

# eurokarst 2022



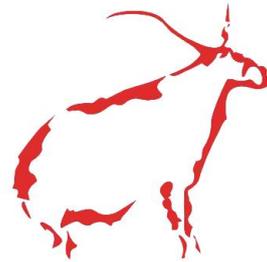
MÁLAGA

22 - 25 June

## The European Conference on Karst Hydrogeology and Carbonate Reservoirs

Field trip guide: field trip to the Nerja cave area – Eastern coast of Malaga province (S Spain)

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## EUROKARST 2022: field trip to the Nerja Cave area - Eastern coast of Malaga province (S Spain)

### Key features

Departure: Saturday 25th June 8:00 am / Arrival: Saturday 25th June 7:00 pm approx.

Instructors: Lucía Ojeda Rodríguez, Cristina Liñán Baena and Iñaki Vadillo Pérez.

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### Location Map

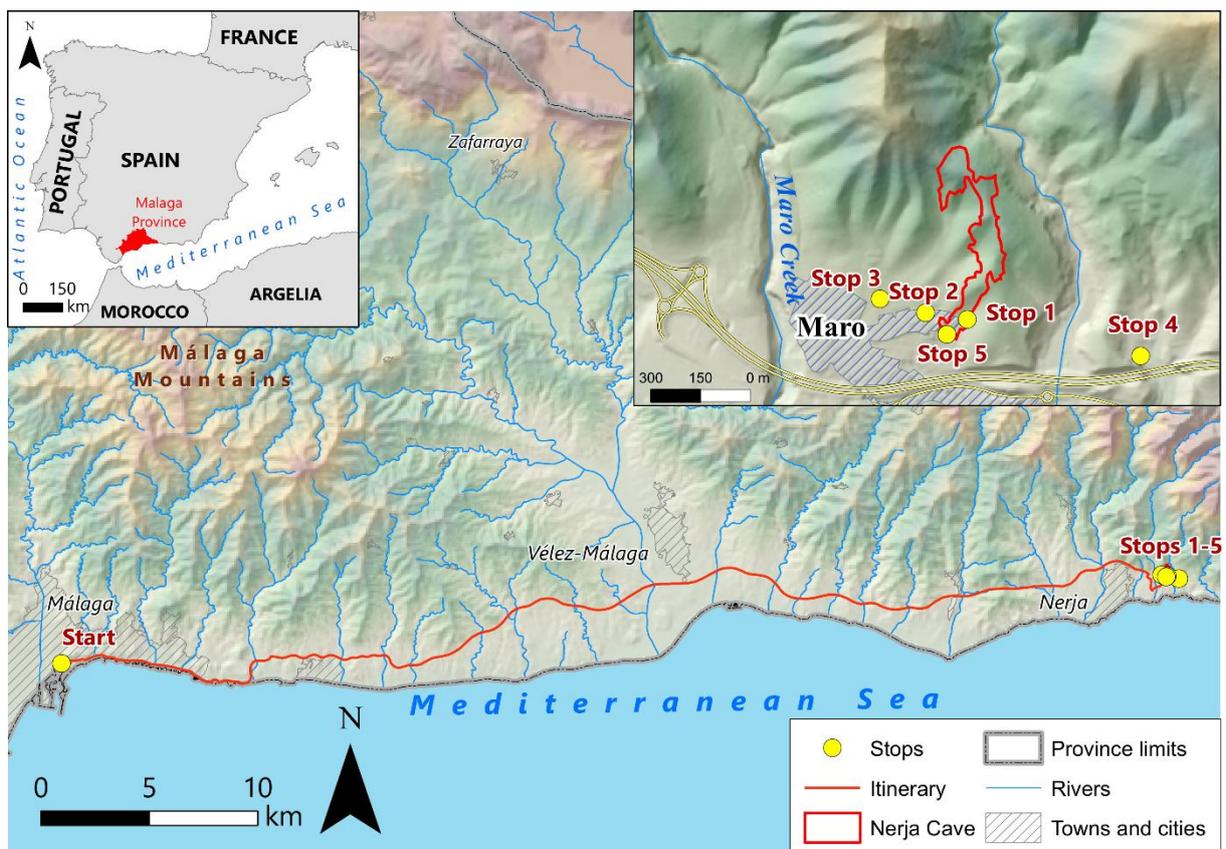


Figure 1. Location map with the route and stops of the field trip to the Eastern coast of Malaga province.

## Introduction

Karstic systems in the province of Málaga occupy a sixth of its surface area. The lithostratigraphic, structural, geomorphologic and hydrogeologic characteristics of the main karstic massifs evidence the extensive development of dissolution processes, with a broad range of exokarstic and endokarstic forms, both ancient and modern (Durán, 1996). This excursion takes place in the surroundings of the southern outcrops of the Sierra Almijara carbonatic aquifer (Figure 1). The main goals of this excursion are to present the ongoing research on the vadose and non-vadose zone surrounding the Nerja Cave.

In the Nerja area, the climate is of a Mediterranean type, basically warm and humid, but with hot, dry summers. The daily mean air temperature ranges from 13.2 °C in January to 25.9 °C in August, with an annual mean value of 18.8 °C (Liñán et al., 2007). The mean relative humidity of the air ranges from 61% to 69 %, with an annual mean of 66 %. Monthly evaporation ranges from 2.3 mm (February and December) to 3.2 mm (July and August), with a mean annual value of 2.8 mm/day. The mean rainfall in the area is 490 mm/year, distributed irregularly, with a marked wet season between October and January and a dry period throughout the summer months.



Figure 2. Panoramic view of the Natural Park of the Maro-Cerro Gordo Cliffs (left) and the Natural Park Tejada- Almijara –Alhama (right).

## Stop 1: Walking trail in the Nerja Cave outdoor area

The trail, about 800 m in length, allows one to know the principal characteristic of the geology and hydrogeology of the southern slope of the mountainous massif of Sierra Almijara. It is a rugged area sparsely covered by pine trees and Mediterranean shrubs, with a top peak slightly higher than 1800 m a.s.l., where the coastal carbonatic aquifers of Nerja and Cerro Gordo are located. It runs over the Nerja Cave's halls on the surface. It ends at a viewpoint where can be seen the Maro and Nerja villages and some cultural heritage elements like medieval watchtowers, sugar factories, and a waterway (Acueducto del Águila), catalogued as "hydraulic heritage".

Sierra Almijara belongs to the Alpujarride Complex of the Internal Zone of the Betic Cordillera. Its lithological sequence is composed of intensely deformed metamorphic rocks: Paleozoic schists at the bottom and Triassic marbles at the top (dolomitic marbles at the bottom and calcareous marbles toward the top). Pliocene conglomerates and sands of marine and continental origin appear discordant over the

metamorphic rocks. Stratigraphically above the Pliocene materials, Quaternary deposits (Pleistocene breccias and upper Pleistocene travertines) are associated with the erosion processes in the surrounding reliefs.

The general geological structure consists of a plurikilometer-size anticline affecting Paleozoic and Triassic rocks of the Almirajara geological unit. The unit is tectonically affected by a set of regional NW–SE faults (Figure 3). One of them, the "Alberquillas fault", is visible from the trail and has been active in recent geological times. This fault has affected the local geomorphology, with the progressive elevation of the northern block since the late Miocene, bringing about the incision of the Maro creek and the perched location of the Nerja cave above groundwater level (Guerra-Merchán et al., 2004).

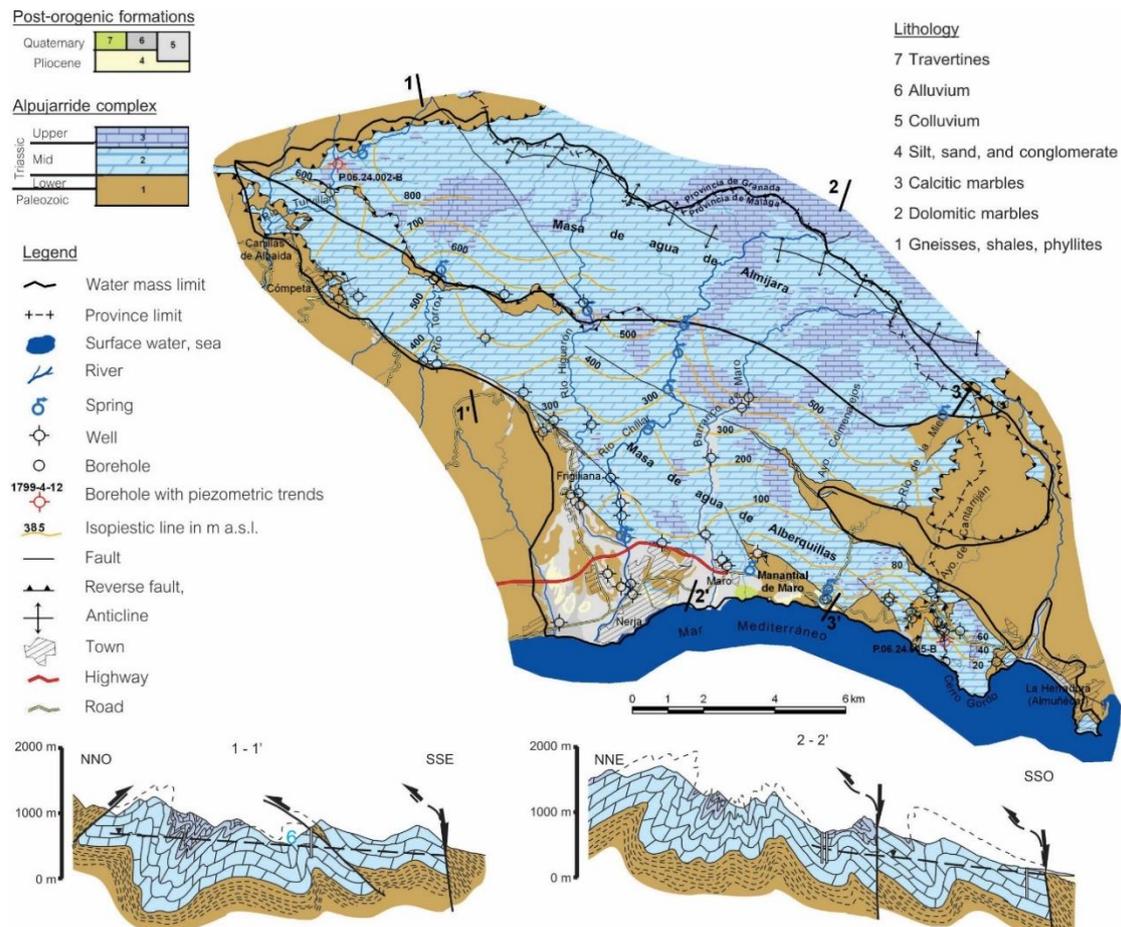


Figure 3. Hydrogeological map of the Almirajara aquifer and hydrogeological cross-sections showing its structural patterns (modified from Pérez & Andreo, 2007).

The marbles, permeable by fissuring, fracturing and karstification, form part of the carbonate aquifer of Nerja - Cerro Gordo, also known as Las Alberquillas aquifer (Figure 3). Recharge in the carbonate aquifer is mainly produced by rainfall infiltration through permeable and interconnected karst features (mostly fractures, fissures, joints, etc.) developed on the surface over the Triassic marbles. Discharge takes place mainly by means of springs with an average outflow of a few hundreds of L/s (Río Chíllar, 350 L/s; Maro, 300 L/s; Río Torrox, 240 L/s) and though to a lesser degree, by pumping and groundwater discharge to the sea, particularly in the Cerro Gordo area (Figure 3) (Andreo et al., 2018).

The exokarstic forms (karren, dolines, sinkholes) are scarce, but there is intense subterranean karstification. Around Nerja Cave, other cavities have been recognised (Figure 4); some of them have access from the surface (Pintada Cave, Km. 301 Cave), and others have been identified by geophysical surveys (Vadillo et al., 2012; Benavente et al., 2017). Since 2013 it has been known that Nerja and Pintada caves are connected (Liñán & del Rosal, 2014), although the physical connection between them is too small to be accessed by speleologists.

## Stop 2: Meteorological station

A weather station belonging to the Spanish Agency of Meteorology (AEMET), located a few meters away from the Nerja Cave, records the external atmospheric parameters every ten minutes: temperature and relative humidity of the air, atmospheric pressure, quantity and intensity of precipitation, and velocity and direction of the wind. The climate in the study area is coastal Mediterranean, with average precipitation slightly below 500 mm/yr, more than 60 % of which falls between October and January. The average temperature ranges from 13 °C in January to 26 °C in August, while average air temperature and relative atmospheric humidity values are 18.8 °C and 66 %, respectively.

The isotopic ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) and hydrochemical composition of the rainwater recorded at the weather station, which infiltrates through fissures and fractures in the marbles and finally drips from the roof of the cave has been characterised (Carrasco *et al.*, 2006). The rainfall (and dripwaters) sporadically present a very high content of  $\text{K}^+$  (up to 49 mg/l) and  $\text{Cl}^-$  (up to 61 mg/l). The transit time (e.g., the time between rainfall reaches the cavity as dripwater) was calculated using  $\text{K}^+$  content, resulting in approximately 2 to 8 months. The range depends on the precipitation quantity and intensity before, during and after the  $\text{K}^+$ - rich rainfall, and the path the water follows through the marbles.

## Stop 3: Research Site (boreholes)

An experimental karst site located near the Nerja Cave has access to nine boreholes drilled some 20 years ago into the vadose zone of the "Las Alberquillas" Triassic carbonate aquifer (RS, Figure 4). Karst openings, cavities and fissures filled with carbonate flowstone deposits were intersected during borehole drilling after recognising negative gravity anomalies in this sector. Later, televiwer logging in the borehole network allowed us to identify several karst features: horizontal and vertical openings and cavities and the relative degree of speleothem development. Since then, the air inside the boreholes of the RS has been studied (Benavente et al., 2010, Ojeda et al., 2019, Ojeda, 2021), revealing  $\text{CO}_2$  concentrations frequently in the range of 20,000 to 40,000 ppmv, with maximum values of almost 60,000 ppmv. There is an active circulation of air masses inside the boreholes between the surface and a reasonably stable, temperate, and humid  $\text{CO}_2$ -rich air reservoir in the vadose zone.

Within the boreholes, there is an interface that distinguishes two separated zones with significantly different concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  (Figure 5). The first zone shows atmospheric values of both  $\text{CH}_4$  and  $\text{CO}_2$ . At a given depth, which varies in the several boreholes, there is a narrow interface where  $\text{CO}_2$  content increases drastically and  $\text{CH}_4$  decreases. This interface oscillates for approximately 10 m from summer to winter because of the drawdown of the vadose air mass associated with advective air processes (Benavente et al., 2015). The second zone is vadose air *sensu stricto*. In the case of  $\text{CH}_4$ , there is a production of biogenic methane associated with sub-atmospheric contents (Ojeda et al., 2019).  $\text{CO}_2$  concentration

increases its content at depth, suggesting the presence of a deep CO<sub>2</sub> source related to the water level (e.g., Atkinson, 1977). The processes of degradation or oxidation of organic matter are supported by the δ<sup>13</sup>C signal.

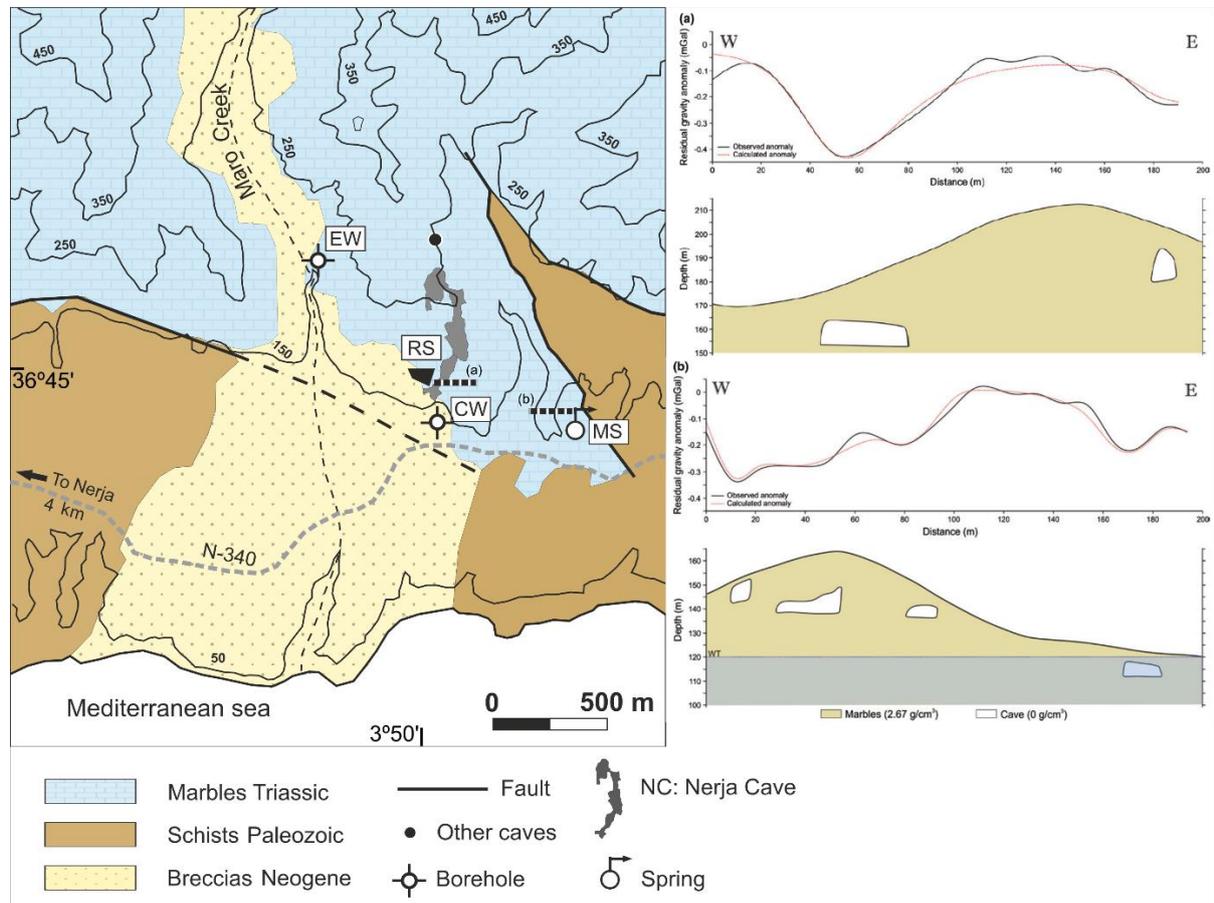


Figure 4. Geological map showing the location of Nerja Cave, the shallow borehole network site (RS), the deeper wells EW (Esparto well) and CW (Cave well), and the Maro Spring (MS). On the right: gravity profile and forward model (bottom). (a) Profile over the NC; (b) Profile over the MS. WT: Water Table. Modified from Benavente et al., 2017.

Other two nearby boreholes Cave Well and Esparto Well (CW and EW in Figure 4), reach the saturated zone of the aquifer below the shallow borehole site and the Nerja Cave. The altitude of the groundwater level is, however, in the range of 60 to 100 m a.s.l., which does not match up with that of the nearby Maro spring (120 m a.s.l.), the principal natural drainage of the aquifer. This suggests: a) the effect of the frequent pumping in this location, and b) the low-permeability boundary between these sectors. In this sense, the karst environment in the study area is characterised by a great vertical heterogeneity, with significant voids and cavities gathered at specific altitudinal intervals but separated by levels of significantly less karstified rock or even bare rock (matrix). This determines the distribution of the water levels in the study area: local perched water levels, as in borehole 6 or the Maro spring system (Benavente et al., 2017), and sites with very low water productivity (e.g., CW), suggesting the existence of spatial differences in the karstification of the marbles. However, laterally, at similar altitudinal levels, the development of the karst openings seems to have more continuity, as suggested by different geophysical techniques (Vadillo et al., 2012; Benavente et al., 2017; Martínez-Moreno et al., 2021). In this context, the cave appears as a vadose subsystem above the groundwater level, with significantly less concentration of CO<sub>2</sub> due to its important natural ventilation.

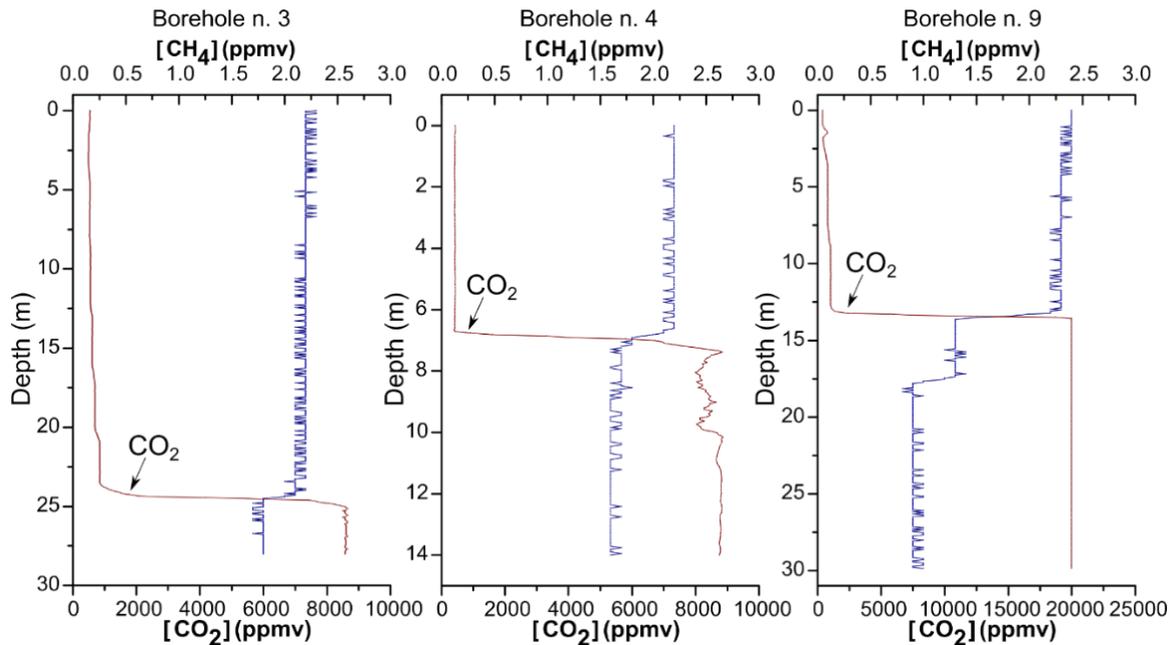


Figure 5. Vertical profiles of CO<sub>2</sub> (red) and CH<sub>4</sub> (blue) concentration in boreholes 3, 4, and 9 (Ojeda et al., 2019).

In order to determine the connectivity between boreholes at the RS, an atmospheric air tracer injection test was carried out (Ojeda, 2021). Tracer testing is a common method in hydrogeology for characterising the hydraulic properties of aquifers. A tracer test requires the use of a substance that, after being released into the subsurface through an injection well, circulates through the system by natural flow patterns. Atmospheric air was chosen as a tracer since the vadose air is CO<sub>2</sub>-rich and presents high <sup>222</sup>Rn activity. Hence, a decline in the CO<sub>2</sub> levels and <sup>222</sup>Rn activity could be observed after injection. This test showed that some boreholes have a direct connection, as depicted by a marked reduction in CO<sub>2</sub> concentration and <sup>222</sup>Rn activity. In contrast, others showed little or no variation, indicating that vadose air flows differently within the karst network and more efficiently through preferential pathways located at particular directions and depths.

#### Stop 4: Maro spring

Maro spring (120 m a.s.l.) is placed ca. 800 m to the East of the Nerja Cave (MS, Figure 4) and is the main point of discharge (300 L/s) of the aquifer where the cavity is located. The outflow suffers an extreme fluctuation because of the rainfall episodes (Figure 6), an indication of the high degree of karstification of the system (Andreo y Carrasco, 1993; Liñán et al., 2000).

Maro spring waters are bicarbonate to sulphate calcic-magnesian type. The average sulphate concentration in the spring is about 200 mg/L. The origin of this sulphate is the gypsum hosted in the dolomitic marbles, as indicated by sulphate isotopic values ( $\delta^{34}\text{S-SO}_4 = 15.4 \text{ ‰}$ ,  $\delta^{18}\text{O-SO}_4 = 12.3 \text{ ‰}$ ; Vadillo et al., 2016), the high correlation between Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>, and the direct observation and subsequent mineralogical characterisation of this mineral in a core sample sampled in a borehole of the research site. Electrical conductivity on average is 700  $\mu\text{S/cm}$ , and the temperature is around 18.8 °C. Waters are slightly over saturated on calcite (SI= 0.43) and dolomite (SI= 0.48). The hydrochemistry evolution (Figure 6) suggests a significant dilution effect, especially distinguished in the conductivity and Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> contents which confirms the karstic type of spring. The high electrical conductivity and the isotopic contents

of the spring (average values  $\delta^{18}\text{O}$ : -7.7 ‰,  $\delta^2\text{H}$ : -45.2 ‰) (Figure 6) lower than the isotopic contents of Nerja Cave dripwaters (average values  $\delta^{18}\text{O}$ : -3.8 ‰,  $\delta^2\text{H}$ : -23.1 ‰), indicate a higher recharge altitude for Maro spring and the existence of longer and deeper flows into the aquifer (Liñán et al., 2002; Vadillo et al., 2016).

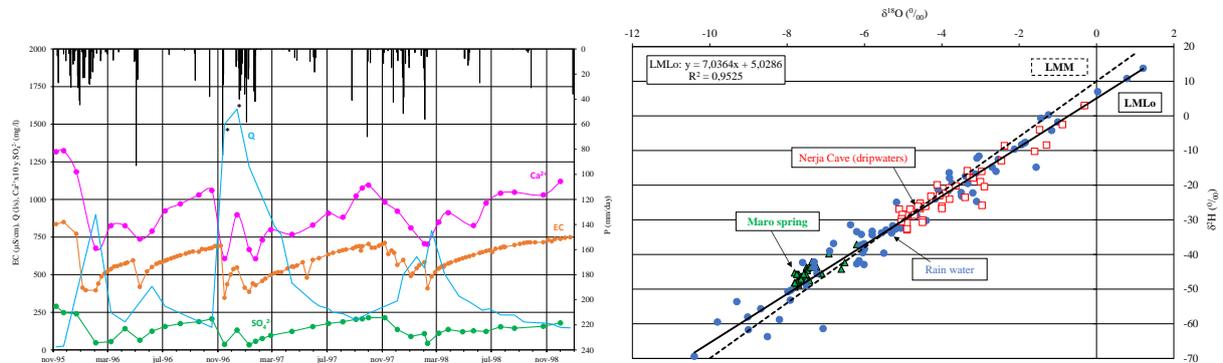


Figure 6. Left: hydrograph of the Maro spring and temporal evolution of the electrical conductivity (EC),  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  contents. (\*) Estimated outflow (Q). Right:  $\delta^{18}\text{O}$ - $\delta^2\text{H}$  diagram obtained from Nerja Cave and surroundings. LMM: world meteoric water line, LMLo: local meteoric water line. Modified from Liñán et al., 2000, 2002.

Two boreholes were drilled near the Maro spring to increase the volume of extracted water. One of them (162 m depth) did not cut the piezometric level, but the other (65 m depth) did when it reached the elevation of the spring. This latter one could not extract more water than the Maro spring. These data suggest that groundwater moves across karstic conduits before reaching the spring. The dynamic water level in the Cave well (400 m to the west of Maro spring, Figure 4) is at 7 m a.s.l. with an outflow of 2 L/s. Another pumping well, some kilometres to the west (Río Chillar), has a dynamic water level at 100 m a.s.l. with pumpings of 100 L/s. This confirms the high variability of piezometric levels and yield of pumping wells, which is an expression of the aquifer's heterogeneity on permeabilities (karstification). The position of Maro spring, perched over the regional water level, would be a consequence of the tectonic uplift of Sierra Almijara and would correspond to an upper level of karstification in this carbonated aquifer.

Recently, a Radon monitoring station was installed in Maro spring in the frame of a scientific collaboration with the University of Sapienza (Roma, Italy). The radon and groundwater hydrochemical data from the spring will be studied to establish their natural variations as a fundamental prerequisite of using Rn as a tracer, or even precursor, of strong earthquakes (Domenico et al., 2018). The study area is strongly seismic, and the final objective is to identify the long-term behaviour of Rn in relation to the seismic cycle.

## Stop 5: Nerja Cave

Nerja Cave was discovered in 1959 and opened to the public one year later. It is one of the most important and large tourist caves in Spain, with about 4,800 m of passages and 450,000 visitors annually. It is also one of the most significant prehistoric sites of the Iberian Peninsula, with more than 600 Pleistocene graphic manifestations. In addition, the Nerja Cave is internationally recognised as a Site of International Geological Relevance, with exceptional geological formations that have enabled the reconstruction of paleoclimate and paleo-earthquakes. Moreover, the cave has three endemic species.

The cavity has a practically horizontal development, lying between 123 and 191 m a.s.l. and covers an area of 35,000 m<sup>2</sup>. It has three known natural entrances: the principal entrance (Tourist entrance) and two

natural sub-circular sinkholes. About a third of the cave, the Tourist Galleries, is open to the public, whilst the other sections, the High Galleries and New Galleries, are only accessed for scientific studies and cave conservation activities. The thickness of the unsaturated zone above the cave is highly variable: from 4 to 50 m in the Tourist Galleries and exceeding 90 m in the non-tourist area.

Since it was discovered in 1959, many multidisciplinary archaeological, geological, hydrogeological, and biological research projects have been carried out in the cave to identify natural and anthropogenic elements and protect their cultural and natural heritage (Carrasco et al., 1995; Docampo et al., 2011; Vadillo et al., 2012; del Rosal et al., 2014).

Hydrogeological studies have been carried in Nerja Cave since 1991 to characterise the dripwater within the cavity, both chemically and isotopically, and to determine the hydrodynamic functioning of the unsaturated zone of the aquifer in which it lies. There are two main types of infiltration water within the cave: one corresponds to the area closest to the entrance, and another represents the rest of the cavity. The first type, with a bicarbonate-sulphate calcic-magnesian facies, presents an average level of electrical conductivity of 1150  $\mu\text{S}/\text{cm}$ . This water is obtained from a nearby borehole, used for the garden irrigation, to later seeps into the cave. The second type has magnesian-calcic bicarbonate facies and a mean electrical conductivity of 468  $\mu\text{S}/\text{cm}$ . It is clearly of meteoric origin, as evidenced by its chemical and isotopic composition (Figure 6). The dripwater is supersaturated in calcite throughout the year and produces calcium carbonate deposits.

Analysis of the natural responses (hydrodynamic, hydrochemical and isotopic) at one of the drip points in the cavity, in terms of the variation in precipitation, reveals the existence of two types of infiltration through the epikarst and the unsaturated zone: one is slow (about 6-8 months), and predominates throughout the year, while the other is rapid (or, relatively less slow; about 1-2 months) and only occurs sporadically when recharge levels are significant in magnitude or intensity.

It has also been determined the main isotopic and hydrochemical content of the condensation water (induced and natural) in the cave (Liñán et al., 2021). Seasonal variations of the isotopic composition were related to the more or less intense evaporation processes that occur inside the cave, depending on the degree of natural ventilation. The higher  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  content in the natural condensation water with respect to induced condensation water evidence the existence of the so-called "*corrosion condensation*" process of the carbonate walls and speleothems of the cave. The high nitrate content in the natural condensation water (mean value up to 46 mg/L) has, most likely, a microbiological origin (presence of *Gammaproteobacteria*, *Nitrosococcaceae* family in the rock substrate), although marine aerosols are not discarded as another possible source for nitrate. Indeed, *Marinobacter*, *Idiomarina*, *Thalassobaculum*, *Altererythrobacter* have recently been found in some Petri dishes placed in different cave halls to study the current carbonate precipitation (Jurado et al., 2022).

Image analysis techniques have been used to quantify the surface occupied by the condensation water and thus quantify the substrate surface potentially exposed to condensation corrosion processes (Figure 7). In Nerja Cave, the areas occupied by the condensation water are highly localised, both spatially and temporally and do not affect rock art. The effect of the corrosion process is not significant concerning their heritage preservation.

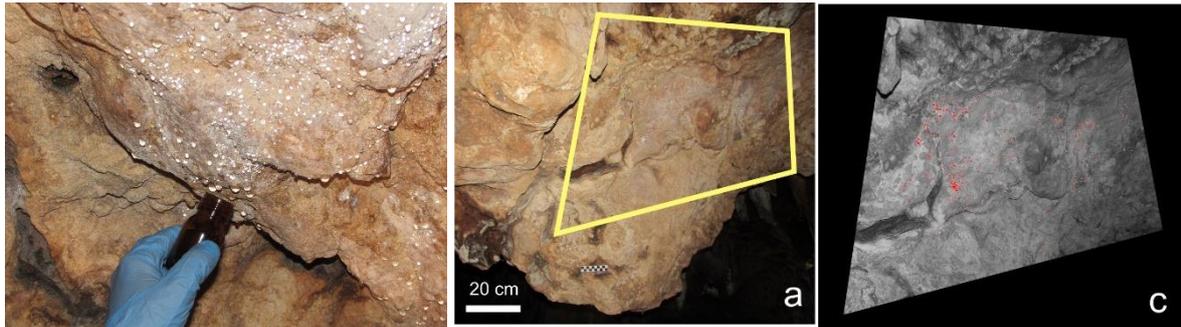


Figure 7. Condensation water sampling method (left) and use of the image analysis: a- sub-area (yellow polygon) used to perform the image analysis; c- sub-area after clipping and quantification of the pixels which correspond to the presence of condensation water (red colour). Modified from Liñán et al., 2021.

The anthropic impact on the cave is an interesting line of research as it is necessary to regulate the visits to the caves for adequate management of this heritage site. The human presence in the cave originates an increase in temperature, humidity and CO<sub>2</sub>. The latest is especially important because CO<sub>2</sub> influences CaCO<sub>3</sub> dissolution and precipitation processes. The produced changes are a function of the number of visitors, the mean stay time, the cave volume and the natural ventilation capacity. The ventilation of Nerja Cave varies seasonally (Liñán et al., 2018, 2020). During the annual cycle, four different ventilation regimes (winter, spring, summer and autumn) and two ventilation modes (DAF and UAF) determine the air exchange and the effect of the anthropogenic impact within the caves. During the winter regime (Figure 8), the strong ventilation regime and the airflow directions from the lowest to the highest entrance contribute to the entry of outside atmospheric air. During the summer regime, the air flows from the highest to the lowest entrances, resulting in very low or even absent ventilation. However, it reduces the anthropogenic impact on the Nerja Cave during the summer when the cave receives the highest number of visitors. The transitional ventilation regimes -spring and autumn- are the most complex of the annual cycle, with changing airflow directions at diurnal and poly diurnal scales.

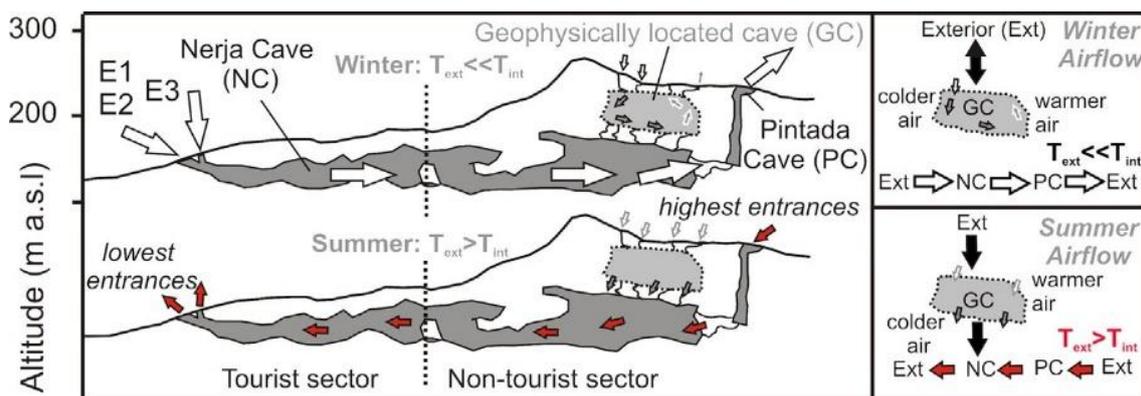


Figure 8. Sketch of the natural ventilation of the Nerja-Pintada cave system depending on the natural ventilation degree and airflow directions: maximum ventilation period (winter, UAF-mode), minimum ventilation period (summer, DAF-mode). Legend: Text: external air temperature,  $T_{int}$ : internal air temperature. E1, E2, E3: lower entrances of the Nerja Cave (Liñán et al., 2020).

Speleothems also have great potential for documenting the records of past climatic conditions. Hydrogen isotope analyses of speleothem fluid inclusions combined with oxygen isotope analyses of speleothem enable the reconstruction of climatic variability in the region (Jiménez de Cisneros & Caballero,

2013). Fluid inclusion isotope analysis drastically improves paleotemperature reconstructions based on speleothem calcite  $\delta^{18}\text{O}$  data. Fluid inclusions trapped in speleothems represent samples of drip water from which the speleothems grew and can provide the  $\delta^{18}\text{O}$  value of cave drip water through time, which is usually the most important unknown in paleotemperature equations. The  $\delta^{13}\text{C}$  values of stalagmite give information on the history of vegetation and climatic conditions. Changes in biological productivity and inorganic processes in response to climatic conditions associated with a climate type originate variations in the  $\delta^{13}\text{C}$  values. Even within the cave, local environmental processes such as evaporation, drip rates, and changes in cave air  $\text{pCO}_2$  controlled by seasonal ventilation can influence the final  $\delta^{13}\text{C}$  values found in the speleothem record.

One of the most recent studies is the research on methane (a potent greenhouse gas) in both the Nerja Cave and the vadose zone, based on seasonal monitoring of  $\text{CH}_4$  and  $\text{CO}_2$  concentration and stable C isotopic ratio (Figure 9) (Ojeda et al., 2019, 2021). The results show that the cave atmosphere is depleted in  $\text{CH}_4$  due to the microbial oxidation (via methanotrophic activity and Proteobacteria) of  $\text{CH}_4$  coming from both the external atmosphere and the vadose/saturated zones of the aquifer (where the  $\text{CH}_4$  is microbially produced, as observed in the borehole research site). This competition process (methanotrophy vs methanogenesis, e.g.,  $\text{CH}_4$  consumption vs  $\text{CH}_4$  production) may be an important factor limiting the sink potential of karst caves.

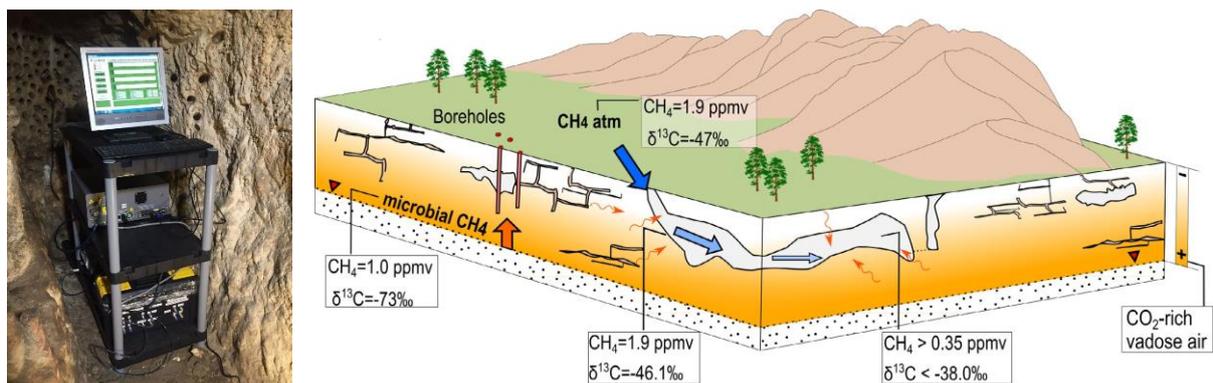


Figure 9. Left: Laser CRDS (Cavity Ring Down Spectroscopy) spectrometer inside Nerja Cave to measure air  $\text{CH}_4$ ,  $\text{CO}_2$  concentration and isotopic composition ( $\delta^{13}\text{C}-\text{CO}_2$  y  $\delta^{13}\text{C}-\text{CH}_4$ ). Right: sketch summarising  $\text{CH}_4$  sources and sinks in the Nerja karst system. Blue arrows: atmospheric methane sources and their progressive depletion inside the cave. Orange arrows: microbial methane source in the vadose zone or in water-filled fractures, migrating towards the cave. A layer of  $\text{CO}_2$ -rich gas is shown (Ojeda et al., 2019).

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