Role of the Soil-Epikarst-Unsaturated Zone in the Hydrogeological Functioning of Karst Aquifers. The Case of the Sierra Gorda de Villanueva del Trabuco Aquifer (Southern Spain)

M. Mudarra and B. Andreo

Abstract Temporal evolutions of discharge, water chemistry (electrical conductivity, temperature, alkalinity, Cl^-, SO_4^{2-}, Ca^{2+}, Na^+, Mg^{2+}) and carbonate controlling variables (PCO_2 and $SI_{calcite}$), together with natural tracers of infiltration (TOC and NO_3^-), monitored in two karst springs of the Sierra Gorda de Villanueva del Trabuco aquifer (Southern Spain), reflect the greater relative importance of the soil-epikarst-unsaturated zone in the hydrogeological functioning of this aquifer. Each recharge event provoked an increase of discharge rates and water mineralization, the latter being due to an increase of alkalinity, and Ca^{2+}, Cl^- and SO_4^{2-} contents, while Mg^{2+} content decreased. Moreover, these variations were mostly accompanied by the rise of TOC content, while concentration of NO_3^- only rose during the first flood episodes (normally in autumn), and progressively fell during winter and spring times. Water temperature varied annually in a similar way to changes in air temperature.

1 Introduction

Hydrogeological responses of karst springs are widely investigated in recent decades with the aim of obtaining basic information about the behavior of the aquifers they drain. In this respect, environmental soil tracers contribute to understand (qualitatively) the hydrogeological functioning of carbonate aquifers

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and some of the hydrogeochemical processes (dynamic of infiltration, transit time, flow conditions, transport, etc.) taking place within them (Batiot et al. 2003; Perrin et al. 2003; Hunkeler and Mudry 2007; Mudarra et al. 2014). Moreover, a detailed and widely monitoring of environmental tracers, jointly with other natural responses, provide insights into the structure and dynamics of karst aquifers, especially regarding to the location of storage (soil-epikarst, unsaturated or saturated zones) and the degree of participation of these in the functioning of the system (Hunkeler and Mudry 2007; Mudarra and Andreo 2011).

In this work, data series of discharge, water temperature, and hydrochemistry (including environmental tracers) from two karst springs located in southern Spain, have been coupled and used with the aim of characterizing the hydrogeological processes (infiltration, residence time, functioning, etc.) that take place within the Sierra Gorda de Villanueva del Trabuco aquifer (Fig. 1). This permits to define the role of the saturated and the unsaturated zones (including soil and epikarst) in the hydrogeological functioning of this aquifer.

2 Study Site

The Sierra Gorda of Villanueva del Trabuco aquifer (6.3 km^2) is located approximately 30 km north of the city of Málaga, Southern Spain (Fig. 1). The altitudes ranging from 800 to 1,450 m a.s.l. in this steep area. The prevailing climate is temperate Mediterranean, with a marked seasonal pattern in the annual distribution of rainfalls (mainly in autumn and winter). The mean annual precipitation recorded during the study period (September 2006–March 2009) was 678 mm (Mudarra 2012), with differences in the quantity year by year: 624 mm (2006/2007), 564 mm (2007/2008) and 847 mm (2008/2009). The mean annual air temperature for the study period has varied between 11.1 °C, in high areas, and 17.1 °C in aquifer borders (Mudarra 2012).

The Sierra Gorda of Villanueva del Trabuco aquifer consists of 400–450 m thick of fractured and karstified Jurassic dolostones and limestones (Martín-Algarra 1987), being bounded at the base by Upper Triassic clays and evaporite rocks (mainly gypsum), while at the top there are Cretaceous-Paleogene marly-limestones and marls (Fig. 1). The geological structure is characterized by a normal limb, with moderate dip (30°), of an anticline fold with vergence toward S-SE, from which overthrust has developed with similar vergence over Cretaceous-Paleogene marls (Fig. 1b). This overthrust individualizes the aquifer of Sierra Gorda de Villanueva del Trabuco of another located to the southeast (aquifer of Sierras de Camarolos and del Jobo). At the north and western borders of aquifer, Flysch-type clays and sandstones outcrops. Aquifer recharge takes place through direct infiltration of rainwater, while discharge is mainly produced through springs located at the northern border of carbonate outcrops (Fig. 1a): Pita spring (24 L/s annual mean discharge rate) situated at 825 m a.s.l., and Eulogio spring (55 L/s) located at 835 m a.s.l.

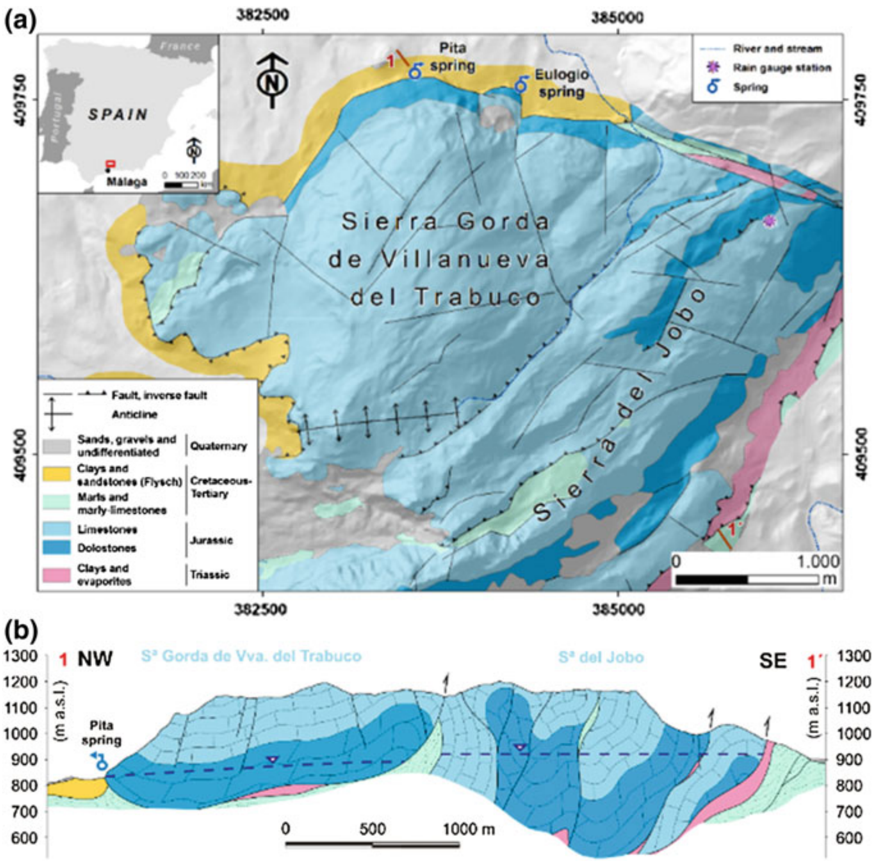

Fig. 1 Geographic location and geological-hydrogeological sketch (**a**) and cross-section (**b**) of Sierra Gorda of Villanueva del Trabuco aquifer. Altitude in meters above sea level

3 Methodology

From September 2006 to March 2009, records of discharge, electrical conductivity (EC) and water temperature, together with the most common hydrochemical parameters (including Total Organic Carbon–TOC-), were monitored in the water drained by Pita and Eulogio springs. In addition, precipitation was also recorded daily at a rainfall station located on the carbonate outcrops (1,130 m a.s.l., Fig. 1a). During the study period, sampling periodicity was adapted to the different hydrological conditions that affected to the aquifer (recharge, recession, depletion): daily in high flow and every 2 weeks during periods of depletion (average sampling periodicity was weekly). The total number of samples obtained was 96 at Pita spring and 87 at Eulogio spring (in 500 ml PVC bottles, stored at 4 °C, analysis within 48 h). In the field, and at the same time as the samples were obtained, water temperature and EC were measured in situ using portable equipment WTW, Cond 315i with a precision of ±0.1 °C and ±1 μS/cm, respectively. In addition to hand measurements, Pita spring was monitored with data logger devices (WTW, Cond 340i), providing an hourly record of water temperature and EC.

The hydrochemical parameters considered were analyzed at the laboratory of the Centre of Hydrogeology of University of Malaga. Alkalinity (TAC) was measured by volumetric titration using 0.02 N H_2SO_4 to pH 4.45. Major components were performed using high pressure liquid ion chromatography (HPLC, Metrohm 791-Basic IC model), with an accuracy of ±0.01 mg/L (previously filtered in line and precolumn-filter). TOC content was measured by combustion (after HCl treatment) of the organic matter present in the samples using a Shimadzu V-TOC carbon analyser, calculated as total carbon (TC) less inorganic carbon (IC). The CO_2 partial pressure (PCO_2) and the saturation index with respect to calcite ($SI_{calcite}$) were calculated using the EQ3NR code (Wolery 1992).

4 Results

Figures 2 and 3 show the temporal evolution of discharge, EC and water temperature values, together with the hydrochemical parameters analyzed in the water drained by Pita and Eulogio springs in the present research; this figure also shows the rainfall recorded in the area for the same time period. Analysis of data obtained in both springs permits to observe relatively quick variations in flow rates as response to precipitation events. These variations are more rapid and accused in Eulogio spring (ranges from 1 to 650 L/s) than in Pita spring (from 7 to 219 L/s). In both cases, increases in discharge rates are accompanied by a sympathetic rise in EC (Figs. 2 and 3), which later falls during the periods of low water conditions. The magnitudes of these increases were proportional to the quantity and intensity of precipitation events. Thus, the maximum variation observed in Pita spring was of 60 μS/cm (autumn 2008), whereas it was of 90 μS/cm (February 2009) in case of Eulogio spring.

The temporal evolution of water temperature at Pita and Eulogio springs presented a seasonal variation mainly influenced by monthly air temperature changes in the area (Figs. 2 and 3): the lowest values (12.6 °C at Pita spring; 12.2 °C at Eulogio spring) occur with the winter minimums of the air temperature (coinciding with high water conditions), whereas the maximum values (13.3 °C at Pita and Eulogio springs) were recorded in summer, during periods of depletion. At Eulogio spring, this seasonal evolution is incomplete due to a lack of measures during the summer months. Additionally, some significant decreases in temperature can exist at this spring (0.4 °C), as consequence of the different recharge events that took place in autumn and winter. Nevertheless, rainfalls had little or no influence on hydrothermal response of Pita spring.

Variations in water mineralization are caused by corresponding changes in Alkalinity and Ca^{2+} content (Figs. 2 and 3), which increase progressively at the same time as the flow rate. During or immediately after recharge events, an

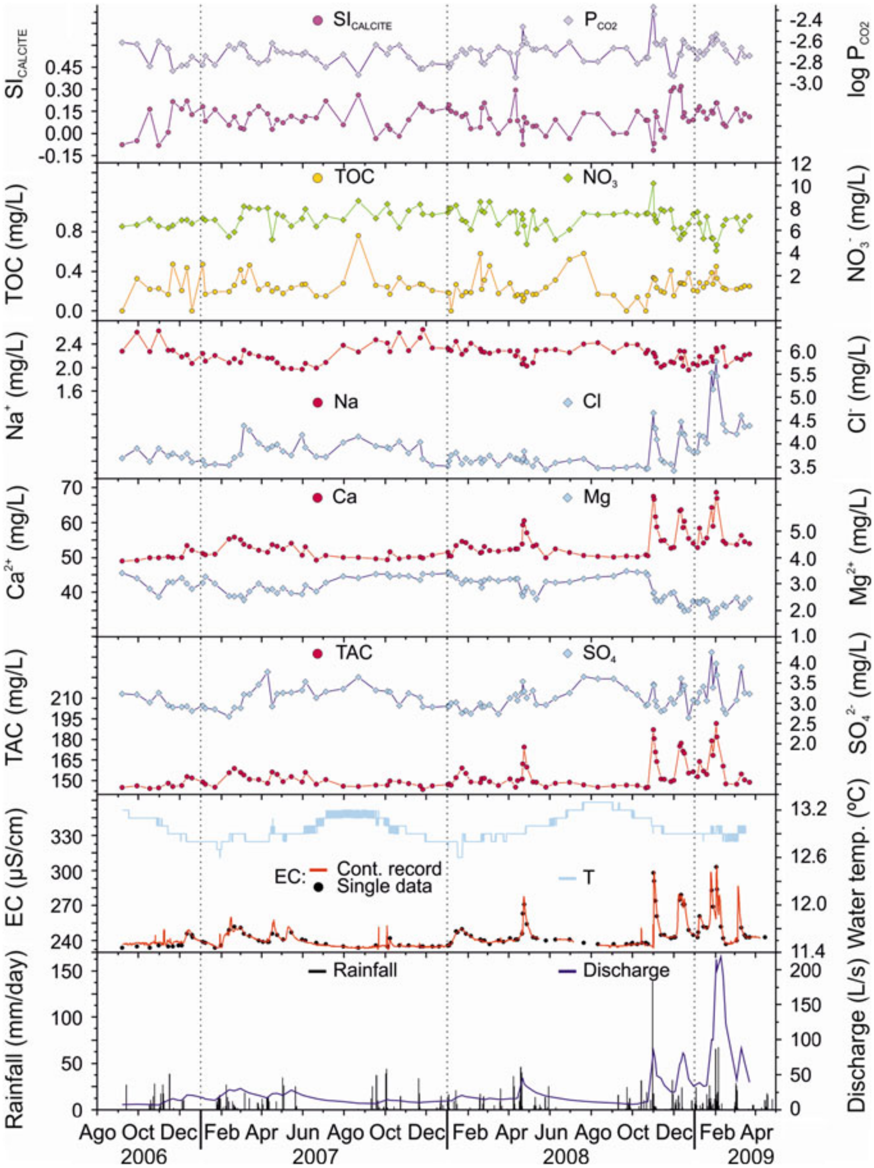

Fig. 2 Temporal evolution of discharge rates, water temperature and the principal chemical components of the water from Pita spring, with respect to precipitation events

increase in Cl^- and, in lesser extent, in SO_4^{2-} contents took place. Variations of all these chemical parameters are slightly higher in the water of Eulogio spring than in that of Pita spring. On the other hand, the greatest concentrations of Mg^{2+} were detected in the spring waters during depletion periods, especially at the

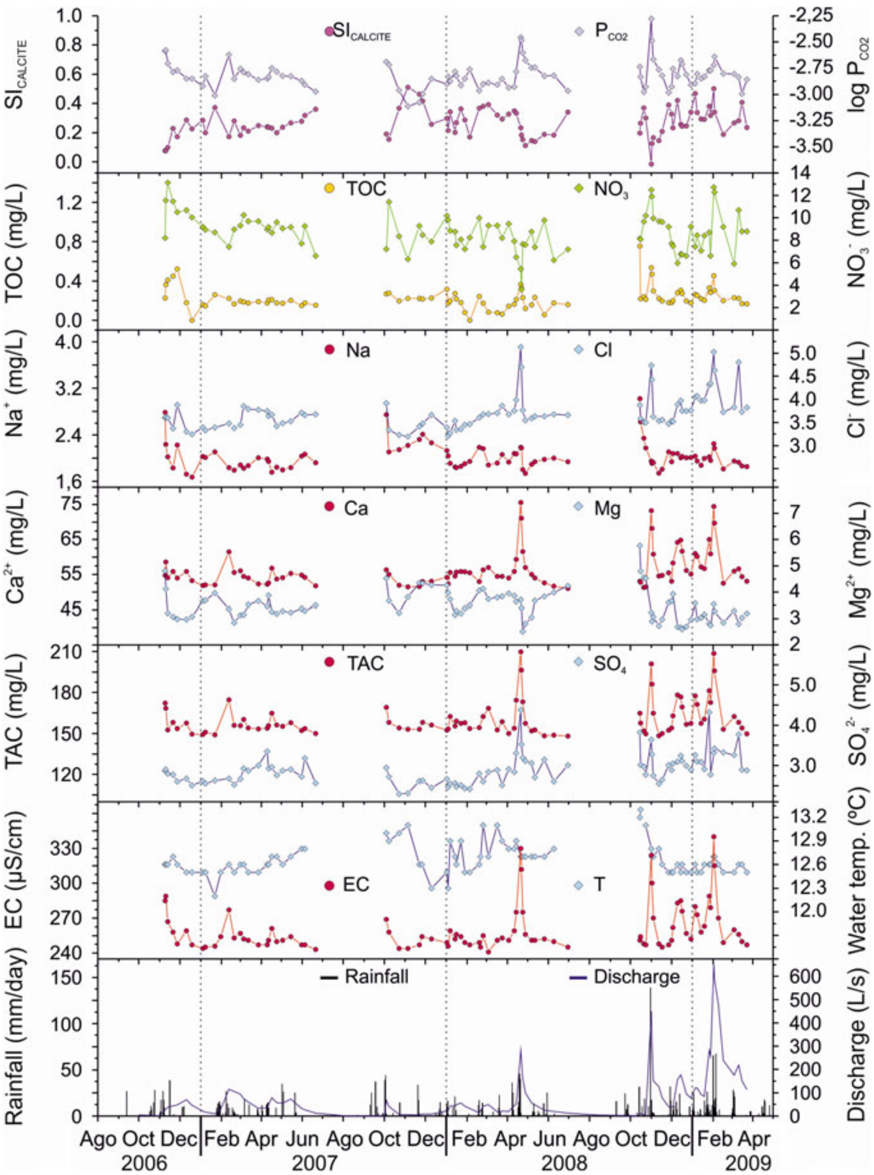

Fig. 3 Temporal evolution of discharge rates, water temperature and the principal chemical components of the water from Eulogio spring, with respect to precipitation events

beginning of the hydrological year, with falls during or immediately after recharges. Na^+ content did not follow the general pattern of EC; on the contrary, they show a general trend similar to Mg^{2+} content, which could indicate, at least partly, the same origin for both in the saturated zone of the aquifer. In fact, temporal evolutions of Na^+ and Cl^- are not always coincident.

With respect to TOC and NO_3^- contents, both natural tracers of recently infiltration, they trended to be higher at the beginning of the hydrologic year (specially at Eulogio spring), when the first recharge events occurred, and fell during the subsequent periods of recession. Other less accentuated increases in TOC content could be observed at springs as consequence of most abundant precipitation events recorded at winter and spring-time. In opposition, the concentration of NO_3^- fell in both springs during the same periods, except at Eulogio spring in February 2009, when the values of this parameter again increased (Fig. 3). During summer of 2007 and, above all, during the summer months of 2008, there was an increase and subsequent decrease in TOC at Pita spring (Fig. 2), which was not caused by precipitation events, but probably by single-point livestock concentrations in the surroundings of the spring (Mudarra 2012).

PCO_2 values calculated in the water of both springs showed similar temporal evolutions and ranges of variation (Fig. 3): they rose during recharge periods and suddenly decreased after few days. This can be specially observed in the precipitation event of November, 2008 (Figs. 2 and 3), which coincided with an increase in TOC and NO_3^- content, coming from the edaphic layer. In general, $SI_{calcite}$ behaves an opposite ways to PCO_2, with decreases in recharge events and increases after these. During the most abundant rainfall, water of both springs are near to equilibrium or slightly subsaturated respect to calcite, whereas in flow recession and in low water condition they tended to be over-saturated. Changes on $SI_{calcite}$ and PCO_2 indicate that, during recharge periods, springs drained very recent infiltrated water, with high CO_2 content from the soil and epikarst. These aggressive waters provoke rapid calcite dissolution (increases in TAC values and Ca^{2+} contents), which favor conditions near to equilibrium in the outflows.

5 Discussion

According to previous authors (Lastennet and Mudry 1997; Emblanch et al. 1998; Batiot et al. 2003; Perrin et al. 2003), the hydrochemical variations recorded at the water drained by Pita and Eulogio springs reflect the greater relative importance of the soil-epikarst-unsaturated zone in the hydrogeological functioning of the sierra Gorda de Villanueva del Trabuco aquifer (Mudarra and Andreo 2011). Each increase of springs flow rates during periods of recharge is followed by a rise in EC values and of the components most influencing it (TAC, Ca^{2+}, Cl^- and SO_4^{2-}), simultaneously to a fall in Mg^{2+} content; the latter indicator of residence time of the water within the aquifer (Batiot et al. 2003), especially in the saturated zone. In addition, these variations are usually accompanied with increases of diverse magnitude in TOC contents. This pattern reveals the arrival to the springs of water that was previously stored in the soil and epikarst, and within the fractures and conduits of the unsaturated zone, where it was affected by evaporation processes and dissolution of carbonate minerals during periods without rainfalls. Later, during high flow conditions, this water was rapidly pushed and mobilized toward springs by new infiltration water (piston effect in the unsaturated zone; Mudarra and Andreo 2011). Likewise, it is possible that a fraction of TAC and Ca^{2+} variations in spring waters would also be a consequence of rapid calcite dissolution in the unsaturated zone of the aquifer by rapid infiltration of water with high CO_2 content (Bakalowicz 1979; Dreybrodt 1988). Nevertheless, aggressive infiltration water, with higher PCO_2 values, would provoke a decrease in $SI_{calcite}$ values during high flow conditions (Figs. 2 and 3).

The above-mentioned hydrochemical variations, although of slight magnitude in some cases (Figs. 2 and 3), took place relatively quickly, which suggests that, in response to rises in flow rate, the water that was previously stored within the fractures of the unsaturated zone is rapidly mobilized toward the springs. During the dry year 2006/2007, the first water arriving at springs was the water from the lower part of the unsaturated zone, which was of greater TAC and had a higher Ca^{2+} content (Fig. 2), followed by the water coming from soil and epikarst (with higher contents of TOC, Cl^{-} and, in some recharges, also NO_3^{-}). The lag between the maximum of TAC and Ca^{2+} content, on the one hand, and those of TOC and Cl^{-} on the other, could be indicative of the transit time of the water through the unsaturated zone, from the soil and epikarst to the spring (exceeding 2 days; Mudarra and Andreo 2011). In opposition, during the most abundant pluviometric events of 2008 and 2009, no lags between these components were detected (Figs. 2 and 3), which could be interpreted as a result of a homogenization of the infiltration water within the unsaturated zone (from soil and epikarst until the lower part of unsaturated zone), previously to the spring discharge.

PCO_2 variations were, in some cases, similar to those of TOC contents, overall at Eulogio spring (Fig. 3). Normally, a simultaneous enrichment of CO_2 and organic matter take place in the edaphic layer. However, an increase of PCO_2 values at the water of Pita spring was observed during some floods, with no changes (or small) in TOC contents (Fig. 2). This might be the result, on the one hand, to the poorly organic matter production in the soil and, on the other hand, to a limited degassing in the unsaturated zone, where low PCO_2 values obtained in soil would be kept.

During low water conditions, the saturated zone also plays a role in the hydrogeological functioning of the aquifer. The greater residence time of the water within the aquifer causes small increases in Mg^{2+} content. However, the very slight increase in the concentration of this cation could be also related to the groundwater flow through the unsaturated zone (Batiot et al. 2003; Mudarra and Andreo 2011). This explanation is consistent with the fact that Pita and Eulogio springs present the lowest mean temperature and EC values of all springs located in the region (Mudarra 2012), being presumably associated with superficial groundwater flows within the aquifer. The time lag observed during some flood events between the maximum of TAC, Ca^{2+} and Cl^{-} content, and the minimum of Mg^{2+}, especially at Eulogio spring (Fig. 3), could be also associated to the transit time of water from the surface to the unsaturated zone (lower than 1 day), minor than from the surface to the saturated zone (greater to 1 day).

6 Conclusions

Pita and Eulogio springs respond to the most important precipitation events with significant increases in groundwater flow (faster and higher in Eulogio spring), sometimes slightly delayed in time. In this case, the mineralization of the water increases rather than decreasing because it contains larger quantities of most of its chemical components (piston effect of the unsaturated zone), except Mg^{2+}, which is indicative of the residence time of the water within the saturated zone of this site. This hydrogeological behavior indicates that the aquifer drained by these springs has a moderate degree of functional karstification, even within the unsaturated zone, which seems to affect its functioning more than does the saturated zone (especially under recharge situations) and provokes a less attenuated response to rainfall events.

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