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## Extended Abstracts

**Editors:**  
Andrzej Zuber  
Jarosław Kania  
Ewa Kmieciak



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author(s): **José Benavente-Herrera**  
University of Granada, Spain, [jbenaven@ugr.es](mailto:jbenaven@ugr.es)

**Iñaki Vadillo-Pérez**  
University of Málaga, Spain, [Vadillo@uma.es](mailto:Vadillo@uma.es)

**Francisco Carrasco-Cantos**  
University of Málaga, Spain, [fcarrasco@uma.es](mailto:fcarrasco@uma.es)

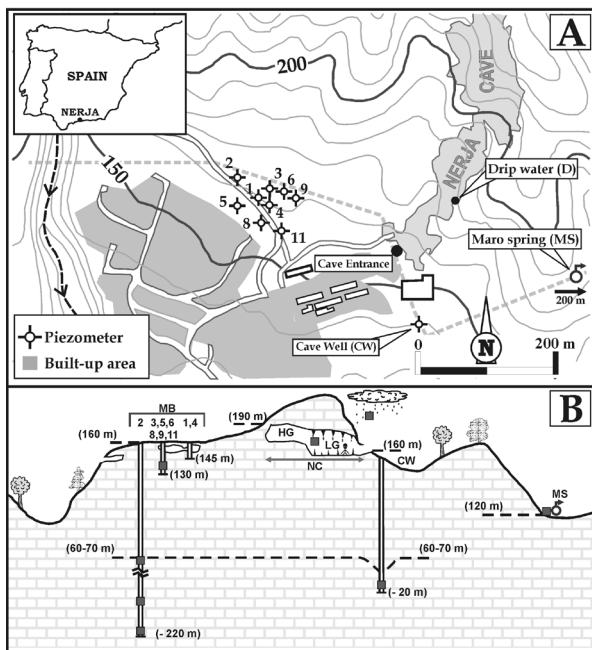
**Cristina Liñán-Baena**  
University of Málaga, Spain, [Cbaena@cuevanerja.com](mailto:Cbaena@cuevanerja.com)

**Albert Soler i Gil**  
University of Barcelona, Spain, [Albertsolergil@ub.edu](mailto:Albertsolergil@ub.edu)

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## INTRODUCTION

This work is based mostly on hydrochemical data obtained in the Nerja Cave experimental site, situated at less than 1 km from the Mediterranean Sea (Fig. 1A). It is located over a regional aquifer made up of fissured and karstified Triassic dolomite marbles which host an important show cave: the Nerja Cave (Malaga province, Andalusia, S. Spain), visited by some 500,000 people each year mostly during summer months.



**Figure 1.** Hydrogeological map of the Nerja experimental site area (A), and idealized cross-section (B) sketching the main characteristics of the monitoring and sampling points. NC: Nerja Cave, LG: Lower Galleries, HG: Higher Galleries, MB: Monitoring Boreholes. Numbers between brackets in part B indicate approximate altitudes in m a.s.l. Discontinuous lines indicate groundwater levels. Grey squares represent the location of the samples considered.

The study site is equipped with 10 boreholes (Fig. 1A). Nine of them –designed by numbers in Figure 1- are small-diameter (90–120 mm) monitoring boreholes (piezometers); other (CW) is a production well which was built to supply the cave facilities. Recently, a new pumping well was drilled nearby, and the CW point — which is 160 m deep — is used for monitoring purposes. With the exception of piezometer 2 (P-2), which is 380 m deep, all the small-diameter boreholes have depths between 15 m and 30 m, and are drilled in the vadose zone of the aquifer (Fig. 1B).

The main discharge from the carbonate aquifer in the study area is the Maro spring (MS, Fig. 1). Its approximate altitude is 120 m a.s.l., and it has an average outflow of 250 L/s, with a range between 20 and 1600 L/s, suggesting relatively well developed karstic conditions (Liñán et al., 2000).

The saturated zone is reached in two boreholes: CW and P-2. The altitude of the groundwater level at these two points is roughly 60–70 m a.s.l. This value does not match with that of the nearby Maro spring altitude (Fig. 1B), suggesting some kind of low permeable boundary between them. The thickness of the saturated zone is thus of approximately 80–90 m in point CW, and 280–290 m in point P-2.

Differences in fissure connectivity probably favour the presence of a sporadic perched groundwater level in the vadose zone which sometimes is found in the lowest meter of piezometer 6 (P-6).

The estimated void volume of the Nerja Cave is 300,000 m<sup>3</sup>. Only one third of the cave — the part labelled as LG in Figure 1B — is open to large-scale visitation along an adapted pathway tour. The average CO<sub>2</sub> content inside this part ranges between approximately 250 ppm in the winter and 2,000 ppm in the summer (Carrasco et al., 1999; Liñán et al., 2008a). Access of visitors to the rest of the cave (HG in Fig. 1B) is restricted.

In previous works (Benavente et al., 2010; Vadillo et al., 2010) we have focused on the interpretation of systematic measurements of the air CO<sub>2</sub> contents in the vadose zone, mostly through logs inside the boreholes. Air temperature and relative humidity values were also registered. These data were compared with those coming from the routine monitoring of the same variables inside the part of the cave that is open to visitors. Such works allow identifying CO<sub>2</sub> concentrations that are frequently in the range of 20,000 to 40,000 ppm in the vadose zone, with maximum values near 60,000 ppm. These values have been validated using a hydrogeochemical simulation model that reproduces the processes affecting the evolution of rain water through the epikarst and vadose zones until its appearance as drip water in the cave. Associated with the dripping, there is an intense CO<sub>2</sub> degassing effect induced by strong cave ventilation. The cave itself appears as an environment relatively depleted in CO<sub>2</sub> within the vadose zone that surrounds it.

The aim of the present work is to present preliminary results concerning hydrochemical data in the saturated zone of the Nerja cave experimental site, and compare them with the information of the nearby vadose environment.

## METHODS

Rainwater samples are routinely taken after precipitation events from a rain gauge collector at the meteorological station (Fig. 1A). Another collector was used to sample the drip water inside the cave (Fig. 1A). These two types of samples have been routinely collected by the cave's scientific staff since 1991, and provide hundreds of samples of both types of waters (Carrasco et al., 2002; Liñán et al., 2008). Measurements of pH, electrical conductivity (EC) and major constituents were carried out within 24 hours 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. For the drip water samples the equilibrium is mainly imposed by the CO<sub>2</sub> content inside the cave.

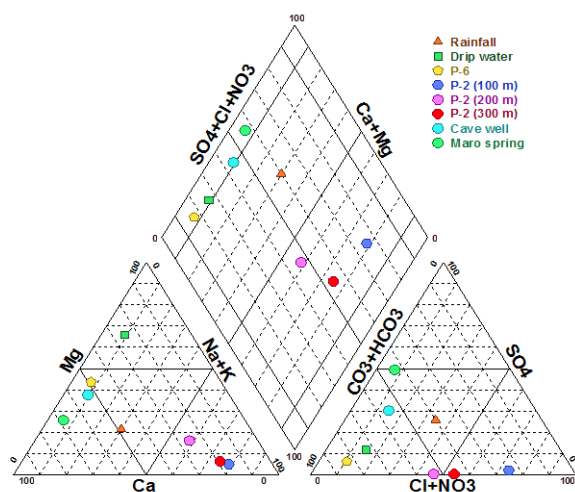
All samples were stored at 4°C and analysed using ion chromatography (Dionex DX-100) at the Nerja Cave Research Centre laboratory.

Sampling in boreholes was carried out with a 0.5 L HDPE bailer. This device allows to sample at different depths in P-6 (100 m, 200 m and 300 m: Fig. 1B). Electrical conductivity (EC), temperature ( $T^{\circ}$ ), redox potential (Eh), pH and dissolved oxygen (DO) measurements were performed in the field with a HACH-LANGE HQ40D device. Major ions were analysed by ionic chromatography with a METROHM 792 Basic IC equipment. A SHIMADZU TOC-VCSN analyser provided the inorganic carbon ( $\text{HCO}_3^-$ ) and total organic carbon (NPOC). Isotopic measurements of dissolved sulphate ( $^{34}\text{S}$  and  $^{18}\text{O}$ ) were performed with Elemental Analysers (Carlo Erba 1108 for sulphur and TC/EA Thermo-Quest Finnigan for oxygen) coupled with an IRMS (Delta C Finnigan Mat). Notation is expressed in terms of delta ( $\text{‰}$ ) units relative to the Vienna Standard Mean Ocean Water (V-SMOW) and Vienna Canyon Diablo Troilite (V-CDT) standards.

Analytical results providing an ionic-balance error of more than 5% have not been taken into account in further interpretation.

## RESULTS, DISCUSSION AND CONCLUSIONS

Table 1 summarizes the main physical-chemical characteristics of the waters studied, which have also been plotted in a Piper diagram (Fig. 2).



**Figure 2.** Piper diagram for the samples of Table 1.

Rainfall (P) and drip water (D) in Table 1 corresponds to average values from hundreds of samples since 1991. The rest are averages of two sampling campaigns in May 2007 and 2008. Data of points P-2 and P-6 are presented here for the first time. Data of points CW and MS can be compared with those of a previous monthly record during 1991 and 1992 (Andreo y Carrasco, 1993). These authors calculate average equilibrium  $\text{PCO}_2$  values in the range of 4,000 ppm (MS) and 14,000 ppm (CW). The comparison between their data and those of Table 1 indicates a slight increase in the concentrations in CW, which can derive from the fact that in the previous study the samples were obtained when the well was currently operating. The MS values show a fair similarity.

Previous studies (Liñán et al., 2008b) show that rainwater composition changes with episodes. Its anomalous average pH is determined by the sampling procedure, as explained before. Drip waters are quite homogeneous in their composition, due to the effect of the residence time in the vadose zone. The bicarbonate, calcium and magnesium contents are due to the high CO<sub>2</sub> partial pressure in the vadose zone (30,000–60,000 ppm: Benavente et al., 2010). This has been validated by the composition of the water sampled in point P-6. The drip water shows the effects of the intense CO<sub>2</sub> degassing and calcite precipitation. The vadose water has a pH near 7.4, but inside the cave it rises up to 8.3 (Table 1).

**Table 1.** Hydrochemical average values of samples. GWL: Groundwater level depth, EC: Electrical Conductivity (microS/cm), TOC: Total Organic Carbon. Concentrations in mg/L.

Name	Reference	GWL	EC	T <sup>a</sup>	pH	Eh	O <sub>2</sub>	TOC	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
Rain Water	P	-	49	-	7.8	-	-	-	8.9	2.35	4.6	2.8	23.6	12.0	10.7	1.8	-
Vadose Water	P-6	28	800	21.9	7.4	+122	6.8	2.5	102.1	55.3	16.4	1.9	521.7	30.9	27.8	18.5	0.1
Drip Water	D	-	459	-	8.3	-	-	2.2	28.6	45.3	9.6	3.7	274.3	34.3	30.5	3.3	-
Piezometer 2	P-2 (100 m)	98	190	20.6	10.3	-41	2.0	17.9	5.8	1.1	22.9	15.5	24.6	1.6	43.3	0.1	0.7
	P-2 (200 m)	-	165	19.5	10.2	-53	2.1	3.4	7.6	2.9	15.3	7.6	46.1	0.2	23.1	0.1	0.5
	P-2 (300 m)	-	170	19.6	10.2	-15	1.7	2.6	5.2	1.0	17.1	10.7	37.1	0.2	25.4	0.1	0.6
Maro Spring	MS	-	666	19.0	7.6	+224	9.2	0.3	119.2	27.2	11.0	1.9	228.6	204.5	20.7	0.8	0.6
Cave Well	CW	62	878	-	7.1	-	-	0.8	112.4	48.3	20.7	2.9	326.5	139.5	34.6	25.2	0.2

Analytical data in the saturated zone (points MS, CW and P-2) show –when compared with the vadose values- a decrease in the Mg/Ca ratio, and an important increase in the sulphate contents. The origin of this ion is from gypsum hosted in the carbonate formation, as suggested by sulphate isotopic values ( $\delta^{34}\text{S}_{\text{SO}_4} = 15.4 \text{ ‰}$ ,  $\delta^{18}\text{O}_{\text{SO}_4} = 12.3 \text{ ‰}$ ).

The composition of P-2 samples is anomalous. There are not significant differences in ion contents with depth. Only TOC shows high values (18 mg/L) related to the proximity of the groundwater level and less than 3 mg/L in the rest. The saturation indices in calcite and dolomite for the two deepest samples indicate oversaturation conditions with respect to both minerals. The sample near the groundwater level approach saturation conditions. Bicarbonate contents (< 50 mg/L), calcium and magnesium (< 10 mg/L) and pH (~ 10.0) in this point suggest an aqueous carbonate environment nearly depleted in CO<sub>2</sub>. This can indicate a groundwater flow in closed conditions with respect to that gas (Appelo, Postma, 2005), which is in sharp contrast with the measured, calculated and modelled values of CO<sub>2</sub> contents in the nearby vadose zone. It seems difficult to admit such differences in the same groundwater flow system, provided the short distances involved. Maybe the P-2 is drilled in a block of the carbonate matrix which is not connected to the CO<sub>2</sub>-rich vadose atmosphere through the karst conduit network where the other points penetrate. Hydraulic testing in this borehole is necessary to check this. Another possibility to check is, provided that the P-2 is hydraulically connected with adjacent sectors, what kind of processes can contribute to the CO<sub>2</sub> depletion. Perhaps most of the gas is lost to the atmosphere due to the ventilation of cavities and big karst conduits in the vadose zone above the groundwater level in P-2.

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