

A Field Analog of CO₂-Closed Conditions in a Karstified Carbonate Aquifer (Nerja Cave Experimental Site, South Spain)

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Abstract We present new data that illustrate the hydrochemical evolution of groundwater along a flow line in the Triassic marbles around the Nerja Cave, South Spain. Water dissolves calcite and dolomite, and then CaSO₄. The environment is locally rich in CO₂ (up to near 60,000 ppmv) and consequently the water increases significantly its content in Ca²⁺, Mg²⁺, HCO₃⁻ and SO₄²⁻ along the flow, with EC values between 500 and 900 μS/cm. The pH values are typically in the 7–8 range, and the equilibrium PCO₂ of the water varies between 10^{-1.5} and 10^{-2.5} atm. In the considered flow line there is a relatively deep borehole (S2: 380 m; 280 m saturated) that shows pH values around 10 and equilibrium PCO₂ of 10⁻⁶ atm, with EC values generally in the 150–200 μS/cm range. Most of its solutes derive from rainwater concentration, together with the dissolution of carbonate minerals in a system closed to CO₂. For this reason we consider S2 to be

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a field analog of such conditions. The nearly stagnant water of this well also shows evidence of sulphate reduction. Unlike its solute contents, isotopically ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) the water of S2 does not show any modification with respect to the other points along the flow line.

1 Introduction and Objectives

When stagnant or quasi-stagnant conditions develop along groundwater flow, it can be expected to find water with very low renewal rate. In addition, it can become isolated from significant CO_2 sources coming from the soil horizons, thus leading to relatively anomalous compositions compared to those arising from the more frequent conditions found in CO_2 -open systems. In this study, by way of repeated hydrochemical sampling, we analyze the composition of the groundwater in what can be conceived as a man-made field analog of the conditions which determine the nearly complete isolation of that water from CO_2 sources. Our analog is a relatively deep (380 m; 280 m saturated), fully cased borehole (S2) drilled during 1999–2001 in a highly karstified Triassic calcite-dolomite aquifer, which also shows some thin interbedded layer of schists (Las Alberquillas aquifer). Our study has the additional interest that the air in the vadose zone around the S2 borehole has high concentrations of CO_2 (up to 60,000 ppmv: Benavente et al. 2010). In the saturated zone of the aquifer, near the studied borehole, there is a pumping well (CW: 150 m depth) used for the supply of the cave facilities. This well was built in 1998 to substitute an adjacent one (165 m, built in 1984), uninstalled at present, which can be used for sampling purposes. Another monitored point is the most significant spring in the area: the Maro spring: MS, with outflow peaks of $> 1 \text{ m}^3/\text{s}$.

Associated to the MS discharge are deposits of travertines. The fourth point considered in our study is an uninstalled well (EW) situated approximately 1 km upstream S2 in the general flow direction. These points belong to a monitoring network (the Nerja Cave Experimental Site, NCES), which also includes a number of shallow boreholes designed to monitor the vadose zone. In Fig. 1 we represent the general location of the study area, and the situation of the NCES and the four sampling points considered. The chemical and isotopic data of samples from these points illustrate the way the groundwater flow modifies its composition in the vicinity of the NCES. In this work we focus on the differences that the water in the S2 presents compared with other nearby points of the saturated zone, and we explain such differences in light of its isolation from the groundwater flow, and particularly due to the local depletion of CO_2 .

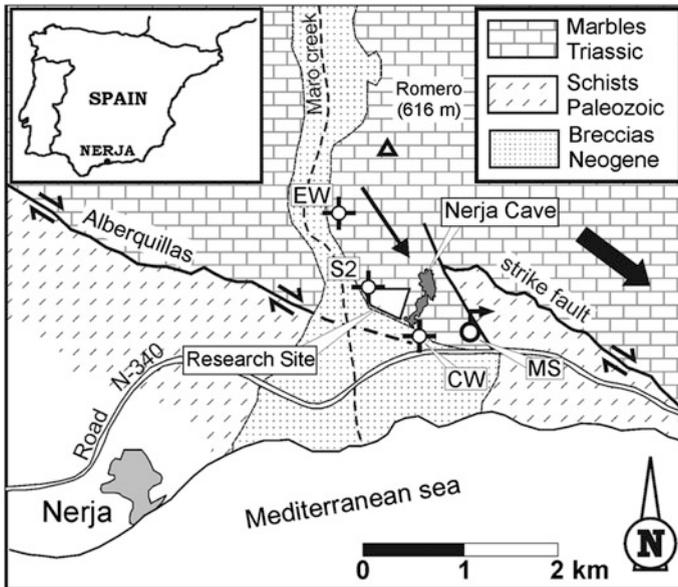


Fig. 1 General location and geological map of the study area showing the situation of the sampling points. Arrows indicate the local and regional flow directions

2 Hydrogeological Setting

The area belongs to the Alpujarride Complex of the Betic Cordillera. In the study area the Triassic carbonate formation dips gently toward the south, and its thickness can be more than 400 m. To the north it becomes folded and fractured. This formation is underlain by a thick sequence of schists, mostly Palaeozoic. To the south of the Nerja Cave, outcrops of the metapelitic materials contact those of carbonate formation by means of the so-called Las Alberquillas fault (Fig. 1), which has proven to be active in recent geologic times. The net outcome of its activity since late Miocene has been the relative elevation of the northern block, in which the cave is developed (Guerra et al. 2004).

The study area has a slightly dry, mild, Mediterranean climate. The general hydrodinamical and hydrochemical characteristics of Las Alberquillas aquifer in the vicinity of the Nerja Cave were stated in the work of Andreo and Carrasco (1993). A regional flow circulation from NW (mountain areas) to SE (Mediterranean Sea) was proposed. Nevertheless, piezometric evidences of lateral disconnection between aquifer blocks, as well as transmissivity measurements indicating values in the 10–1,000 m²/d range suggested that local flow systems were likely to occur (Andreo and Carrasco 1993). One of these systems develops around the Nerja Cave, draining toward the points MS and CW. The 50 m difference in the water level altitude is a consequence of the heterogeneities mentioned before. Groundwater level is some

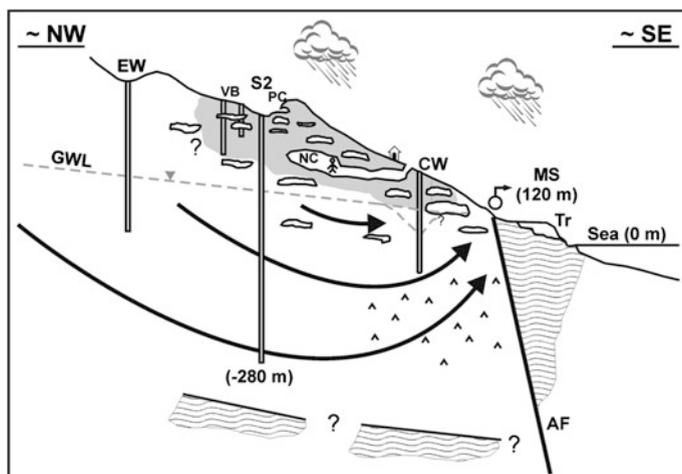


Fig. 2 Hydrogeological sketch (not to scale) of a cross section along the main flow in the aquifer in the study area. Some flow lines and altitudinal data are included. *GWL* groundwater level. *VB* vadose boreholes. *Tr* travertines. *NC* Nerja Cave. *PC* Pintada Cave. *Curved lines* represent schists. *Chevron symbols* represent CaSO_4 dissolution. *Shaded sectors* represent the recorded CO_2 -rich vadose environment. See text and Fig. 1 for references of the sampling points (*EW*, *S2*, *CW* and *MS*)

meters below the Nerja Cave floor. The aquifer crops out in a rugged mountainous area, with peaks of more than 1,500 m a.s.l. Its recharge comes mainly from the precipitation over the permeable outcrops. The main hydrochemical signature of this local system, pointed out in previous works (Andreo and Carrasco 1993; Liñán et al. 2000), is the important increase in calcium and sulphate contents of the groundwater drained by these two points and the relatively high equilibrium PCO_2 values in *CW* water: from 8,500 (late summer) to 19,500 ppmv (springtime). Figure 2 depicts schematically a hydrogeological cross-section which intends to coincide with the flow direction and includes the points considered in this study. As can be seen in the figure, there are a number of cavities, the most important of them open to tourist visits is the Nerja Cave (*NC*). Other cavities have been recognized both above and below the *NC* (as, for instance, Pintada Cave: *PC* in Fig. 2); some others have been crossed by the vadose boreholes (*VB*) and finally others have been identified by geophysical surveys (Vadillo et al. 2012). Most of these caves are developed mainly in the horizontal direction, although it is logical to imagine that vertical discontinuities can interconnect them and favor the general vadose ventilation which typically follows different patterns in summer than in winter (Benavente et al. 2011). Even artificial conducts can play the same role, as is the case of a shaft drilled between *PC* and *NC*.

3 Methods

Hydrochemical sampling has been done at different dates from 2005 to 2013. Samples in MS and CW (when pumping) were taken directly in the outflow. Sampling in EW, S2 and CW (when not in operation) was carried out with a 0.5 L HDPE bailer. This device allows to sample at different depths (100, 200 and 300 m in S2). Electrical conductivity (EC), temperature (T), redox potential (ORP), pH and dissolved oxygen (DO) measurements were performed in the field. Major ions were analyzed by ionic chromatography. An elemental analyzer provided the inorganic carbon (HCO₃⁻) and total organic carbon (NPOC). Isotopic measurements of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were obtained by laser spectroscopy and expressed in terms of delta (‰) units relative to the Vienna Standard Mean Ocean Water (V-SMOW). The precisions are ± 0.5 ‰ ($\delta^2\text{H}$) and ± 0.1 ‰ ($\delta^{18}\text{O}$). Analytical results providing an ionic-balance error of more than 5 % have not been taken into account in further interpretation. The code PHREEQC (Parkhurst and Appelo 1999) was used in speciation calculations as well as in hydrochemical modeling.

Rainwater samples are taken after precipitation events from a rain gauge collector at the NCES. This task is done by the cave's scientific staff and provides hundreds of samples. Measurements of pH, EC and major constituents were carried out within 24 h of sampling. Both types of samples can thus stay some hours in the collector devices before their analysis. So, for the rainwater samples an equilibration process with the carbonate dust in atmosphere is likely to occur.

A permeability (“slug”) test was carried out in S2 by way of introducing 15 L of water, then measuring the decay or recovery of the water level back toward the static condition as a function of time. The interpretation was done by the Hvorslev (1951) method. The result of the “slug” test in S2 indicates a value of hydraulic conductivity of the order of 10^{-9} m/s.

4 Results

Table 1 shows the analytical results obtained in point S2, and the average values of other points of interest (CW, EW and MS) and rain samples. Figure 3 is a Piper plot of the different analysis in the previous table. Figure 4 is a binary plot of the contents of the two stable isotopes of the water molecule analyzed. The altitude of the water level in S2 is near 60 m a.s.l. with few variations along the sampling campaigns. Water from S2 has generally pH values in the 10–11 range. Temperature is variable depending on the dates, whereas in winter it increases slightly with depth: from 19.4 to 19.6 °C, in summer the maximum values (22–24 °C) are found just below the water level. In most of the samples the EC ranges between 150 and 200 $\mu\text{S}/\text{cm}$. The maximum DO value is 3 mg/L. TOC is usually in the 2–10 mg/L range, although one sample shows an exceptionally high value of 26 mg/L. Calculated equilibrium PCO₂ values are near $10^{-6.5}$ atm. Saturation

Table 1 Dates and depth of sampling, and analytical results of the samples of the studied points

SAMPLE	DATE	EC	T	pH	DO	TOC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	F ⁻	δ ² H	δ ¹⁸ O	
BOREHOLE S2	100 m	Jul-2005	178	22,6	10,20	1,3	-	-	-	-	37,30	35,82	3,07	1,91	0,65	-	-	
	100 m	Feb-2006	212	19,6	10,15	2,1	9,59	6,08	1,06	27,23	15,16	35,90	43,32	1,63	0,14	0,74	-	-
	150 m	Feb-2006	168	19,5	10,34	1,7	2,79	5,65	0,94	18,03	8,59	36,60	25,01	0,36	0,09	0,54	-	-
	200 m	Feb-2006	165	19,5	10,19	2,1	3,41	7,64	2,87	15,28	7,63	46,10	23,12	0,22	0,07	0,47	-	-
	250 m	Feb-2006	200	19,6	9,63	2,1	1,82	8,84	9,55	14,82	7,52	81,00	22,38	0,18	0,07	0,38	-	-
	300 m	Feb-2006	170	19,6	10,24	1,7	2,59	5,16	1,03	17,06	10,71	37,10	25,40	0,22	0,07	0,57	-	-
	100 m	May-2007	167	21,6	10,44	1,9	26,24	5,55	1,20	18,59	15,85	13,22	-	-	-	-	-	-
	110 m	May-2007	163	21,4	10,53	1,7	6,96	5,27	0,54	17,48	10,11	11,73	-	-	-	-	-	-
	150 m	May-2007	166	22,6	10,52	1,6	8,33	5,45	0,70	17,47	9,32	11,66	-	-	-	-	-	-
	100 m	Jun-2011	181	24,1	10,34	2,9	-	5,86	0,76	24,00	10,85	-	24,26	4,99	0,76	0,45	-38,57	-6,13
	200 m	Jun-2011	182	23,0	10,44	3,0	-	5,39	0,19	25,16	11,08	-	23,77	4,94	0,81	0,45	-39,24	-6,41
	100 m	Jan-2012	184	19,4	10,60	1,8	-	5,53	0,36	24,64	10,64	-	24,56	5,14	0,81	0,42	-38,08	-6,76
	150 m	Jan-2012	182	19,6	10,55	1,4	-	7,36	0,36	24,34	10,99	-	24,05	5,09	0,70	0,43	-38,07	-6,75
	100 m	Jun-2013	173	23,0	10,28	2,1	2,67	9,87	0,77	19,32	18,33	55,40	38,74	5,15	1,00	0,41	-40,68	-6,75
	150 m	Jun-2013	172	22,3	10,32	1,0	2,73	9,79	0,77	20,29	8,58	52,00	25,92	5,06	0,76	0,41	-40,55	-6,85
	100 m	Oct-2013	210	21,5	10,14	1,3	5,28	15,71	2,50	29,19	8,02	26,75	36,95	6,86	0,85	0,56	-39,35	-6,66
		Max	212	24,1	10,60	3,0	26,24	15,71	9,55	29,19	18,33	81,00	43,32	6,86	1,91	0,74	-38,07	-6,13
		Min	163	19,4	9,63	1,0	1,82	5,16	0,19	14,82	7,52	11,66	22,38	0,18	0,07	0,38	-40,68	-6,85
RAIN WATER	m	49	-	7,80	-	-	8,90	2,35	4,60	2,80	23,60	10,70	12,00	1,80	-	-30,90	-5,16	
ESPARTO WELL	m	553	20,2	7,17	6,1	1,49	20,49	17,67	6,62	2,38	224,38	27,13	17,17	3,38	0,11	-34,18	-5,89	
CAVE WELL	m	900	21,8	7,23	6,3	0,94	95,68	48,44	22,04	9,46	232,15	41,00	159,30	12,55	0,20	-38,56	-6,64	
MARO SPRING	m	722	19,3	7,62	8,9	0,36	113,90	30,09	11,30	2,40	204,72	20,18	200,23	1,44	0,50	-44,22	-7,65	

All the contents in mg/L, except EC ($\mu\text{S}/\text{cm}$), T ($^{\circ}\text{C}$) and stable isotopes (‰). (*m* mean value, *max* maximum, *min* minimum)

indices (SI) with respect to calcite, dolomite and gypsum are near 1.0, 2.5 and – 3.0, respectively. The hydrofacies correspond mostly to the Na–Cl and Na–HCO₃ types (Fig. 3). Nitrate contents are generally less than 1 mg/L.

Groundwater sampled in EW, CW and MS shows average EC values in the 500–900 $\mu\text{S}/\text{cm}$ range, and pH between 7.1 and 7.7. Average temperature ranges between 19 and 22 $^{\circ}\text{C}$. DO is in the 6–9 mg/L range, and TOC is below 1.5 mg/L. Calculated equilibrium PCO₂ average values are 10^{-2.4} atm (MS), 10^{-1.8} (CW) and 10^{-1.6} (EW). Approximate average values for the SI in MS are 0.2 (calcite), 1.4 (dolomite) and –1.3 (gypsum); in CW are 0.1 (calcite), 1.2 (dolomite) and –1.4 (gypsum); in EW are –0.5 (calcite), 0.3 (dolomite) and –2.8 (gypsum). The hydrofacies of EW is Mg–HCO₃, for MS it is Ca–SO₄, and in the case of CW it has mixed features: Ca, Mg–SO₄–HCO₃. Average nitrate contents are > 1 mg/L, with a maximum of near 12 mg/L in CW.

The isotopic composition (Fig. 4) in S2 shows differences in function in the dates and depth of samples. Overall, there is no significant deviation with respect to the position of the average CW water in the diagram. The other two groundwater plots are clearly out of the S2 composition, indicating lower (MS) and higher (EW) contents. The point representing average local precipitation has highest contents. In the points of the June 2011 campaign, it is particularly noticeable the difference in contents with the sampling depth. The same can be identified in the June 2013 campaign (Fig. 4).

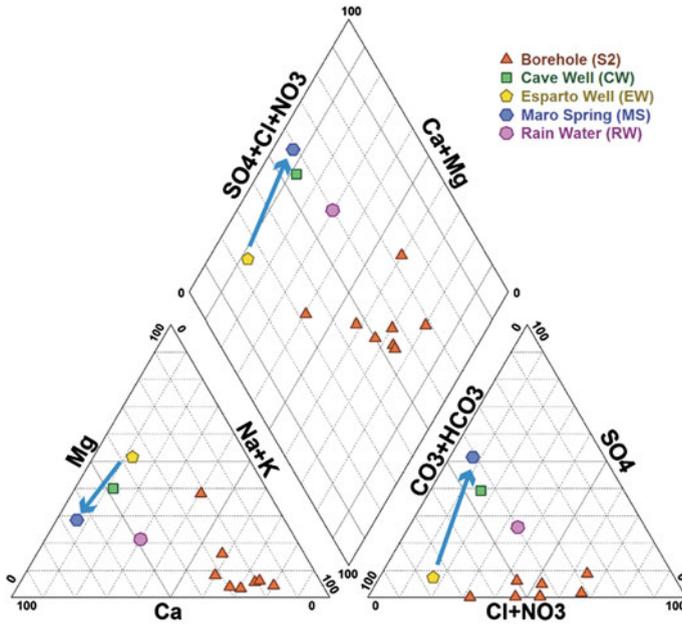


Fig. 3 Piper plot of the samples of Table 1. The arrow shows the main flow path

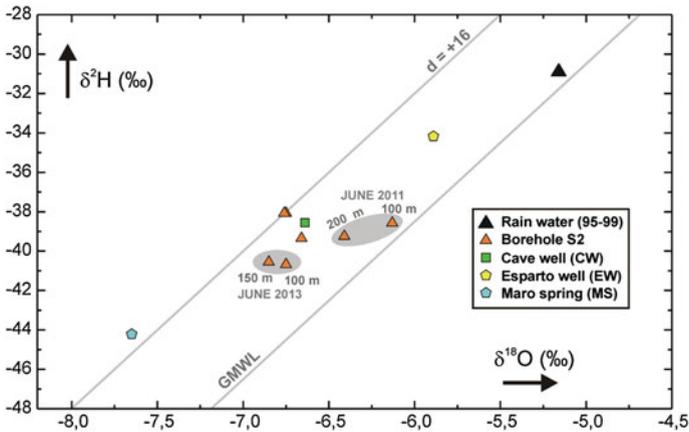


Fig. 4 Plot of the isotopic compositions of samples of Table 1

5 Discussion

In correspondence with Andreo and Carrasco (1993), Table 1 indicates similar results in the case of MS. CW composition in our study indicates higher values of EC and T, and particularly SO₄²⁻ and Ca²⁺. Chloride and nitrate remain quite

similar, and HCO_3 decreases. These changes may be induced by the extraction regime in the new well, with the consequence of getting water coming from deeper flows with higher contents in dissolved gypsum (Fig. 2). This mineral phase was confirmed by $\delta^{34}\text{S}$ values (15, 3 ‰).

MS chemical composition is similar to CW, although more diluted due to the effect of local recharge inputs favored by a karstic network. Due to this, it is colder with high DO and pH average values. Karstic influence in the hydrodynamical and hydrochemical data in this spring was deduced in a previous study (Liñán et al. 2000). In fact, Moral and Benavente (2010) suggested that the spring could be linked with a cave system (Fig. 2). The hydrochemical evolution from EW to MS involves: (1) the dissolution of calcite and dolomite along the saturated flow or by the effect of local recharge in the sector of high CO_2 vadose contents (Benavente et al. 2010) and (2) the dissolution of CaSO_4 (Fig. 3) which happens at the level of CW and MS points. It is worth to point out that neither gypsum nor anhydrite has been identified in outcrops of the study area, but these minerals are common in materials with similar degree of metamorphism in geologically similar nearby areas. Due to its hydrogeological character, in MS one could expect influences of both deep flow lines as well as near surface ones. Although water mixing happens, its isotopic composition (Fig. 4) reveals recharge at higher altitudes than the other points. On the contrary, the EW isotopic composition indicates a lower altitude of recharge (Fig. 2). Nitrates and, specially, TOC are regarded as good tracers for local recharge in the area (Batiot et al. 2003). Its average contents in EW, CW and MS corroborate the relatively higher influence of this recharge in the first point. Nitrate in CW is anomalously high (>10 mg/L), and is interpreted as a particular incidence of recycled water percolating from the garden sector near the entrance to the Nerja Cave, a circumstance which has been identified in previous studies (Liñán et al. 2008).

Although during the drilling operations it was found a number of karstification evidences in the saturated zone, and it was able to identify inputs of water at different levels of the column, the water sampled in S2 can be considered in the present conditions nearly stagnant, provided the very low value of permeability found on it. This is the consequence of being completely cased with unscreened tube after its drilling. In spite of its situation in the flow line joining roughly EW with CW and MS (Fig. 2), its composition does not reflect at all the general hydrochemical processes mentioned above. Water inside S2 has Cl^- , Na^+ and K^+ contents which are likely to be derived from simple concentration of precipitation water. The comparison with P composition indicates that some sulphate has suffered reduction, which is in accordance with the low DO values and the decrease in HCO_3^- . TOC values are, in some of the S2 samples, anomalously high (>5 mg/L: Table 1), even taking into account the relatively high values found in previous surveys (from 1 to 5 mg/L: Batiot et al. 2003). It is suggested that oxidation of this OC favors sulphate reduction. It is particularly illustrative the nearly depletion in CO_2 that the very low PCO_2 value and high pH value suggests. It is likely that water in S2 has evolved toward equilibrium in calcite and dolomite in a CO_2 -closed system.

The isotopic contents of the S2 samples are, however, fully coherent with its supposed recharge sources. They are quite similar to the data in the nearby CW. Furthermore, it is possible to identify in the S2 isotopic contents the effects of a certain stratification which is congruent with the basic flow net depicted in Fig. 2. This circumstance can be inherited from the moment of its drilling, ended in 2001, and not subjected to further modifications. Chemically, however, the water has experienced the significant modifications commented above.

6 Conclusion

In Nerja research site (South Spain) located over a karstified Mediterranean carbonate environment (calcite and dolomite Triassic marbles) it was found an analog to groundwater conditions in a CO₂-closed system. The analog is a borehole (S2) with an unscreened casing in all its length (380 m). Water column inside S2 reaches nearly 200 m. Sampling in S2 shows pH values around 10 and PCO₂ of 10⁻⁶ atm. With EC values of less than 200 μS/cm, most of its solute contents seem to derive from the concentration of rainwater, together with the dissolution of carbonate minerals in a system closed to CO₂ and sulphate reduction process. The latter can be linked with the relatively high TOC values. These hydrochemical characteristics contrast with those that have been identified in the groundwater flow system in which the point S2 is included. The general trend is the dissolution of calcite and dolomite in an environment that, for the local recharge through the vadose zone near the cave, is marked by equilibrium with very high PCO₂ values. Near the main natural outflow of the system-Maró spring—the main hydrochemical process is the dissolution of CaSO₄.

The water isotopic data obtained for the S2 are coherent with the flow model proposed for the study area. In this case, the data for what can be considered nearly stagnant water are similar to a nearby pumping well, although their hydrochemical characteristics are completely different.

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