National Cave
and Karst Research Institute
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NCKRI SYMPOSIUM 9 Proceedings of the 17th Multidisciplary Conference on Sinkholes and the Engineering and Environmenal Impacts of Karst

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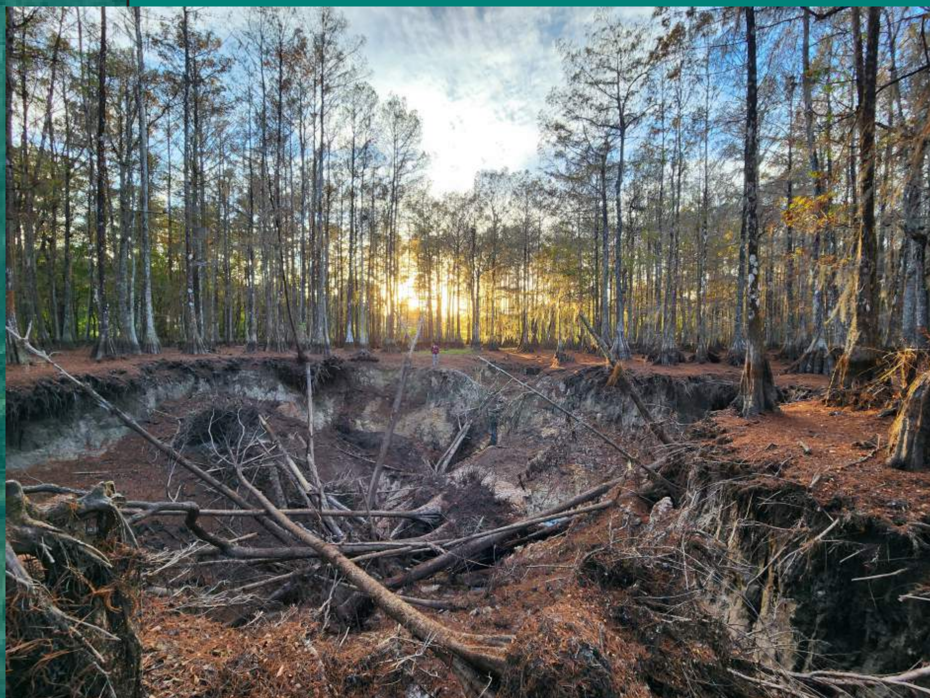
NCKRI SYMPOSIUM 9

Proceedings of the 17th Multidisciplinary Conference on Sinkholes and the Engineering and Environmental Impacts of Karst

Edited by: Lewis Land, Clint Kromhout, and Simeon Suter



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NATIONAL CAVE AND KARST RESEARCH INSTITUTE
SYMPOSIUM 9

PROCEEDINGS OF THE 17th MULTIDISCIPLINARY CONFERENCE ON

SINKHOLES AND THE ENGINEERING AND ENVIRONMENTAL IMPACTS OF KARST

EDITORS:

Lewis Land
National Cave and Karst Research Institute

Clint Kromhout
Florida Geological Survey

Simeon Suter
Pennsylvania Geological Survey

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FOREWORD

Welcome to sunny Tampa, Florida, and to our first in-person Multidisciplinary Conference on Sinkholes and the Engineering and Environmental Impacts of Karst in five years. The Sinkhole Conference series, as it is more commonly known, got its start in the state of Florida in 1984 thanks to the efforts of the late Barry Beck. Although several subsequent conferences have been held in this state since the series began, this is the first to be held in Tampa. The National Cave and Karst Research Institute (NCKRI) assumed responsibility from PE LaMoreaux & Associates, Inc. (PELA) for managing the Sinkhole Conference series in 2011. PELA continues to serve as a co-sponsor, and this year it is our pleasure to be sharing our hosting duties with the University of South Florida, which is serving as the conference venue thanks to the support of its School of Geosciences.

As most of you are certainly aware, Florida's unique geology is ideally suited for a sinkhole-themed conference. Karst phenomena are abundant throughout the state, both onshore and offshore, and most of the Florida Platform is underlain by a regional karstic aquifer. We will visit some of these karst features during the scheduled field trips on Monday and Friday. The research documented in this proceedings volume continues a long history of karst investigations in Florida dating back almost a century.

As senior editor I would like to thank my assistant and associate editors for their efforts in producing this proceedings volume, the authors for contributing their papers, as well as all those on the Organizing Committee who have contributed to making this event happen.

Lewis Land, Proceedings Editor
National Cave and Karst Research Institute
Carlsbad, NM USA

Edited by:

Lewis Land
National Cave and Karst Research Institute
400-1 Cascades Ave.
Carlsbad, NM 88220 USA
575-932-9912
lland@nckri.org

Clint Kromhout
Florida Geological Survey
Florida Dept. of Environmental Protection
3000 Commonwealth Blvd, Suite 1
Tallahassee, FL 32303 USA
850-617-0332
clint.kromhout@floridadep.gov

Simeon Suter
Pennsylvania Geological Survey
3240 Schoolhouse Road
Middletown, PA 17057-3534
717-702-2047
ssuter@pa.gov

VERTICAL SHAFT MONITORING TO ASSESS MIXING PROCESSES IN KARST AQUIFERS

Beatriz de la Torre Martínez
Department of Geology and Center of Hydrogeology of the University of Malaga (CEHIUMA), Boulevard Louis Pasteur, 31, Malaga, Spain, 29010, delatorrem@uma.es

Matías Mudarra Martínez
Department of Geology and Center of Hydrogeology of the University of Malaga (CEHIUMA), Boulevard Louis Pasteur, 31, Malaga, Spain, 29010, mmudarra@uma.es

Bartolomé Andreo Navarro
Department of Geology and Center of Hydrogeology of the University of Malaga (CEHIUMA), Boulevard Louis Pasteur, 31, Malaga, Spain, 29010, andreo@uma.es

José Manuel Gil Márquez
Department of Geology and Center of Hydrogeology of the University of Malaga (CEHIUMA), Boulevard Louis Pasteur, 31, Malaga, Spain, 29010, josemgil@uma.es

Abstract

Karst springs often are the key to inferring the global functioning of their whole catchment area. The drainage of such springs represents the total amount of effective infiltration on the recharge area, regardless of the transit time of these flow components within the carbonate aquifer. However, springs rarely provide information about sub-catchments or compartments nor enable access to intermediate positions upstream of the groundwater outlet.

Jarastepar massif is an alpine karst aquifer affected by a major tectonic contact of the Betic Cordillera (South Spain). The aquifer is drained by three permanents springs placed on metamorphic rocks (75% of the annual recharge), as well as by an overflow spring (25%), known as Pozancón, sited between the recharge area (Jurassic limestones) and the permanent springs. This outlet corresponds to a vertical cave 30 m deep, linked to horizontal conduits, where the accessible water table varies from 643 (low water) to 664 m a.s.l. (overflowing threshold). Aerial drainage (up to 25 m^3/s) is only visible during the most significant recharge events for several hours.

The analysis of the discharge and water level series recorded at the outlet has allowed defining four hydrodynamic stages with different proportions of flows in mixing processes: 1) *piston-flow* (deep saturated zone) during the first hours after recharge, 2) *outflowing* (fast flow -~15 hours- from the ground) when water table exceeds the overflowing threshold, 3) *declined* piezometric level just after visible drainage stops but recharge water still arrives to the shaft, and 4) *depletion* as the lowest hydraulic head (dry season). These hydrodynamic stages coincide with changes in the slope of the flow (level) duration curve. Altogether, flows from different compartments of the aquifer and with different residence times can be detected in a small alpine system with a clear karst behavior if observations at an intermediate point is available.

Introduction

Karst aquifers are one of the primary potable water sources since they provide 9.2% of the world's drinking water and contribute to 13% of the total global withdrawal of groundwater (Stevanović, 2019). Records from karst springs are key to obtaining quantitative information on karst aquifers' hydrogeological functioning and water resources (Malík, 2015). Flows from such springs represent the total amount of effective infiltration on the recharge area, regardless of the time any component of these flows has spent moving through the carbonate aquifer. However, these observation points rarely provide information about sub-catchments / compartments or enable access to intermediate positions between recharge and discharge areas.

Recession curve analyses of the spring hydrographs have commonly been used to characterize karst aquifers, evaluate hydraulic properties, and estimate groundwater resources (Padilla et al., 1994; Dewandel et al., 2003;

Kovács et al., 2005; Fiorillo, 2014). In other cases, time series analysis, considering rainfall as input and complete spring discharge series as output, helps to infer the hydrodynamic behavior of these systems (Mangin, 1984; Pulido-Bosch et al., 1995; Panagopoulos and Lambrakis, 2006; Katsanou et al., 2011). Using autocorrelation and cross-correlation functions can efficiently describe an aquifer's global response time and its capacity to attenuate the input signal (Panagopoulos and Lambrakis, 2006).

Some authors have adapted the previous methodologies to treat piezometric data records instead of flow rates. For example, the Master Recession Curve (MRC) method, consisting in an automated procedure that plots the recession curves and analyses them using linear and nonlinear regression (Posavec et al., 2006, 2010), has been progressively improved for karst aquifers research (Arnold et al., 1995; Posavec et al., 2006; Hatipoglu-Bagci and Sazan, 2014). Another approach for hydrodynamic analysis uses flow-level-duration curves. This method represents a cumulative frequency curve showing the percent of the time during which the discharge (or water level) is equal to or exceeds a specified threshold in each period. This approach contributes to assessing the range and variability of spring discharge (Hartmann et al., 2013; Kovačič, 2010; Malík, 2015).

The combination of hydrodynamic responses with hydrochemical variations recorded in springs permits understanding the hydrogeological functioning of karst systems and inferring the mixing process along flow paths. Thus, Celle-Jeanton et al. (2003) deduced the participation of different vertically distributed compartments of a French Jura karst aquifer from the combination of chemical (NO_3^-, Mg^{2+} and Total Organic Carbon -TOC-) and isotopic ($\delta^{13}C_{TDIC}$) parameters. Emblanch et al. (2003) used $\delta^{13}C_{TDIC}$ as an isotopic tracer to quantify the role of the unsaturated zone in different hydrodynamic stages of the Vaucluse Karst systems.

In this work, the time series of hydraulic head, groundwater temperature, and electrical conductivity, recorded at the bottom of a vertical shaft with access to water table dynamics, have been jointly analyzed to gain deeper insight into the mixing processes occurring upstream of the main outlets of an alpine karst aquifer. Water level variations and the hydrochemical and isotopic signals (major dissolved ions, TOC, and $\delta^{13}C_{TDIC}$) recorded during three years have been used to characterize up to 4 hydrodynamic stages with implications in the origin and mixing of groundwater before being drained by the permanent springs of the aquifer.

Pilot site

The study area considered in this research (Sierra de Jarastepar aquifer) is in the western part of the province of Malaga, in Southern Spain (Figure 1A). Topography is rough, with altitudes ranging from 400 to 1427 m a.s.l. The climate is temperate Mediterranean, with rainfalls occurring mainly during the spring and autumn. Mean historic annual precipitations and temperature air values are close to 1000 mm and 14ºC, respectively. From September 2014 to September 2017, the research period considered in this work, the average precipitation value was 934 mm, whereas the mean air temperature was 15.8ºC (De la Torre, 2020).

From a geological point of view, the carbonate aquifer beneath Sierra de Jarastepar (Figure 1B) presents a complex geological structure, defined by the overthrust (toward NW) of two main tectonic units of the Betic Cordillera: the External Zone and the Internal Zone. The Internal Zone occurs in the southeast part of the study area as a narrow and elongated NE-SW outcrop composed of Triassic carbonate rocks, overthrust above rocks of the External Zone to the northwest. Rocks of the External Zone consist of Jurassic dolostones and limestones (500-550 m thick), underlain by Triassic clays and evaporitic rocks and overlain by Cretaceous-Paleogene marly limestones and marls (Martin-Algarra, 1987). Between both tectonic units, flysch-type clays and sandstones are discontinuously imbricated. In detail, the geological structure of the External Zone formations is characterized by the normal limb, with moderate dip (25º–35º), of a NE–SW anticlinorium fold. On the other hand, carbonate rocks from the Internal Zone consist of a tectonic slice whose stratified layers plunge moderately toward the SE (Figure 1C). The entire structure has been affected by more recent fractures of NE–SW, NW–SE, and E-W directions.

In hydrogeological terms, the principal carbonate aquifer of the pilot site is made of fractured and karstified Triassic and Jurassic carbonate rocks (38 km^2), limited in almost all their borders by low permeability materials (Triassic clays, Cretaceous-Paleogene marls, and Paleozoic metapelites). The SE border corresponds with a major tectonic contact between Triassic dolomitic rock and metapelites (Figure 1B). Water recharge occurs by rainwater infiltration, which is faster over the karstified outcrops of Jurassic limestones (Figure 1B). In addition, concentrated infiltration occurs through several swallow holes. Discharge mainly takes place by three permanent springs located at the southern border of the carbonate outcrops (Figure 1B) and through two overflow springs (named Pozancón and Alfaguara), sited near the tectonic contact between the Jurassic limestones and the outcrops of flysch-type clays and sandstones (Figure 1B, C, and D). Previous studies highlighted the considerable hy-

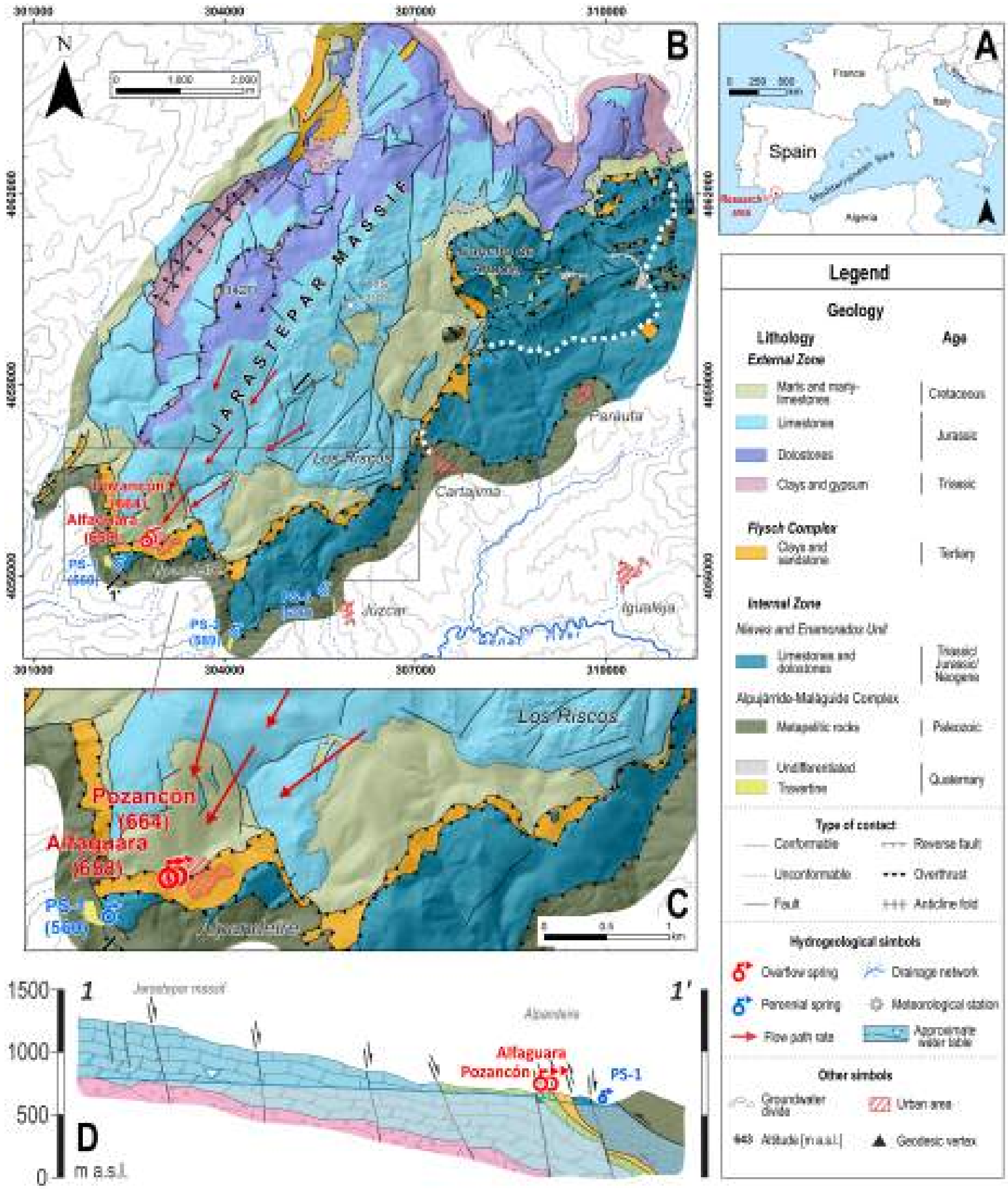

Figure 1. *A) Geographic location; B-C) geological sketch; (D) cross-section (modified from De la Torre et al., 2020 and Gil-Márquez et al., 2020) of Jarastepar massif and surrounding areas.*

drogeological complexity of the site, related to the geological-structural framework, which affects the spatial distribution of groundwater flow patterns, both in terms of speed and water quality (De la Torre et al., 2020; Gil-Márquez et al., 2020).

Pozancón shaft is a subvertical cave (Figure 2) approximately 30 m deep with a 40 m horizontal route, which becomes an overflow spring during major recharge events. Access to the piezometric level of the aquifer is possible in intermediate and low water conditions. Pozancón shaft is closely interconnected with Alfaguara spring (Figure 2), and the latter (658 m a.s.l.) emerges first during rainfall. Only if the recharge is relevant, the piezometric level rises enough to give rise to visible discharge through Pozancón overflowing threshold at 664 m a.s.l. Speleological explorations prior to this study allowed the description of the Pozancón shaft as a vertical cave that presents horizontal development towards the northeast in the saturated level (Figure 2). The maximum diameter of the entrance mouth is 8 m and gradually decreases until its narrowest passage (1.5 m), which is between 9 and 13 m deep. From this point, a partially flooded room culminates in a siphon, through which a horizontal conduit can be observed, still not fully explored.

Methods

Hourly data of rainfall and air temperature were measured by a meteorological station (*DAVIS*, *VantagePro2* model) installed at 1317 m a.s.l. over the Jurassic carbonate outcrops (Figure 1B). Continuous records of water level (cm), temperature (ºC) and electrical conductivity (μS/cm) in Pozancón shaft were recorded through an *OTT* sensor, *ecoLog 800* model. Variations in the natural responses (hydrodynamic, hydrochemical, and hydrothermal) are extensive to Alfaguara spring, given its proximity (Figure 2). Dataset was collected with an hourly interval from October 1, 2014 to September 30, 2017. The accuracy of the device is respectively ±1 cm (hydraulic head), ±0.01 °C (temperature), and ±1% for the electrical conductivity.

In addition, 140 field trips were carried out during the study period for water sampling and for *in situ* measurements of electrical conductivity (EC) and temperature (T_w). A rating curve for the springs aerial drainage was designed based on 28 single measurements of the joint discharge (Alfaguara and Alfaguara + Pozancón) rate obtained using sodium chloride or salt (NaCl) as a tracer by applying the instantaneous injection method and an *ETRELEC™ Salinomadd* (Meléndez and Bros, 2010). The resulting rating curve was composed of two equations (Figure 3): one when only Alfaguara was active and another more for the simultaneous drainage of Pozancón + Alfaguara, with correlation coefficients of 0.99 and 0.92, respectively.

Chemical and $\delta^{13}C_{TDIC}$ isotopic analyses were carried out at the Laboratory of the Center of Hydrogeology of the University of Malaga (CEHIUMA). Alkalinity (HCO_3^-) was determined by volumetric titration using 0.02 N H_2SO_4 to pH 4.45. Chemical analyses of the major components were performed through high pressure ionic

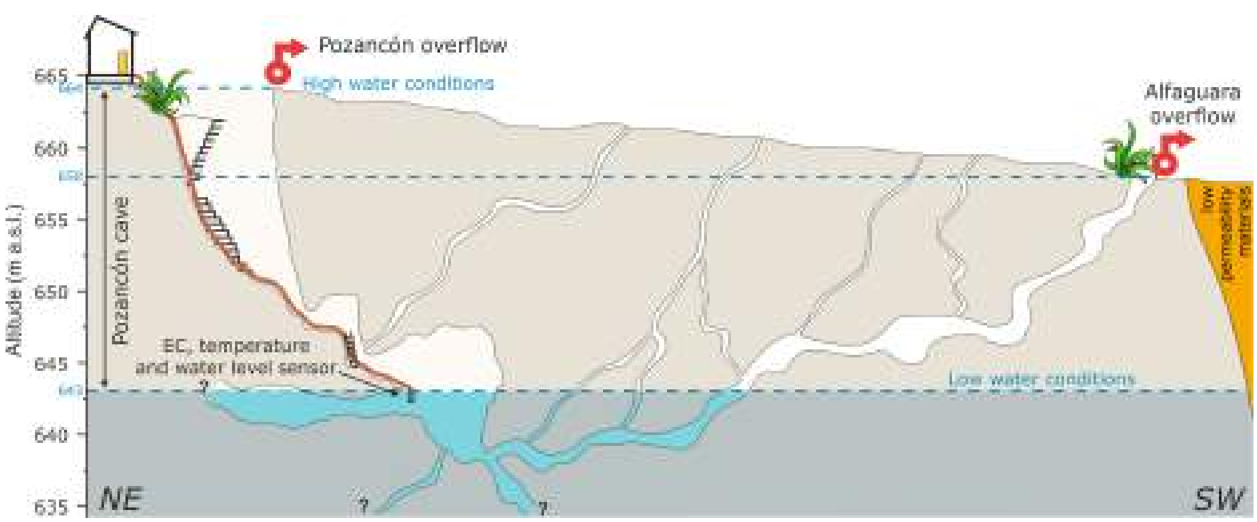

Figure 2. *Sketch of the Pozancón shaft and Alfaguara spring.*

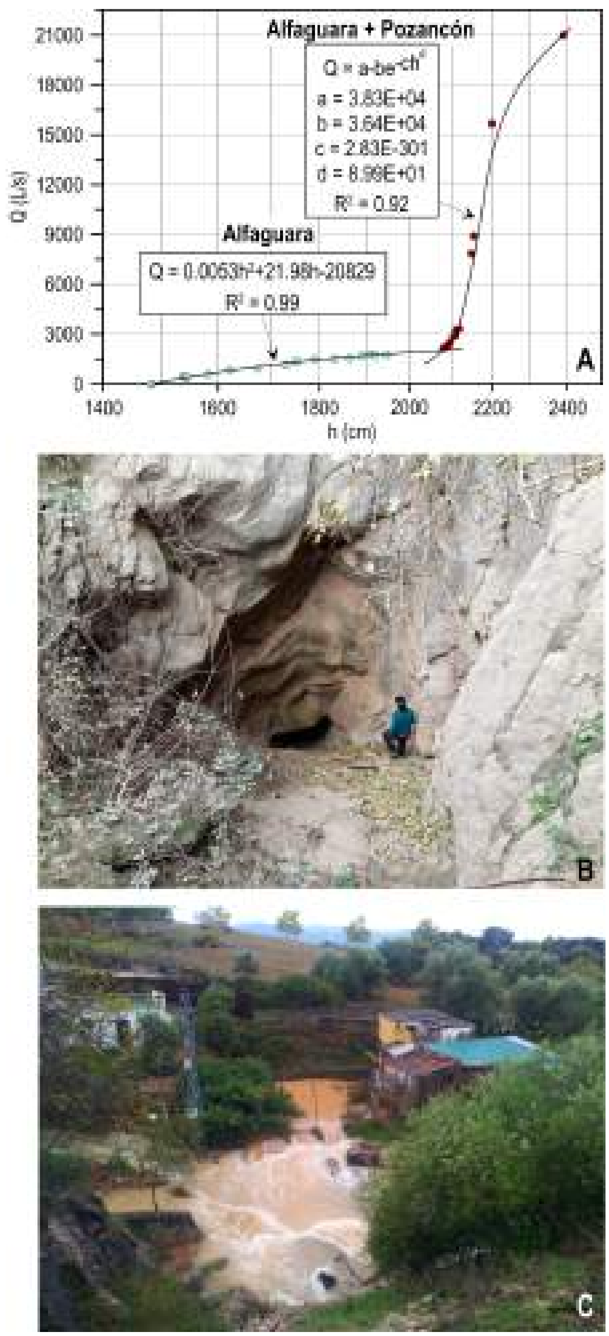

Figure 3. *A) Rating curve for Alfaguara and Alfaguara+Pozancón springs. Q, discharge; h, height of water level. B) Vertical cavity (Pozancón spring) at the bottom of which the water level, electrical conductivity, and temperature sensor (OTT, ecoLog 800®) were installed. Location shown in Figure 2. C) Pozancón spring during one recorded overflow event (October 2015).*

chromatography (HPIC METROHM™ Compact 930 IC Flex and METROHM™ Compact 881 IC Pro). Total organic carbon (TOC) was measured with a SHIMADZU™ V-TOC carbon analyzer. The Isotopic signature of total dissolved inorganic carbon ($\delta^{13}C_{TDIC}$) was analyzed with a PICARRO™ G1111-I Analyzer for Isotopic CO_2, coupled with an OI-A™ Aurora 1030 TOC Analyzer. Values of $\delta^{13}C_{TDIC}$ are given in parts per mil relative to V-PDB (*Vienna-Pee Dee Belemnite*).

Time series analyses, such as signal processing methods, are commonly used in hydrological studies to gain a basic understanding of karst aquifers. Generally, a quantitative treatment is carried out according to the proposed methodology by Mangin (1975; 1984), based on the recession curve analysis of karst springs. However, a different methodology has been used here to obtain hydraulic parameters from intermittent outlets, since data consists of piezometric levels and not only discharge. The procedure used applies a set of algorithms (linear and non-linear regression) programmed in Excel-Visual Basic, which allows the combination of each depletion curve into a single plot defined by a simple exponential model. This methodology has been successfully applied in other karst systems (Posavec et al., 2006).

Correlation and spectral analyses were also used, which are a type of time series analysis for studying transfer functions between input (effective rainfall) and output (discharge or water level variations) using statistical functions (Mangin, 1975; 1984; Massei et al., 2006; Paiva and Cunha, 2020).

The analysis of flow-duration curves has also been carried out, although in this case corresponds to the potentiometric-duration curve, based on the continuous series of the piezometric level recorded in the Pozancón shaft. The probabilistic plot curve from this approach represents the percentage of days in which the piezometric level is equal to or lower than a given one. So that, it expresses the frequency with which a certain level occurs (Custodio and Llamas, 1983). If this frequency is divided by the number of days considered, the result is the occurrence probability of a given level. Changes in the slope of this curve (probability vs. piezometric level) denote variations in the speed of water level changes (Mangin, 1970; 1975). Thus, a higher slope represents an increase in the percentage of levels for a certain number of classes; that is, a slower variation of the levels. On the contrary, a smaller slope represents faster variations of the levels for certain classes.

Results and interpretations

Records of hydraulic heads in Pozancón shaft are characterized by rapid variations because of recharge events, as shown in Figure 4. The joint discharge of Alfaguara + Pozancón presented an average value over 2 m^3/s (1961 L/s), if only effective drainage periods are considered, with a maximum flow peak of 21.4 m^3/s (21433 L/s; November 2014). The magnitude of the hydrodynamic response is proportional to the cumulative rainfall and the initial hydraulic conditions in the aquifer. Accordingly, this information testifies that the aquifer there has clear karst behavior with a good connection between the conduit network and the spring.

Figure 5 shows the average recession curve (red line) obtained from all recession segments recorded in Pozancón during the study period. The analysis of the recession curve according to the simulation of the average value of recession constant (α) showed a good fit ($R^2 = 0.95$), with a value of $-7.65 \cdot 10^{-1}$ $days^{-1}$, which is the highest estimated through this analysis in karstic aquifers (Katsanou et al., 2015; Arbi-Kurniawan et al., 2019).

The autocorrelation function (ACF) of daily precipitation falls quickly and reaches the confidence level (rk = 0.2) after 2 days (Figure 6). This indicates that no memory effect is detected in daily rainfall, so it can be considered a purely stochastic process. The full-time series of water level recorded in the Pozancón shaft reaches rk = 0.2 after 18 days (Fig. 6). However, when performing an annual autocorrelation (by hydrological year), the confidence level varies between 7 (2014/2015) and 16 days (2016/2017). This reflects the low memory effect of the aquifer sector drained through Pozancón, comparable to other well-karstified carbonate aquifers (Mangin, 1984; Liñán, 2003; Rahnemaei et al., 2005). The

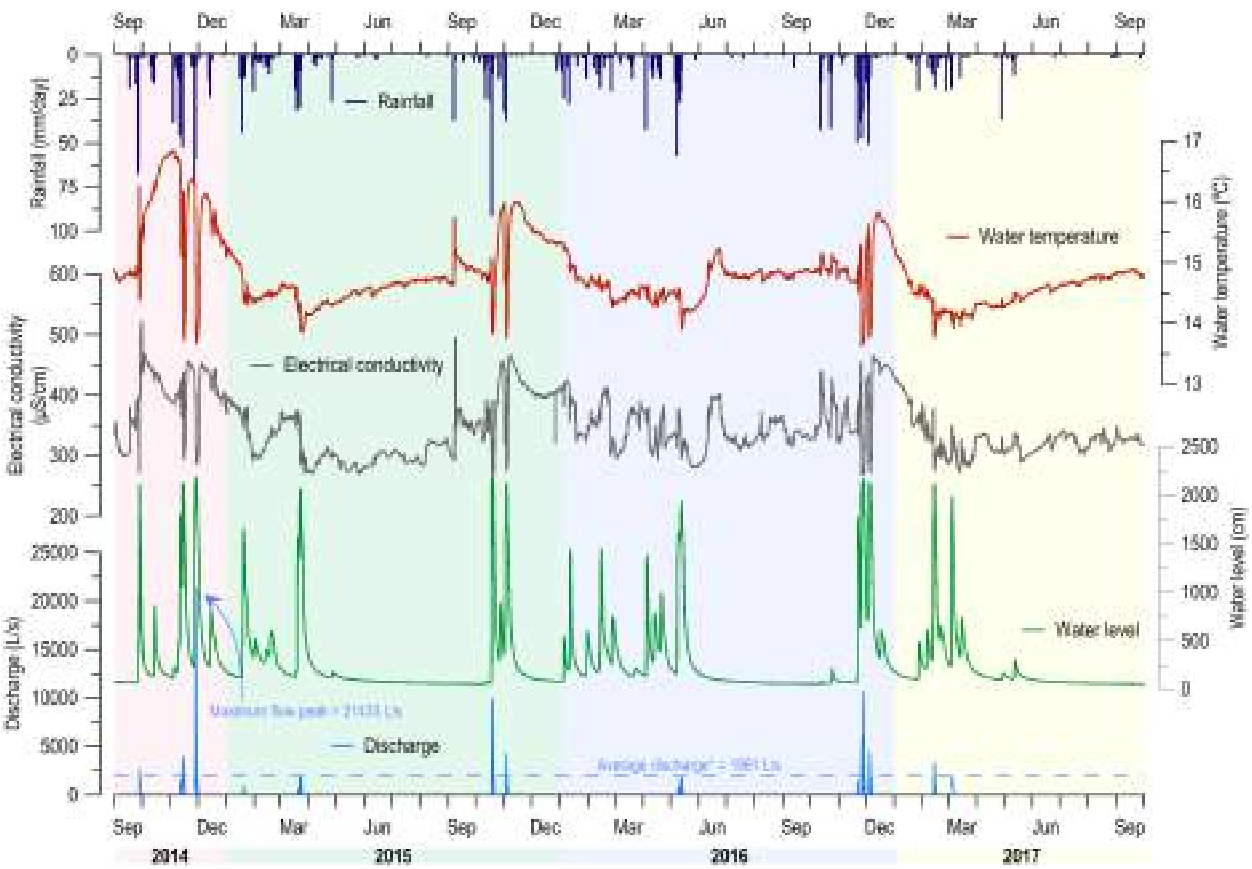

Figure 4. *Temporal evolution of discharge rate (Pozancón+Alfaguara), water level (Pozancón), electrical conductivity, and water temperature recorded in Pozancón shaft during the study period, together with precipitation events (Modified from De la Torre et al., 2020). *Average discharge value if only effective drainage situations are considered.*

rapidly decreasing trend of the autocorrelation functions means a limited storage capacity of the aquifer and that groundwater is released from the system immediately (during aerial drainage). Furthermore, functions show a more rapid decline within the first four days, followed by a slightly slower decline up to 10 days (Figure 6). The first time-lag would be related to the influence of karst conduits (rapid flows), while the second one has a certain influence of diffuse drainage (flow through fractures and bedding planes). The autocorrelation disappears (rk ≈ 0.0) around 40 days, which as in other karst systems is attributed to the influence of aquifer reserves (Rahnemaei et al., 2005; Paiva and Cunha, 2020).

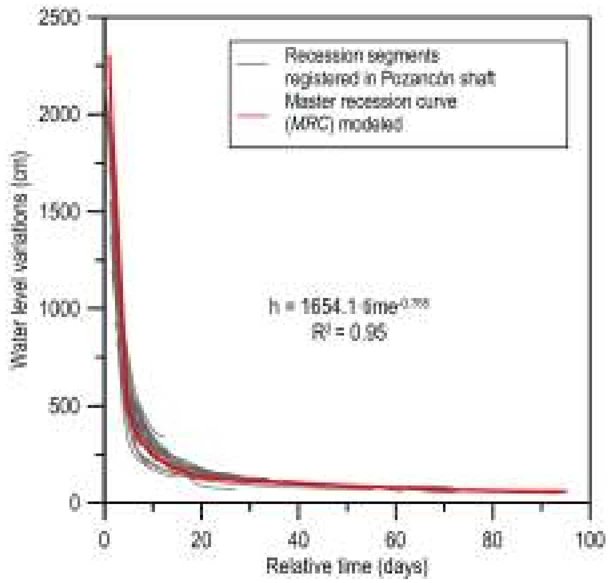

Figure 5. *Representation of the modeling of the master recession curve (MRC) obtained from the methodology proposed by Posavec et al. (2006) for the record of water level in Pozancón shaft.*

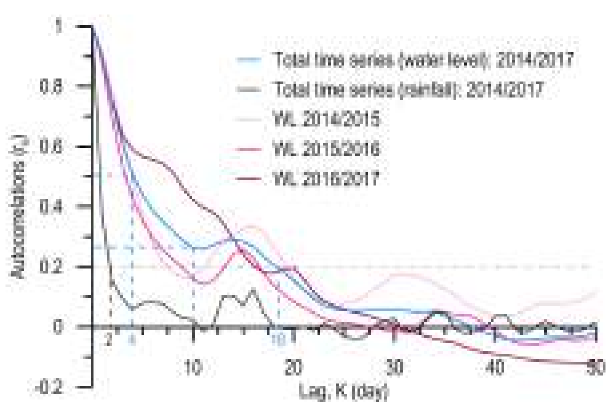

Figure 6. *Autocorrelation function for daily series of water level registered in Pozancón shaft and rainfall recorded in the meteorological station located in the central part of the recharge area (see situation in Figure 1B) during the study period (October 2014 to September 2017).*

Figure 7 shows the results of the flow-level-duration curve analysis carried out in the framework of this work. The piezometric data series recorded in the Pozancón shaft has been divided into 0.5 m classes, and the accumulated frequency has been calculated. The results indicate that 50% of the time water level is lower than 643 m a.s.l. (Figure 7A). The cumulative probability of the classified water levels, on a probabilistic scale, allows the distinguishing of five different stages (S_1-S_5) according to changes in the slope (Figure 7B).

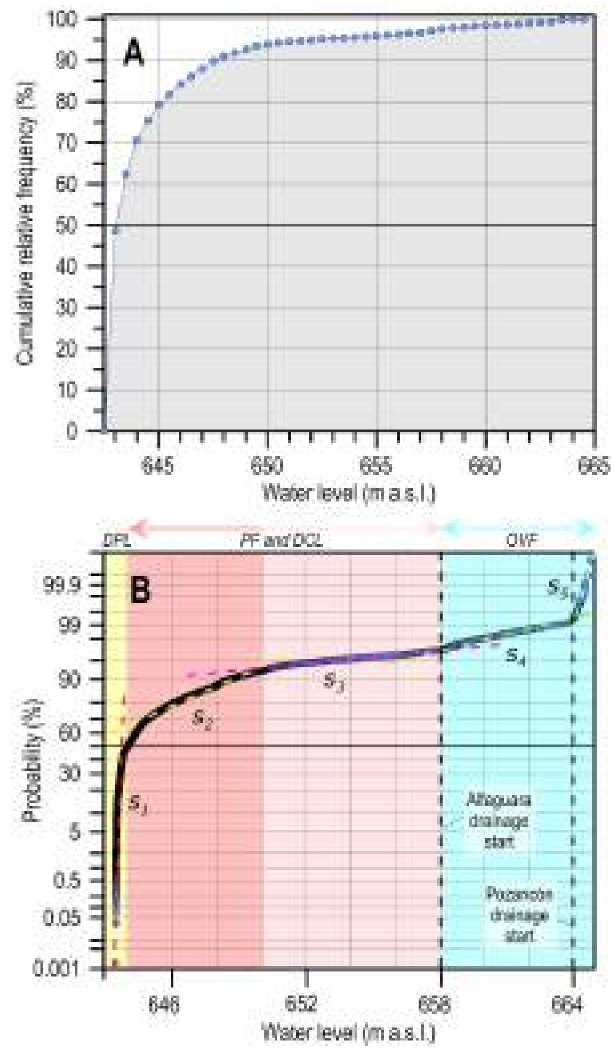

Figure 7. *Analysis of flow–level-duration curves carried out in the framework of this work, in arithmetic scale (A) and probabilistic scale (B). Hydrodynamic conditions: DPL, depletion; PF, piston-flow; DCL, decline; OVF, overflow.*

S_1: Hydraulic head is less than 644 m a.s.l., related to the end of depletions. In this case, the water level variation is very slow, which translates into a very high slope of the curve.
S_2: Hydraulic head varies between 644 and 650 m a.s.l., coinciding with rises and declines of water level. The slope is notably lower with respect to S_1, because variations of water level within Pozancón shaft occur a little bit more quickly.

S_3**:** Corresponds to piezometric level of between 650 and 658 m a.s.l., a stage related to rises and declines but, unlike S_2, coincides with situations before or after periods of visible discharge.

S_4: Hydraulic head varies between 658 and 664 m a.s.l., variations in water level are slower than in the previous stage. This is related to situations where Alfaguara presents aerial drainage, but the water level does not exceed the Pozancón overflow threshold.

S_5: Water level is higher than 664 m a.s.l., when Alfaguara and Pozancón overflows have simultaneous aerial drainage because of significant recharge events. The steep slope is because these level variations occur slowly, in accordance with the geometric characteristics of this point (Pozancón spring), so that small rises in water level cause considerable increases in the discharge.

The significant change in slope observed between S_1 and S_2 (Figure 7B) could be favored by the difference between a lower development of the karst network in the strip where a 50 % probability of piezometric level variations accumulates, S_1 (between 643 and 644 m a.s.l.), and the section immediately above, S_2 (between 644 and 650 m a.s.l.), in which this statistical value is lower (35 %) and whose karst development would possibly be higher. On the other hand, the slope difference between S_4 and S_5 is conditioned by the beginning of the Pozancón drainage (from 664 m a.s.l.) since this is the highest overflow level.

Simultaneously to the hydrodynamic recording, periodic hydrochemical and isotopic analyses were performed and a continuous recording of the groundwater temperature and electrical conductivity in Pozancón shaft (Figure 4). The joint analysis of all this information has allowed defining four hydrodynamic stages with different proportions of flows in mixing processes:

1. *Piston-flow* (deep saturated zone), during the first hours after recharge.
2. *Outflowing* (fast flow –during the first 15 hours- from the soil), when water table exceeds the overflowing threshold (referred to the drainage of Alfaguara and Pozancón jointly; that is, S_4 and S_5).
3. *Declined* water level, when aerial drainage stops but recharge water still arrives to the shaft.
4. *Depletion*, the lowest hydraulic head (dry season). These hydrodynamic stages coincide with changes in the slope of the flow (level) duration curve (Figure 7B). It should be remembered that the visible discharge of Alfaguara and Pozancón has been treated jointly (S_4+S_5).

The highest values of electrical conductivity and water temperature (461 µS/cm; 16.9 ºC) were recorded at the first impulse detected after recharge events as the result of a significant *piston-flow* effect, and immediately after the overflow springs stopped the aerial drainage, during *decline* period (Figure 4). These rises in mineralization and temperature values are directly associated with increased numbers in the concentration of HCO_3^-, Ca^{2+}, and Mg^{2+} (De la Torre et al., 2020). In addition, the highest mean TOC values for a stage (0.94 mg/L, *piston-flow*; 0.82 mg/L, *decline*) were also recorded during these hydrodynamic conditions (Fig. 8). Meanwhile, the less negative values of $\delta^{13}C_{TDIC}$ (up to -8.2 ‰; Fig. 8) were recorded in the water samples collected in the Pozancón shaft when the water level was ascending (*piston-flow*), between 644 and 658 m a.s.l. However, the most negative values were recorded during times of *decline* (Figure 8) and not during periods of *overflow*, as would be expected. This is because the flows drained by the overflow springs during periods of aerial drainage correspond to recently infiltrated water, much of which has been infiltrated through concentrated recharge (swallow hole). The residence time of these flows in the aquifer is short (hours or a few days), and they have a $\delta^{13}C_{TDIC}$ signal with a greater influence from rainfall (-8.0 ‰; Clark and Fritz, 1997). However, when the effective drainage ceases and the *decline* conditions recorded in Pozancón begin, the proportion of recently infiltrated water progressively decreases and the fraction of water from diffuse recharge through soil (-22.0 ‰; Clark and Fritz, 1997) increases.

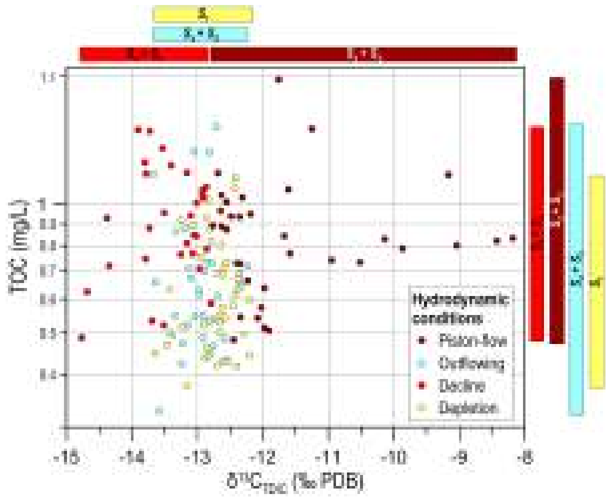

Figure 8. *Relationship between TOC concentration and $\delta^{13}C_{TDIC}$ signal of water samples collected at Pozancón shaft during different hydrodynamic conditions.*

When the water table is above the threshold defined by Alfaguara altitude (658 m a.s.l.) in the first place and Pozancón threshold (664 m a.s.l.) afterward, a marked decrease in mineralization and water temperature is recorded (Fig. 4), reaching values of 246 µS/cm and 13.7 ºC, respectively. Similarly, the $\delta^{13}C_{TDIC}$ signal varies towards more negative values, up to -13.7 ‰. These hydrochemical characteristics coincide with the hydrodynamic conditions of high waters, presented as *overflowing* steps (Figure 7B; > 658 m a.s.l.), in which the predominant flows are recently infiltrated waters from the soil. On the other hand, the periods of low water correspond to the *depletion* steps (Figure 7B; < 644 m a.s.l.). During this time, minimal hydrochemical, hydrothermal, and isotopic variations were recorded. The mean values of EC and water temperature were 320 µS/cm and 14.7 ºC, respectively. However, a slight increasing trend appears during the progressive decrease of the water table in the dry months. Thus, as the piezometric level slowly descends, the flows present a greater proportion of water with a longer residence time in the aquifer, with $\delta^{13}C_{TDIC}$ values that vary between -12.8 ‰ and -12.4 ‰, from the beginning of the dry season to the end of it. Therefore, the combined analysis of water level, mineralization, water temperature, hydrochemistry, and isotopic values have evidenced the hydrodynamic behavior of the Jurassic sector drained by the overflow springs and permitted to identify flows from different compartments of the aquifer and with distinct residence times.

Conclusion

In this research, the joint analysis of hydrodynamic time series, hydrochemical data (major dissolved ions, TOC), and stable isotopes ($\delta^{13}C_{TDIC}$) has provided a deep understanding of the origin and characteristics of groundwater-flow paths at different compartments of a highly karstified aquifer and of the temporal dynamics of mixing processes within it. Results indicate that the Jurassic carbonate sector that constitutes the Jarastepar aquifer exhibits a typical behavior of a karstic aquifer with a highly developed drainage network. Furthermore, it has been possible to define four hydrodynamic stages with different mixing and distinct hydrochemical and isotopic characteristics: *piston-flow* (deep saturated zone), *outflowing* (fast flow from the soil), *declined* piezometric level, and *depletion* (dry season). During the *piston-flow* and *declined* steps, the highest mineralization and water temperature were recorded, while the $\delta^{13}C_{TDIC}$ isotopic signal was the least negative. This shows that the piston-flow waters have a higher fraction of water with a longer residence time than those corresponding to the declined steps. Less mineralization and lower mean $\delta^{13}C_{TDIC}$ values were recorded in the overflow or low water episodes. This is a consequence of a greater contribution of flows with an isotopic signal closer to that of rainwater (-8 ‰), for overflow situations, and with a certain evolution towards an equilibrium with bedrock (0 ‰), for dry periods. In general, these hydrodynamic stages coincide with that inferred from the analysis of flow–level-duration curve performed in the framework of this work.

The evidence of rapid flows denotes the high vulnerability of karst systems to contamination processes, as well as the participation of each of the compartments or zone of the aquifer (soil-unsaturated zone-saturated zone) in its hydrogeological functioning. The results highlight that the management and protection of groundwater continue to be challenging, so it is necessary to keep working to understand karst aquifers better.

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