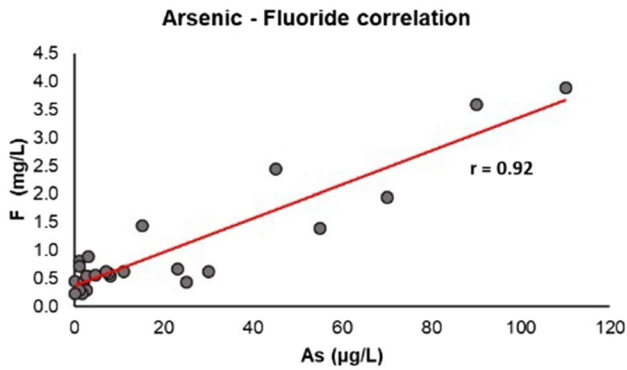


Fig. 6 As and F linear correlation

550 mV, it is assumed that the species that are moving from adsorption sites to the solution are arsenates (AsO_4^{2-}) as occurs in the unconfined aquifer throughout the South of Córdoba and La Pampa province (Argentina) (Smedley et al. 2002; Bécher Quinodóz et al. 2019).

It should be noted that As has a high statistically significant correlation with F ($r=0.92$, p value 0.01, Table 4 and Fig. 6) and also a similar spatial distribution, corroborating that a common geochemical environment may favor their passage to the solution. The spatial distribution of the $\text{Na}^+/\text{Ca}^{2+}$ ratio shows the dominance of Na^+ in those environments where eolian and re-transported eolian sediments predominate (Unit 1.a and Unit 2). Also, a coincidence between high values of $\text{Na}^+/\text{Ca}^{2+}$ ratio values and high As and F values is notorious. The highest values of both ions are located in the western sector (Unit 1.a), linked with a specific lithology and sodium and higher pH waters.

Table 5 Rotated component matrix for 11 chemical variables

	Component		
	1	2	3
pH	0.312	0.787	0.028
EC	0.943	0.239	0.146
HCO_3^-	-0.070	0.711	0.167
SO_4^{2-}	0.965	-0.121	0.006
Cl^-	0.849	-0.171	0.022
Na^+	0.844	0.451	0.178
K^+	0.384	0.380	0.651
Ca^{2+}	0.538	- 7.26	-3.24
Mg^{2+}	0.144	0.262	0.890
As	0.168	0.918	0.231
F	-0.044	0.847	0.331

Bold values indicate correlation coefficients that explain each PC (principal component)

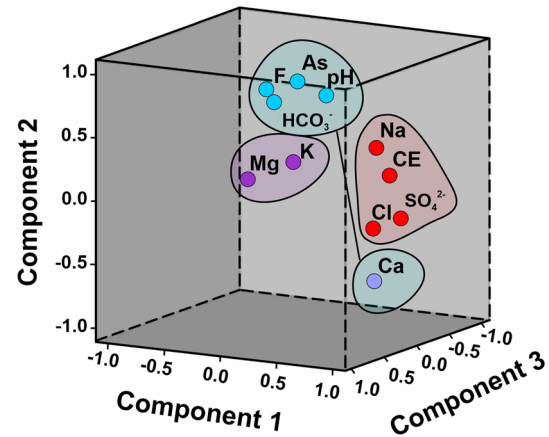


Fig. 7 Main components matrix

The multivariate analysis (PCA) allowed for summarizing all the data set information into a smaller set of factors or components. The rotated component matrix can be seen in Table 5 and the principal components in Fig. 7. The three factors identified by the PCA explain 83.5% of the accumulated variance. Each of them provides an approximation to the dominant hydrogeochemical processes in the study basin. In general terms, PC 1 and PC 2 reflect a similar percentage of variance (34.8% and 33.9%, respectively), which are considerably higher than that obtained for PC 3 (14.7%). As can be seen in Table 5 and Fig. 7, the matrix loadings of the first factor indicated a strong positive correlation of EC, SO_4^{2-} , Cl^- , and Na^+ . It was interpreted as the “water salinity” factor attributed to the influence of precipitations and to water–sediment interaction demonstrating that the saltier the water the higher is the concentration of SO_4^{2-} and Cl^- . Following the results of Pramparo et al. (2022) the sodium type in saltier water observed in the sedimentary aquifer can be attributed to reverse ion exchange, where Ca^{2+} retention in sediments (e.g., illite) and release of Na^+ into solution is favored. Factor 2 exhibited chemical variables with a strong-to-moderate positive association: HCO_3^- , As, F, and pH, all of them opposite to Ca^{2+} . This factor explains the trace elements geochemistry in this basin that is, As and F stability in solution in alkaline sodium water with the highest pH, opposite to calcium waters. The last factor explains a minimum part of the variance and is represented by the chemical variables Mg^{2+} and K^+ which can come in low concentrations from mineral weathering and precipitations.

Conclusion

In the upper and middle basin of the Las Peñas stream, the hydrochemistry of the groundwater is strongly controlled by the main geomorphological/lithological features. In Las

Peña's basin, a mountainous recharge area, groundwater originates from rainfall supply, which obviously influences groundwater chemistry. However, it is concluded that the strongest control over the groundwater chemical composition is exerted by the main geomorphological/lithological characteristics. The natural groundwater chemistry in the Main relict paleosurface with sedimentary cover (sodium bicarbonate waters) responds mainly to the slow flow velocities circulation (as a result of low topographic and hydraulic gradients) and the presence of eolian sediments, both aspects that control the presence of saltier groundwater. In the Piedmont, the variability of groundwater chemistry (sodium bicarbonate and sulfate waters) is due to the lithological and hydrodynamic aquifer heterogeneities. In this unit, low flow velocities and longer water residence time, particularly in those flatter areas with thick layers of eolian sediments, give more opportunities for water–mineral contact and favor different types of hydrochemical reactions that supply ions. The dominance of sodium in these environments is attributed to reverse cation exchanges in fine sediments. On the other hand, the greatest slope and the domain of crystalline rocks in the central area (Dissected paleosurface with outcropping rocks and valleys filled with sediments) define a low salinity groundwater type. Here, recently infiltrated water (mainly rainwater) has short circulation times through rocks and valley sediments which partially diminish groundwater enrichment with solutes from weathering processes (hydrolysis of silicates). In addition to this process, the dissolution of dispersed carbonates, and the alkalinity generated by soil CO₂ are added, allowing the increment of the calcium and bicarbonate ions, which defines the chemical water type.

Specifically, in relation to arsenic values in groundwater, it is clear that they are also controlled by geomorphological and lithological features which in turn controlled the groundwater dynamics and chemistry. The highest As values were found in the geomorphological unit where loess sedimentary layers predominate, especially in the main relict paleosurface area in the upper basin. The lowest values appear in the central rocky environment where groundwater flows faster and the rock–water contact is lesser. Thus, and taking into account that the highest values are located in the loess environment of the relict paleosurface and to a lesser degree extent in the piedmont, it is assumed that the abundant volcanic glass, which is known as an arsenic bearer, is the most probable source of this chemical element. Also, the desorption surface processes from Fe- and Mn-oxy hydroxides are considered a probable origin in these areas. As it is known, not only the source but a specific geochemical environment for the transference of chemical elements from minerals to groundwater is needed. In this way, the results of data treatment, including multivariate statistical analysis,

demonstrated that high dissolved arsenic contents, very well correlated with elevated fluoride values, were able to enter and be stable in the high pH sodium bicarbonate groundwater. Further studies of batch lab tests are needed to confirm the role of volcanic glass, carbonates, and other minerals in groundwater composition and also in relation to the desorption processes from oxyhydroxide minerals.

Finally, it may be highlighted that the presence of high As concentration dissolved in water is widely known in the sedimentary aquifer system of the fluvio-eolian plain of Córdoba province. However, it should be noticed that under certain geochemical controls and the local influence of relief and lithology, it is possible to find As in solution even in concentrations above the permissible limits for human consumption in mountain environments (regional recharge areas), where usually groundwater evidence excellent aptitude.

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Data availability The data set generated during the current study are included in the article. More data are, however, available from the corresponding author on a reasonable request.

Declarations

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

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

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