

## Assessing interactions between groundwater and surface water in a Pampean stream

F. Becher Quinodoz, M. Blarasin, H. Panarello and E. Ducos

### ABSTRACT

In the south of Córdoba (Argentina), groundwater from the unconfined aquifer, presents scarce suitability due to high values of salts, sulfates, arsenic and fluorides. This situation makes it necessary to explore other possibilities, for example, conjunctive use of groundwater and surface water. The objective of this work was to describe the dynamic and geochemical relationships between surface water and groundwater in the medium-low basin of the Ají stream. The conceptual model was supported by the use of stable  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$  isotopes and it was validated through numerical modeling and  $^{222}\text{Rn}$  activity results. The stream water is sodium bicarbonate fresh type (460–1,400  $\mu\text{S}/\text{cm}$ ). The aquifer presents fresh to salt water (720–14,000  $\mu\text{S}/\text{cm}$ ), from sodium bicarbonate to sodium chloride type. The isotopic results show that there is a straight mixing line between surface water and groundwater samples. The geochemical numerical modeling revealed that in the mixing models between stream and aquifer, for hydraulically linked samples, the aquifer only provides 2% of the total stream flow. This was validated through  $^{222}\text{Rn}$  results, which led us to the estimation of about 2% of groundwater supply in summer.

**Key words** | geochemical modeling, groundwater, radon, stable isotope, surface water

**F. Becher Quinodoz** (corresponding author)  
CONICET-UNRC,  
Ruta 36 km 602,  
Rio Cuarto,  
Córdoba,  
Argentina  
E-mail: [fbecher@exa.unrc.edu.ar](mailto:fbecher@exa.unrc.edu.ar)

**M. Blarasin**  
Dpto. Geología,  
Universidad Nacional de Rio Cuarto (UNRC),  
Ruta 36 km 602,  
Rio Cuarto,  
Córdoba,  
Argentina

**H. Panarello**  
**E. Ducos**  
Instituto de Geocronología y Geología Isotópica,  
(INGEIS-CONICET-UBA)  
Buenos Aires,  
Argentina

### INTRODUCTION

Although water law and water policy often consider groundwater and surface water as separate resources, both water bodies are functionally interdependent. Surface-water bodies such as rivers, lakes and wetlands can receive groundwater inflow, recharge the groundwater or do both actions in different sectors or seasons. This interaction between water systems leads to the mixing of their water qualities (Winter 1999; Sophocleous 2002; Hancock *et al.* 2005; Goldscheider *et al.* 2006). High quantities of nutrients or other dissolved chemicals derived from natural processes and human activities in surface water can be transferred to the connected groundwater system and vice versa. Thus, the interaction of ground water and surface water has been shown to be a significant concern in issues related to water supply, water quality and degradation of aquatic environments (Winter 1999). The interactions of streams, lakes, and wetlands with groundwater are governed by the

positions of the water bodies with respect to groundwater flow systems, geologic characteristics of their beds, and their climatic settings (Tóth 1999; Winter 1999).

Despite the fact that groundwater and surface water interactions are controlled by their hydraulic connection and may be considered essentially one resource, the interactions are difficult to observe and measure (Winter 1999; Sophocleous 2002; Custodio 2005). All methods have shown significant uncertainty, as usually happens when humans try to quantify nature.

In the south of Córdoba Province (Argentina), the most used hydrological resource is groundwater from the unconfined aquifer, which quite often presents scarce suitability for several uses due to high values of salts, sulfates, arsenic and fluorides. This situation and the high salinity of confined aquifers in some areas make it necessary to explore other possibilities, for example, conjunctive use of groundwater

and surface water. In this framework, a sector of a basin located in this region was selected for the investigation. The objective of this work is to show the dynamic and geochemical relationships between surface water and groundwater in the low basin of the Ají stream situated in the sandy plain in the south of Córdoba Province (Argentina, Figure 1). The results were interpreted to obtain a hydrogeochemical conceptual model which could be used as a tool for hydrological and environmental management. The conceptual model was supported by the use of stable  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$  isotopes and was validated through numerical geochemical modeling and the preliminary results of  $^{222}\text{Rn}$  activity in water.

## METHODS

The regional geological and hydrological features were identified in the field and hydrogeological data were obtained from 25 wells, most of them penetrating the upper 20 m of the unconfined sedimentary aquifer. Climatic and land use features were analyzed for the study area. The historical precipitation data were collected from 'La Perdiz' station ( $33^\circ 54' 52.54''\text{S} - 64^\circ 24' 16.39''\text{W}$ ). In this first stage of the study, the hydrological survey was carried out in summer and the stream flow was measured in this season in different gaging sections. Twenty-five groundwater and surface water samples were obtained and field parameters were measured

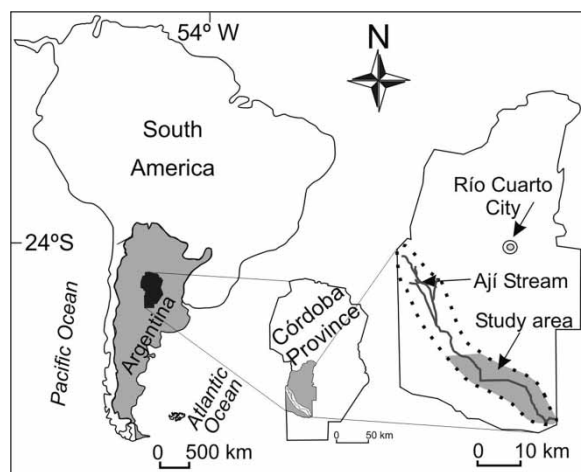


Figure 1 | Study area.

*in situ*: pH (Electrode Orion 9104), electrical conductivity (EC) (Hanna Instruments, HI 9033) and temperature (T) (YSI Model 95 Handheld Temperature System).

The samples were collected in 1 L plastic bottles and were analyzed within 24 h of collection, in the laboratory of the National University of Río Cuarto. The following parameters were analyzed:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  (American Public Health Association (APHA) et al. 2005).

Stables isotopes ( $^2\text{H}$  and  $^{18}\text{O}$ ) analyses were done in the Institute of Geochronology and Isotope Geology (INGEIS-CONICET-UBA) by means of Off-Axis Integrated Cavity Output Spectroscopy (OICOS) (Lis et al. 2008), DLT-100 Liquid-Water Isotope Analyzer from LGR Inc. Results were expressed in the usual form, i.e.  $\delta(\text{‰})$  defined as:

$$\delta = 1000 \frac{R_S - R_{ST}}{R_{ST}} \quad (1)$$

where  $R$  = isotope ratio  $^2\text{H}/^1\text{H}$  or  $^{18}\text{O}/^{16}\text{O}$ ;  $\delta^2\text{H}$  or  $\delta^{18}\text{O}$ , isotopic deviation in ‰, respectively.  $S$  denotes sample and  $ST$  reference standard. Uncertainties are  $\pm 1\text{‰}$  for  $\delta^2\text{H}$  and  $\pm 0.3\text{‰}$  for  $\delta^{18}\text{O}$ . Reference standard is V-SMOW (Gonfiantini 1978).

Although this work was carried out in the medium-low basin as a result of a requirement of a water company, some samples were collected in the upper and middle basin to improve hydrological interpretations. Moreover, and even though this research was carried out in summer, an expeditious survey was carried out in winter to measure EC and isotope values. The numerical geochemical models were developed using the PHREEQC software (Parkhurst and Appelo 1999) taking into consideration the major ions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and the stable isotopes ( $\delta^{18}\text{O}/\delta^2\text{H}$ ). The activity of  $^{222}\text{Rn}$  in surface water and groundwater was measured *in situ* in five samples using the RAD7 radon detector (DurrIDGE Co.) belonging to INGEIS.

## RESULTS AND DISCUSSION

### Climatic and geological characterization

Climatic changes which occurred in South America during the Quaternary provoked deflation and deposition of large

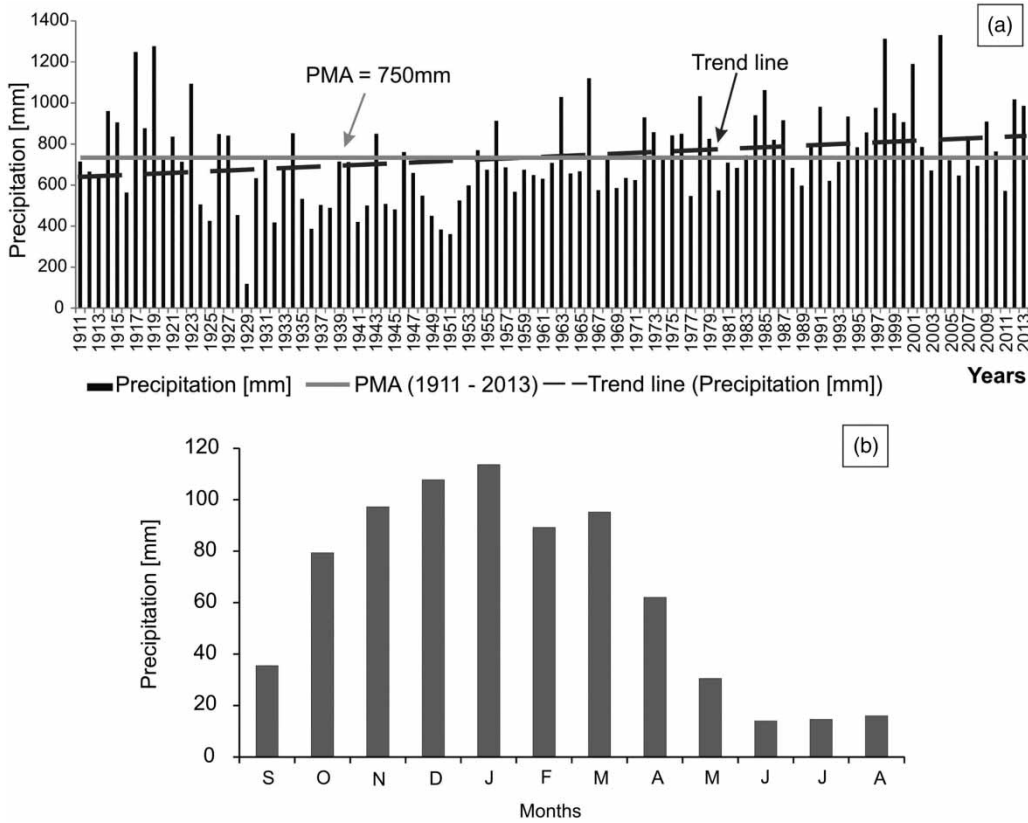


Figure 2 | (a) Annual rainfall chronological curve. (b) Distribution of precipitations.

masses of silt and fine sand which formed loess and loessoid units of regional extension in several areas of the continent. The winds derived from the Patagonian ice field during the Last Glacial Maximum transported to the Pampean plain

silts and fine sands formed by frost action in the Andean Mountains Range. In humid periods, these loessical and sand plains were crossed by different fluvial systems while, in the interfluvial areas, soils were developed (Iriondo 1997).

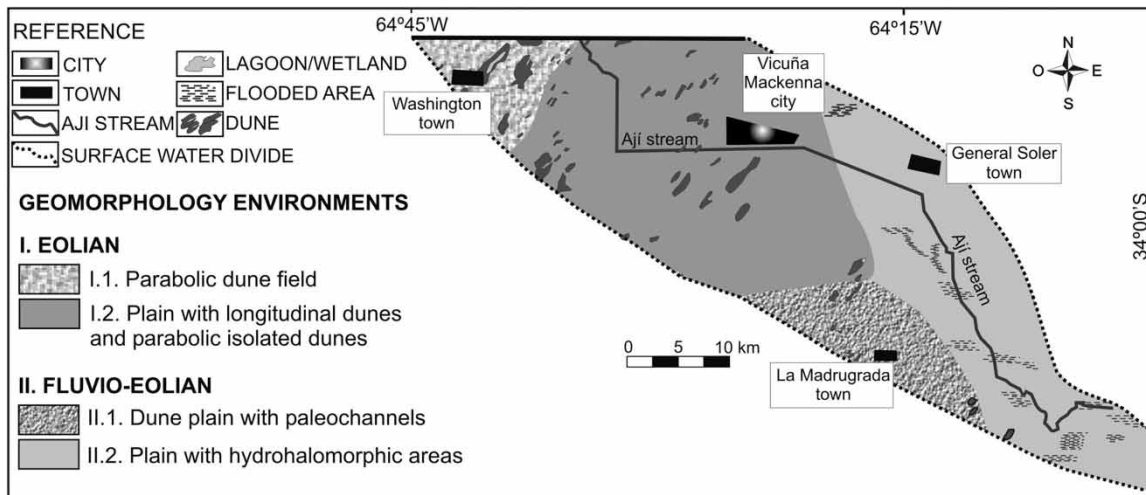
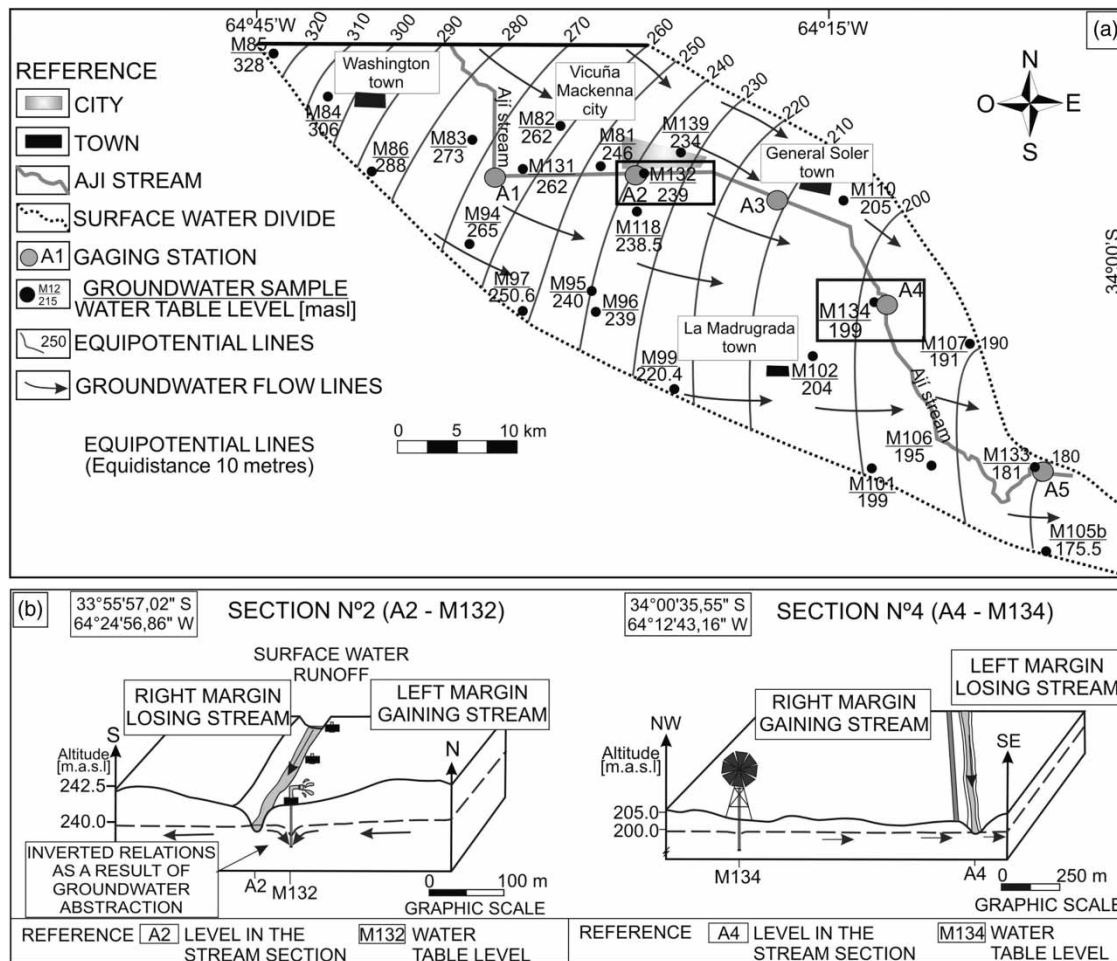


Figure 3 | Geomorphological map.

**Table 1** | (a) Stream flow (Q) in Aji stream (summer) and (b) (winter)

Gaging stations	Latitude	Longitude	Area [m <sup>2</sup> ]	Mean velocity [m/s]	Flow (Q) [m <sup>3</sup> /s]
<b>Summer</b>					
A1	33°55'47.36" S	64°32'25.45" W	2.18	0.37	0.81
A2	33°55'47.98" S	64°24'52.81" W	2.67	0.31	0.83
A3	33°57'09.04" S	64°17'17.98" W	2.29	0.34	0.78
A5	34°08'39.70" S	64°05'16.89" W	2.49	0.29	0.74
<b>Winter</b>					
A1	33°55'47.36" S	64°32'25.45" W	1.44	0.34	0.50
A2	33°55'47.98" S	64°24'52.81" W	1.83	0.29	0.54
A3	33°57'09.04" S	64°17'17.98" W	1.08	0.42	0.46
A5	34°08'39.70" S	64°05'16.89" W	1.28	0.28	0.36



**Figure 4** | (a) Equipotential map for the unconfined aquifer. (b) Hydraulic relation between stream and aquifer in sections A<sub>2</sub> and A<sub>4</sub>.

At present, the studied area (2,500 km<sup>2</sup>) has a subhumid climate, characterized by an annual rainfall of 750 mm (Figure 2(a)), of which 85% is concentrated in spring-summer (September–March), (Figure 2(b)). The regional rainfall salt concentration is in the order of 30 mg/L and, according to its chemical composition it supplies bicarbonate, sulfate, chloride, sodium, calcium and magnesium ions to the groundwater (Cabrera *et al.* 2013).

The area has a flat to gently undulated relief, with longitudinal and parabolic dune systems of different origin and age which are crossed by the Ají stream fluvial strip (Bécher Quinodóz 2014). The upper basin of this stream is located in the Comechingones Mountains (Córdoba Province), outside the studied area, where the

Precambrian-Paleozoic bedrock outcrops. In the fluvial system, erosion processes prevail. Both lateral and vertical fluvial incisions were identified while floods occasionally occur in the low basin. The most relevant geomorphological units can be observed in Figure 3. The unconfined aquifer is formed by sandy-silt brown sediments with dispersed calcareous nodules or layers (calcretes).

### Hydrodynamic and hydrochemical characteristics

The Ají stream starts at the confluence of the Cortaderas and Zelegüa streams with some supply from the Suco lagoon. From the middle basin, it is a permanent stream as the result of groundwater contribution. The flow varies between

**Table 2** | Topographic and hydrogeological data

Name	Latitude	Longitude	Well depth (m)	Topographic elevation (m)	Water table depth (m)	Water table level (m)
M81	33°55'45.84"S	64°27'18.66"O	15	249.0	3.0	246.0
M82	33°53'54.31"S	64°30'13.25"O	15	265.5	3.5	262.0
M83	33°54'19.72"S	64°33'45.75"O	20	276.5	3.5	273.0
M84	33°52'25.14"S	64°41'20.34"O	15	309.0	3.0	306.0
M85	33°50'52.93"S	64°46'25.32"O	15	335.0	7.0	328.0
M86	33°58'11.84"S	64°40'18.85"O	20	291.5	3.5	288.0
M94	34°01'42.31"S	64°36'11.01"O	20	268.0	3.0	265.0
M95	34°01'15.40"S	64°27'26.95"O	20	242.5	2.5	240.0
M96	34°01'45.36"S	64°27'18.98"O	20	241.5	2.5	239.0
M97	34°05'39.58"S	64°32'14.47"O	20	253.0	2.5	250.5
M99	34°08'19.88"S	64°23'00.64"O	18	223.4	3.0	220.4
M101	34°10'33.64"S	64°14'19.21"O	15	202.5	3.5	199.0
M102	34°03'49.22"S	64°16'16.05"O	20	206.5	2.5	204.0
M103a	33°56'58.51"S	64°25'02.27"O	14	241.0	3.0	238.0
M105a	34°11'19.83"S	64°04'05.74"O	15	178.0	2.5	175.5
M106	34°09'53.66"S	64°10'53.11"O	15	198.5	3.5	195.0
M107	33°59'41.66"S	64°06'31.29"O	20	193.5	2.5	191.0
M110	33°56'57.11"S	64°14'28.33"O	15	207.5	2.5	205.0
M118	33°57'00.73"S	64°25'00.52"O	15	241.5	3.0	238.5
M131	33°55'38.57"S	64°31'55.40"O	15	264.0	3.0	261.0
M132	33°55'47.98"S	64°24'52.81"O	10	242.0	3.0	239.0
M133	34°08'39.70"S	64°05'16.89"O	10	183.5	2.5	181.0
M134	34°00'23.59"S	64°12'30.78"O	15	201.5	2.5	199.0
M138	33°31'39.95"S	64°56'26.36"O	20	505.0	7.0	498.0
M139	33°54'59.60"S	64°22'17.63"O	15	236.5	2.5	234.0
M140	33°19'32.93"S	64°51'38.46"O	20	631.0	10.0	621.0

summer ( $0.8 \text{ m}^3/\text{s}$ ) and winter (in the order of  $0.40 \text{ m}^3/\text{s}$ ) with an average water velocity of  $0.33 \text{ m/s}$  (Table 1).

As can be seen in the unconfined aquifer equipotential map and the hydrogeological sections (Figure 4(a) and 4(b)) the hydraulic relationships are variable but, in most reaches, the watercourse is a gaining stream as a result of groundwater contribution. In the upper basin, groundwater does not influence the stream water (Bécher Quinodó 2014). Hydrogeological data are shown in Table 2.

Surface water salinity shows a notable homogeneity along the studied stream reach. Thus the EC was from  $458 \mu\text{S/cm}$  to  $1,410 \mu\text{S/cm}$  in the flow direction and all the samples were classified as sodium bicarbonate geochemical type (Table 3, Figure 5). Measurement of winter EC in surface water ( $467\text{--}1,414 \mu\text{S/cm}$ ) showed that there is almost no salinity change in relation to summer, indicating high influence of the fresh water that flows from the mountains.

The groundwater from the unconfined aquifer exhibits variable EC from  $650 \mu\text{S/cm}$  (fresh water) linked to recharge in dunes (Bécher Quinodó 2014), up to  $14,000 \mu\text{S/cm}$  (salty

water) in the hydrohalomorphic areas (Figure 3). Groundwater shows a geochemical evolution in the flow direction from fresh to salty water, changing from sodium bicarbonate to sodium sulfate and, finally, to sodium chloride geochemical type (Table 4, Figure 5).

The analyses of relationships show that surface water exhibits marked homogeneity, with freshwater from the beginning to the end of the studied area (Figure 5), despite having traveled tens of kilometres and maintaining, in most sections, hydraulic connection with an aquifer that provides brackish to salty groundwater. This situation allows the interpretation that the aquifer has little influence on the mixture.

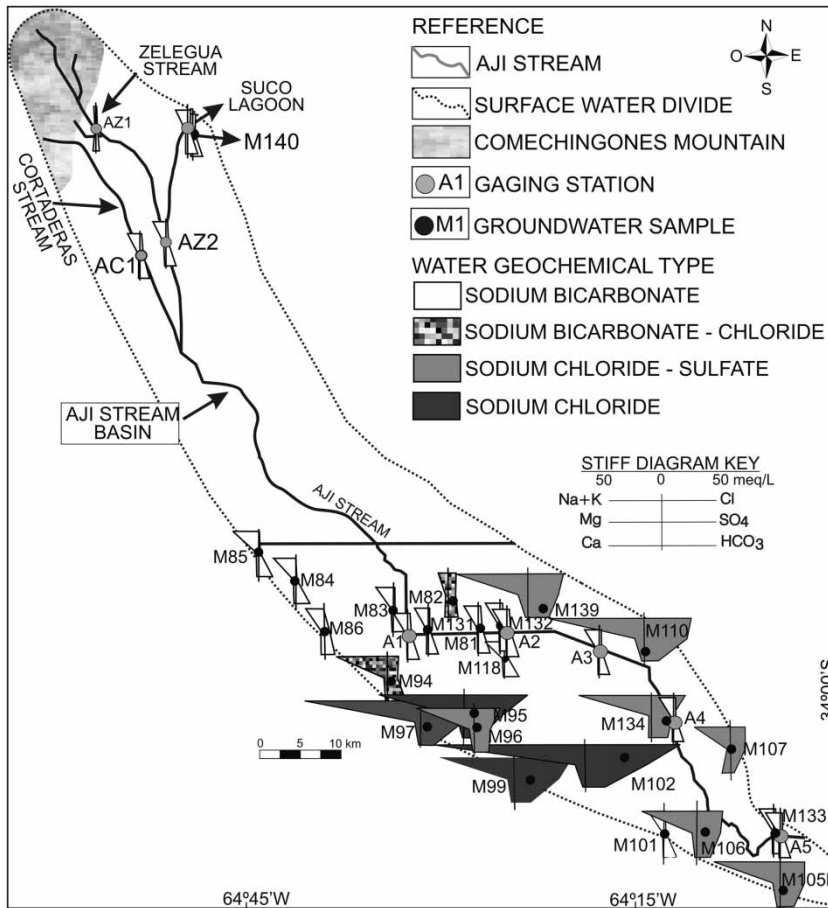
### Stable isotope composition of surface and groundwater

Isotopic results ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) show that groundwater and surface water exhibit more depleted values at the western part of the basin. This situation can be explained because the rainfall water that recharges the aquifer and surface water bodies in the piedmont area of the Comechingones

Table 3 | Major ions and stable isotope concentrations in surface water in 2013

Name	Date	EC ( $\mu\text{S/cm}$ )	pH	$\text{CO}_3^{2-}$ (mg/L)	$\text{CO}_3\text{H}^-$ (mg/L)	$\text{SO}_4^-$ (mg/L)	$\text{Cl}^-$ (mg/L)	$\text{Na}^+$ (mg/L)	$\text{K}^+$ (mg/L)	$\text{Ca}^+$ (mg/L)	$\text{Mg}^+$ (mg/L)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
S. Lagoon	Summer (15/03/2013)	1,266	8.7	46	480.0	103.6	82.9	242.7	15.4	20.0	13.2	-2.0	-11.6
A <sub>Z1</sub>		458	8.2	0	185.0	43.3	16.6	30.9	5.3	38.4	4.9	-5.2	-26.6
A <sub>Z2</sub>		1,050	8.5	21.82	502.5	88.0	42.9	273.0	7.0	12.0	21.0	-5.1	-25.9
A <sub>C1</sub>		1,025	8.4	9.70	490.0	107.8	42.9	257.8	5.6	16.0	8.8	-5.1	-25.5
A <sub>1</sub>		1,212	8.9	26.7	535.0	123.4	51.4	282.1	9.2	20.0	12.7	-4.9	-24.7
A <sub>2</sub>		1,272	8.8	26.7	532.5	113.0	60.0	291.2	9.8	19.2	17.1	-4.4	-23.5
A <sub>3</sub>		1,333	8.2	0	625.0	88.9	71.4	264.9	10.8	24.0	12.2	-4.5	-23.1
A <sub>4</sub>		1,368	8.8	33.9	517.5	102.5	71.4	315.5	11.0	21.6	14.6	-4.5	-23.3
A <sub>5</sub>		1,410	8.6	12.1	565.0	113.0	82.9	291.2	17.6	20.0	17.1	-4.2	-23.0
S. Lagoon	Winter (12/08/2013)	1,266	8.7	46	480.0	103.6	82.9	242.7	15.4	20.0	13.2	-2.0	-11.6
A <sub>Z1</sub>		467	8.2	0	187.5	47.2	17.1	36.4	5.4	40.0	4.9	-5.3	-26.7
A <sub>Z2</sub>		1,080	8.7	21.82	527.5	92.5	45.7	273.0	7.2	13.6	21.0	-4.7	-23.6
A <sub>C1</sub>		1,076	8.6	12.12	512.5	123.4	45.7	257.8	5.7	17.6	8.8	-4.7	-24.4
A <sub>1</sub>		1,270	8.2	0	585.0	144.2	57.1	297.3	7.3	17.6	8.8	-4.4	-22.9
A <sub>2</sub>		1,329	8.3	0	585.0	144.2	62.9	308.4	7.6	17.6	16.1	-4.3	-22.1
A <sub>3</sub>		1,406	8.4	4.85	590.0	144.2	91.4	328.6	7.8	17.6	20.5	-4.3	-22.7
A <sub>4</sub>		1,410	8.5	12.12	575.0	144.2	97.1	328.6	7.8	17.6	16.6	-4.2	-22.9
A <sub>5</sub>		1,414	8.6	12.12	575.0	113.0	102.9	328.6	7.9	17.6	29.3	-4.1	-21.8





**Figure 5** | Water geochemical type in the stream and the unconfined aquifer.

Mountains (Figure 5) comes from depleted rains originated in a wet warm front that comes from the Atlantic Ocean (1,000 km away). This front has suffered isotopic impoverishment as a consequence of continental and altitude effects (Cabrera *et al.* 2010; Bécher Quinodóz 2014). Moreover, Figure 6 shows that there is a straight mixing line between surface water and groundwater samples. The most depleted are those surface water samples related to the rainy season and clearly linked to the flows coming from the mountains.

In some samples, the similarity between aquifer and stream isotopic features are closely linked to induced recharge from the stream freshwater when groundwater is extracted in wells located at the stream side (Figure 4(b), Section A<sub>2</sub>). This singular situation holds an environmental positive connotation, because the induced recharge improves the groundwater condition. More studies are necessary to evaluate the winter behavior, but preliminary  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  isotope

results showed more fractionation in winter stream samples as a result of evaporation. The surface water will also be more enriched in winter as a result of the aquifer contribution.

### Numerical geochemical model

Numerical modeling was carried out for summer, taking into account the explained hydrological features and linking the different sampled sections (Figure 7), in order to evaluate the adjustment to the conceptual model.

Taking into account the conceptual model, it was considered that A<sub>Z2</sub> (upper basin) is a mixture between A<sub>Z1</sub> (surface water from mountain area) and SL (surface water from Suco lagoon). Table 5 shows chemical and isotope data of samples used in the numerical models.

The results (Table 5) showed that to obtain the sodium bicarbonate water type of Zelegüa stream in A<sub>Z2</sub> (final

**Table 4** | Major ions and stable isotope concentrations in groundwater in Summer 2013

Name	EC ( $\mu\text{S/cm}$ )	pH	$\text{CO}_3^{2-}$ (mg/L)	$\text{CO}_3\text{H}^-$ (mg/L)	$\text{SO}_4^-$ (mg/L)	$\text{Cl}^-$ (mg/L)	$\text{Na}^+$ (mg/L)	$\text{K}^+$ (mg/L)	$\text{Ca}^+$ (mg/L)	$\text{Mg}^+$ (mg/L)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
M82	1,700	7.8	0	460.0	259.5	222.9	242.7	19.3	80.8	54.6	-4.5	-24
M83	1,650	8.2	0	800.0	88.0	65.7	385.2	11.4	24.8	26.3	-4.5	-25
M84	1,670	8.6	24.2	825.0	92.5	28.6	448.9	8.2	4.8	9.3	-4.6	-24
M85	1,950	8.2	0	900.0	146.3	85.7	520.7	9.2	7.2	11.2	-4.1	-22
M86	1,850	8.3	0	715.0	332.7	51.4	348.8	9.1	17.6	14.6	-4.6	-24
M94	4,250	8.2	0	1,000.0	499.9	388.6	1,061.7	19.9	21.6	33.7	-4.6	-24
M95	8,990	7.9	0	545.0	1,543.4	2,057.1	2,042.5	65.6	144.0	165.9	-4.1	-24
M96	5,020	8.2	0	835.0	714.3	857.1	1,294.2	29.9	44.0	69.3	-4.2	-23
M97	9,540	7.9	0	700.0	1,867.0	1,828.6	2,548.0	41.8	70.4	77.6	-4.7	-29
M99	7,600	7.6	0	435.0	1,602.9	1,657.1	1,820.0	37.8	222.4	185.4	-4.6	-28
M101	1,470	8.5	19.4	705.0	102.5	34.3	321.5	7.0	6.4	13.2	-4.6	-24
M102	14,040	8.0	0	835.0	2,565.9	3,171.4	3,731.0	75.0	168.0	204.9	-4.4	-23
M103	650	7.7	0	347.5	32.3	14.3	72.8	19.0	32.0	30.7	-4.4	-24
M105b	5,740	8.4	12.1	907.5	1,168.2	885.7	1,415.6	28.1	33.6	64.9	-4.8	-25
M106	5,230	8.1	0	705.0	1,016.8	828.6	1,162.8	32.8	51.2	58.5	-4.4	-24
M107	3,580	7.6	0	360.0	758.8	562.9	697.7	27.5	100.8	11.2	-4.4	-23
M110	9,190	7.5	0	837.5	1,995.9	1,631.4	2,184.0	74.4	65.6	123.4	-4.4	-23
M118	2,970	8.6	38.8	935.0	206.8	205.7	551.1	39.6	34.4	37.6	-4.4	-23
M131	1,198	8.2	0	620.0	102.5	62.9	273.0	8.8	14.4	13.2	-4.7	-24
M132	1,270	8.2	0	575.0	102.5	57.1	291.2	12.9	18.4	11.2	-4.4	-24
M133	1,410	8.8	26.7	542.5	102.5	85.7	291.2	10.8	21.6	15.1	-4.4	-24
M134	6,820	7.5	0	1,012.5	997.5	1,200.0	1,698.7	49.8	56.8	32.7	-4.4	-23
M138	1,450	7.9	0	725.0	113.0	42.9	306.4	6.3	23.2	49.3	-5.1	-26
M139	7,830	7.9	0	1,250.0	1,348.5	1,214.3	1,739.1	40.4	56.0	112.2	-4.7	-27
M140	1,393	7.7	0	677.5	98.4	68.6	291.2	15.7	24.8	10.2	-2.2	-10

solution), the initial solutions must be mixed in a ratio 92/8 ( $\text{AZ}_1/\text{SL}$ ) and cation exchange and salt dissolution processes ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) must be produced.

The  $\text{A}_1$  sample was considered a mixture (Table 6) of  $\text{A}_{Z2}$  (surface water, Zelegüa stream),  $\text{A}_{C1}$  (surface water, Cortaderas stream) and  $\text{M}_{83}$  (groundwater from unconfined aquifer). The results (Table 6) showed that to obtain the sodium bicarbonate water type of Ají stream in the  $\text{A}_1$  section (final solution), the initial solutions must be mixed in a ratio 19/72/9 ( $\text{A}_{Z2}/\text{A}_{C1}/\text{M}_{83}$ ) and cation exchange and salt dissolution processes ( $\text{CaCO}_3; \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) must be produced.

The  $\text{A}_3$  sample was considered a mixture (Table 7) of  $\text{A}_1$  (surface water of Ají stream, which is identical to  $\text{A}_2$ ) and  $\text{M}_{139}$  (groundwater from unconfined aquifer).

The results (Table 7) showed that to obtain the sodium bicarbonate water type of Ají stream in the  $\text{A}_3$  section (final solution), the initial solutions must be mixed in a ratio 98/2 ( $\text{A}_1/\text{M}_{139}$ ), and cation exchange and salt dissolution processes must be produced ( $\text{CaCO}_3; \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

#### Application of $^{222}\text{Rn}$ for assessment of the relationship between surface water and groundwater

In order to add quantitative evidence to the conceptual hydrogeological model, a preliminary characterization of the stream-aquifer relationships was made using dissolved  $^{222}\text{Rn}$  in water. The characterization of  $^{222}\text{Rn}$  activity in



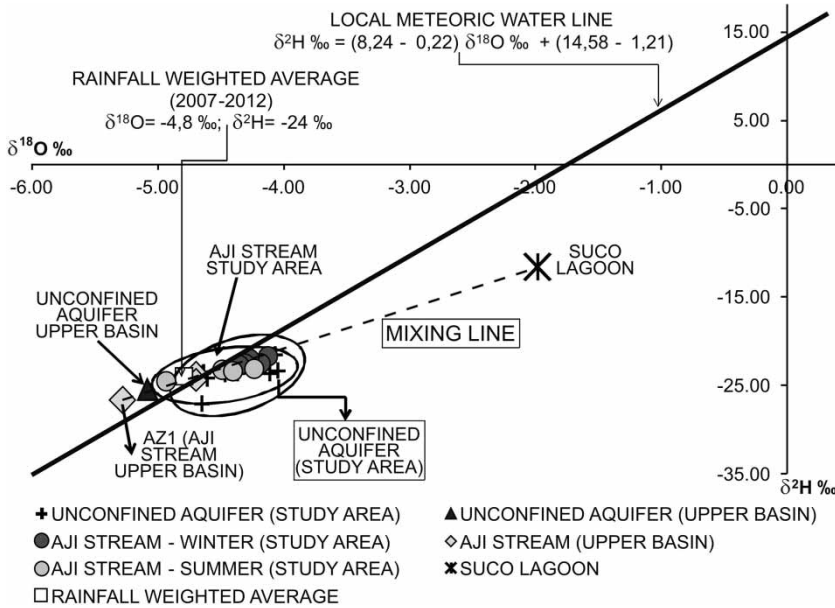


Figure 6 | δ²H vs δ¹⁸O for the Aji stream and the unconfined aquifer samples.

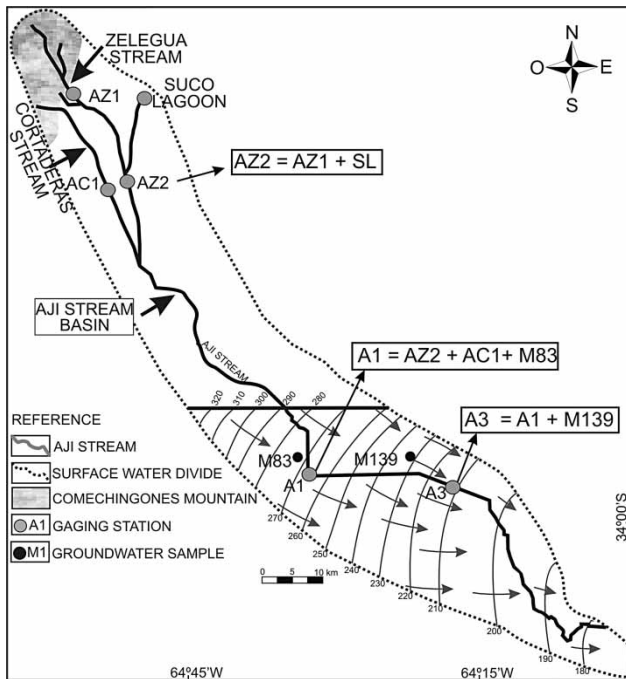


Figure 7 | Location of the modeled sites.

groundwater and surface water was performed by punctual water measurements at five sites (stream and wells), (Table 8, Figure 8) located along the entire basin.

Suco Lagoon, located in the upper basin (outside the study area) showed results which were consistent with large surface runoff contribution (2.2 pCi/L). On the other hand, the Aji stream within the study area, with a flow of about 0.8 m³/s at the selected gaging station, showed low <sup>222</sup>Rn values (4.5 pCi/L). This value, higher than that of Suco lagoon, was consistent with the hydrological section location, i.e. the low basin where the stream receives groundwater supply. The unconfined aquifer near the gaging station exhibited high <sup>222</sup>Rn values, typical of groundwater contained in the regional aeolian sediments (Bécher Quinodóz 2014). The highest value (351 pCi/L) corresponded to a confined aquifer (C<sub>100</sub>) and it was probably related to the aquifer depth and slow groundwater flow (Figure 8). At the A<sub>3</sub> gaging station, an estimation of groundwater contribution was performed, taking into account the <sup>222</sup>Rn mass balance method (Ellins et al. 1990) and using the following equation:

$$\frac{Q_{gw}}{Q_{sw}} = \frac{R_{nsw} - R_{nf}}{R_{ngw} - R_{nf}} \quad (2)$$

where  $Q_{gw}$ : groundwater flow;  $Q_{sw}$ : surface water flow;  $R_{nsw}$ : <sup>222</sup>Rn activity in surface water;  $R_{ngw}$ : <sup>222</sup>Rn activity in groundwater and  $R_{nf}$ : regional background of <sup>222</sup>Rn activity in surface water.

**Table 5** | (a) Samples used in the numerical modeling and (b) results of numerical modeling carried out with PHREEQC

<b>(a)</b>						<b>Cl<sup>-</sup></b>	<b>Na<sup>+</sup></b>	<b>K<sup>+</sup></b>	<b>Ca<sup>+</sup></b>	<b>Mg<sup>+</sup></b>	<b>δ<sup>18</sup>O</b>	<b>δ<sup>2</sup>H</b>
<b>Sample</b>	<b>EC (μS/cm)</b>	<b>pH</b>	<b>CO<sub>3</sub><sup>-2</sup> (mg/L)</b>	<b>CO<sub>3</sub>H<sup>-</sup> (mg/L)</b>	<b>SO<sub>4</sub><sup>-</sup> (mg/L)</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(‰)</b>	<b>(‰)</b>
SL (IS)	1,266	8.7	46	480.0	103.6	82.9	242.7	15.4	20.0	13.2	-2.0	-11.6
A <sub>Z1</sub> (IS)	458	8.2	0	185.0	43.3	16.6	30.9	5.3	38.4	4.9	-5.2	-26.6
A <sub>Z2</sub> (FS)	1,050	8.5	21.82	502.5	88.0	42.9	273.0	7.0	12.0	21.0	-5.1	-25.9
<b>(b)</b>												
<b>Sample</b>	<b>Mixture fraction</b>	<b>NaX (mol/L)</b>	<b>CaX<sub>2</sub> (mol/L)</b>	<b>MgX<sub>2</sub> (mol/L)</b>	<b>CaSO<sub>4</sub>·2H<sub>2</sub>O (mol/L)</b>							
SL (IS)	0.08	0.24	0.17	0.05	0.08							
A <sub>Z1</sub> (IS)	0.92	2.46	1.78	0.55	0.82							

IS: initial solution; FS: final solution

**Table 6** | (a) Samples used in the numerical modeling and (b) results of numerical modeling carried out with PHREEQC

<b>(a)</b>						<b>Cl<sup>-</sup></b>	<b>Na<sup>+</sup></b>	<b>K<sup>+</sup></b>	<b>Ca<sup>+</sup></b>	<b>Mg<sup>+</sup></b>	<b>δ<sup>18</sup>O</b>	<b>δ<sup>2</sup>H</b>
<b>Sample</b>	<b>EC (μS/cm)</b>	<b>pH</b>	<b>CO<sub>3</sub><sup>-2</sup> (mg/L)</b>	<b>CO<sub>3</sub>H<sup>-</sup> (mg/L)</b>	<b>SO<sub>4</sub><sup>-</sup> (mg/L)</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(‰)</b>	<b>(‰)</b>
A <sub>Z2</sub> (IS)	1,050	8.5	21.82	502.5	88.0	42.9	273.0	7.0	12.0	21.0	-5.1	-25.9
A <sub>C1</sub> (IS)	1,025	8.4	9.70	490.0	107.8	42.9	257.8	5.6	16.0	8.8	-5.1	-25.5
M <sub>85</sub> (IS)	1,650	8.2	0.00	800.0	88.0	65.7	385.2	11.4	24.8	26.3	-4.5	-25.1
A <sub>1</sub> (FS)	1,212	8.9	26.7	535.0	123.4	51.4	282.1	9.2	20.0	12.7	-4.9	-24.7
<b>(b)</b>												
<b>Sample</b>	<b>Mixture fraction</b>	<b>NaX (mol/L)</b>	<b>CaX<sub>2</sub> (mol/L)</b>	<b>KX (mol/L)</b>	<b>CaCO<sub>3</sub> (mol/L)</b>	<b>CaSO<sub>4</sub>·2H<sub>2</sub>O (mol/L)</b>						
A <sub>Z2</sub> (IS)	0.190	0.20	-0.10	0.02	0.09	0.03						
A <sub>C1</sub> (IS)	0.720	0.78	-0.41	0.05	0.35	0.04						
M <sub>85</sub> (IS)	0.090	0.10	-0.05	0.006	0.04	0.02						

IS: initial solution; FS: final solution.

**Table 7** | (a) Samples used in the numerical modeling and (b) results of numerical modeling carried out with PHREEQC

(a) Sample	EC ( $\mu\text{S}/\text{cm}$ )	pH	$\text{CO}_3^{2-}$ (mg/L)	$\text{CO}_3\text{H}^-$ (mg/L)	$\text{SO}_4^{2-}$ (mg/L)	$\text{Cl}^-$ (mg/L)	$\text{Na}^+$ (mg/L)	$\text{K}^+$ (mg/L)	$\text{Ca}^{2+}$ (mg/L)	$\text{Mg}^{2+}$ (mg/L)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
A <sub>1</sub> (IS)	1,212	8.9	26.7	535	1,23.4	51.4	282.1	9.2	20.0	12.7	-4.9	-24.7
M <sub>139</sub> (IS)	7,830	7.9	0	1,250	1,348	1,214	1,739	40.4	56.0	112.2	-4.7	-27
A <sub>3</sub> (FS)	1,333	8.2	0	625	88.9	71.4	264.9	10.8	24.0	12.2	-4.5	-23.1
(b) Sample	Mixture fraction	$\text{NaX}$ (mol/L)	$\text{CaX}_2$ (mol/L)	$\text{CaCO}_3$ (mol/L)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (mol/L)							
A <sub>1</sub> (IS)	0.98	-0.12	0.63	-0.48	-0.45							
M <sub>139</sub> (IS)	0.02	-0.02	0.01	-0.03	-0.02							

IS: initial solution; FS: final solution.

**Table 8** |  $^{222}\text{Rn}$  concentration (pCi/L) in the surface and ground water

Sample	$^{222}\text{Rn}$ concentration (pCi/L)
1. Suco lagoon	2.2
2. Unconfined aquifer upper basin (M <sub>140</sub> )	246
3. Ají stream (A <sub>3</sub> )	4.5
4. Unconfined aquifer study area (M <sub>139</sub> )	274
5. Confined aquifer study area (C <sub>100</sub> )	351

The  $^{222}\text{Rn}$  regional background value in surface water was tentatively established at 1 pCi/L, on the basis that generally there is no  $^{222}\text{Rn}$  in surface water (Ellins *et al.* 1990). This result indicates that, at the sampling moment, surface flow predominated and groundwater contribution was approximately only in the order of 2% (Table 9, Figure 8).

## CONCLUSIONS

The explained surface water-groundwater relationships showed the control exerted by the relief, the lithology and the climate. The chemical composition of both hydrological systems is essentially the result of different water velocity in each body. This situation leads to mixing processes between surface water and local, intermediate or regional groundwater giving rise to the observed geochemical pattern. The aquifer-stream relationships in the studied stream reach, as was observed from the hydraulic data, showed effluent/influent varying spatially as a result of the fluvial geomorphology and human actions, although a natural gaining stream type prevails.

The isotopic behavior ( $\delta^2\text{H} - \delta^{18}\text{O}$ ) of both hydrological systems also indicates water mixtures. This point is validated by  $^{222}\text{Rn}$  and the numerical geochemical modeling which indicates also a small contribution from the aquifer (~2%) in summer.

Taking into account the isotopic and modeling results and although fresh surface water flows in areas with high groundwater salinity (up to 14 mS/cm in the low basin), it may be established that there is strong predominance of surface water in the summer mixing process. As a result of surface water high velocity and the incoming of such small groundwater quantities, salts that come from the aquifer are diluted.

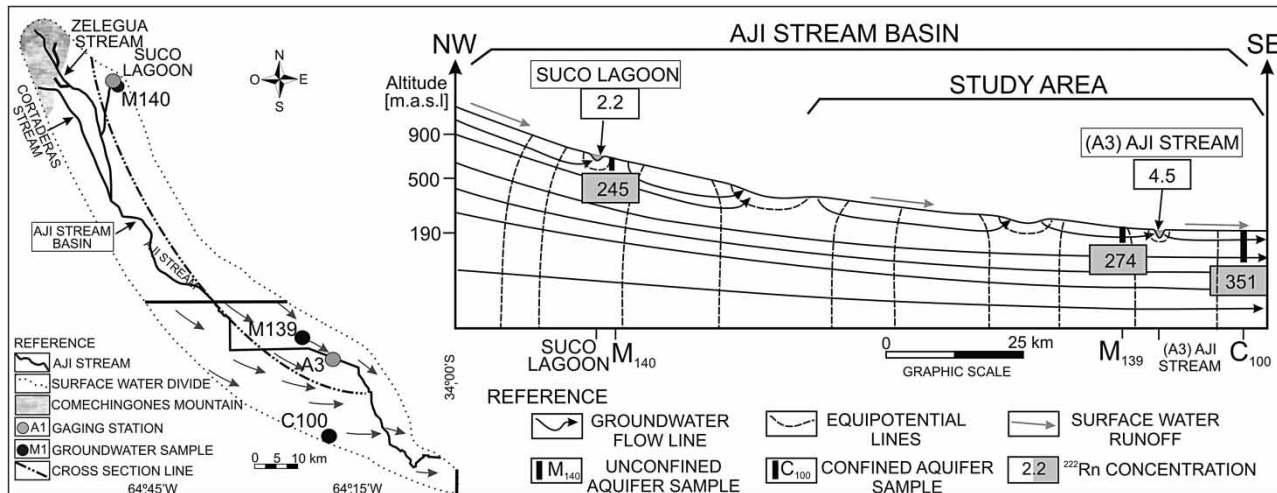


Figure 8 | Cross section of a groundwater-surface water relationship scheme taking into account  $^{222}\text{Rn}$  values.

Table 9 | Results of calculation of the %Q<sub>gw</sub> in the A<sub>3</sub> section

Station	Q <sub>sw</sub> (m <sup>3</sup> /s)	$^{222}\text{Rn}_{sw}$ (pCi/L)	$^{222}\text{Rn}_{gw}$ (pCi/L)	$^{222}\text{Rn}_f$ (pCi/L)	Q <sub>gw</sub> (m <sup>3</sup> /s)	% Q <sub>sw</sub>
A3 (Ají stream)	0.8	4.5	274	1	0.013	1.60

Furthermore, the stream water samples and those extracted from adjacent wells exhibit the same low salinity (in the order of 0.4 g/L) and geochemical type (sodium bicarbonate) due to induced recharge from stream to aquifer during pumping. This is a promising situation for conjunctive use of surface water and groundwater for different purposes. In this regard, the first measurements in the winter season showed that the stream water has low electrical conductivity and it is still influenced by the fresh water coming from the mountains. Thus, it was considered a vital water supply offer and some wells located beside the stream have already been built to generate induced recharge of surface fresh water towards the aquifer. More studies are required, especially extensive and thorough sampling in the two contrasting seasons, if a more comprehensive description of the entire basin is to be attempted.

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