ORIGINAL ARTICLE

Piezometric and hydrogeochemical characterization of groundwater circulation in complex karst aquifers. A case study: the Mancha Real-Pegalajar aquifer (Southern Spain)

Antonio González-Ramón · Manuel López-Chicano · Juan Carlos Rubio-Campos

Abstract A small karst aquifer of great structural complexity has been subjected to significant resource withdrawal over recent decades. This exploitation aroused social conflict due to the effect it has had on emblematic springs. This research has analysed piezometric data collected over the course of 12 years and the spatial hydrochemical data supplied by the main water points associated with it. The spatial and temporal evolution of the main chemical species in the groundwater and the hydrogeochemical processes affecting them have been studied, modelling them with the programme PHREEQC. These data suggest a complicated model of hydrogeological function with sectors storing water at different depths and connected to each other locally as determined by the geological structure.

Keywords Karst aquifers · Hydrochemistry · Piezometry · Intensive exploitation · Betic Cordillera

Introduction

Karst aquifers in structurally complex zones usually reflect this complexity in their hydrogeology and patterns of groundwater circulation. This is even truer if they are subjected to intensive exploitation of their hydrological resources and there are isolated compartments in the hydrogeological system. The geological complexity sometimes allows hidden exchanges of water between different permeable formations and for there to be a natural flow of water between them. In such cases, the hydrogeological function can be difficult to discern (García-Aróstegui et al. 2006; Simsek et al. 2008; Abu-Jaber and Kharabsheh 2008).

In southern Spain, the emplacement of the Internal Zones of the Betic Cordillera during the Neogene led to the destructuring of the Mesozoic platform forming the continental boundary of the Iberian basement, resulting in the deposition of significant amounts of calcareous sediments alternating with marls. The tectonic thrusting produced, by the end of the Neogene, a rosary of remnants of Jurassic and Cretaceous carbonate masses that had formed part of that platform. These masses are the so-called External Zones of the Betic Cordillera (Blumenthal 1927; Fallot 1948; Azema et al. 1979), which consist of a great number of ranges of different length, isolated by marly Triassic, Cretaceous, and Miocene materials, and with hugely complex geological structures.

All of these ranges enclose groups of aquifers that are fundamental to the water supply of settlements in the region, and that are quite difficult to study due to their hydrogeological features. On many occasions, exploitation of the groundwater from these aquifers has been undertaken without prior planning and without sufficient knowledge of their hydrogeological function. As a result, there have been cases of undesirable effects that have produced social conflicts (González-Ramón and Rubio-Campos 2008).

One of these conflicts took place over a small aquifer near the city of Jaén (Fig. 1) in Andalusia, southern Spain.

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This aquifer is used to supply the needs of three nearby towns totalling a population of 15,000.

The exploitation of its resources by means of water wells affected the discharges of its main springs, and particularly of spring S-1, located in the town centre of Pegalajar and an emblematic site for the town. The social conflict generated thereby led, in 1992, to the start of legal actions to declare over-exploitation of the aquifer. These actions culminated in 2007 with the writing and approval of the Extractions Regulatory Plan (CHG 2006), as covered in Spanish legislation.

Due to the intensive exploitation carried out over the course of decades, there is no relevant information on discharge flows for the springs. Therefore, the research has focussed on a study of piezometric data, supported by hydrochemical data supplied mainly by water pumped from the wells for urban supply. This approach, although unconventional as regards karst aquifer research, has allowed us to define a working hydrogeological model coherent with existing observations.

The main goal of this work has been to expand our knowledge of the mechanisms governing the hydrogeology of karst aquifers with complex geological structures in Mediterranean climates. More specific aims include the following: (a) to study the intensive use of groundwater, the sustainability of the water extraction and the possibility to recover the affected spring for this extraction; (b) to propose a conceptual model of groundwater flow consistent with piezometric and hydrochemical observations; (c) to define a geochemical model for the groundwater evolution.

Study area

The Mancha Real-Pegalajar aquifer extends over some 30 km^2, with an area of permeable outcrops covering 27.4 km^2, and consists of upper Cretaceous carbonates averaging around 300 m in thickness (Rubio-Campos et al. 2003). Resources for an average year have been calculated at a little over 5 hm^3, with extractions for urban supply calculated at 1.5 hm^3 a year (González-Ramón 2008); there is no exploitation for irrigation.

Its surface area can be divided into two main outcrops, termed the Serrezuela de Pegalajar and the Sierra de Mojón Blanco (Figs. 1, 2), with elevations ranging from 470 to 1,495 masl. The lowest elevation is the course of the Guadalbullón River's southwestern boundary, and the highest is the peak of Mojón Blanco. The Guadalbullón
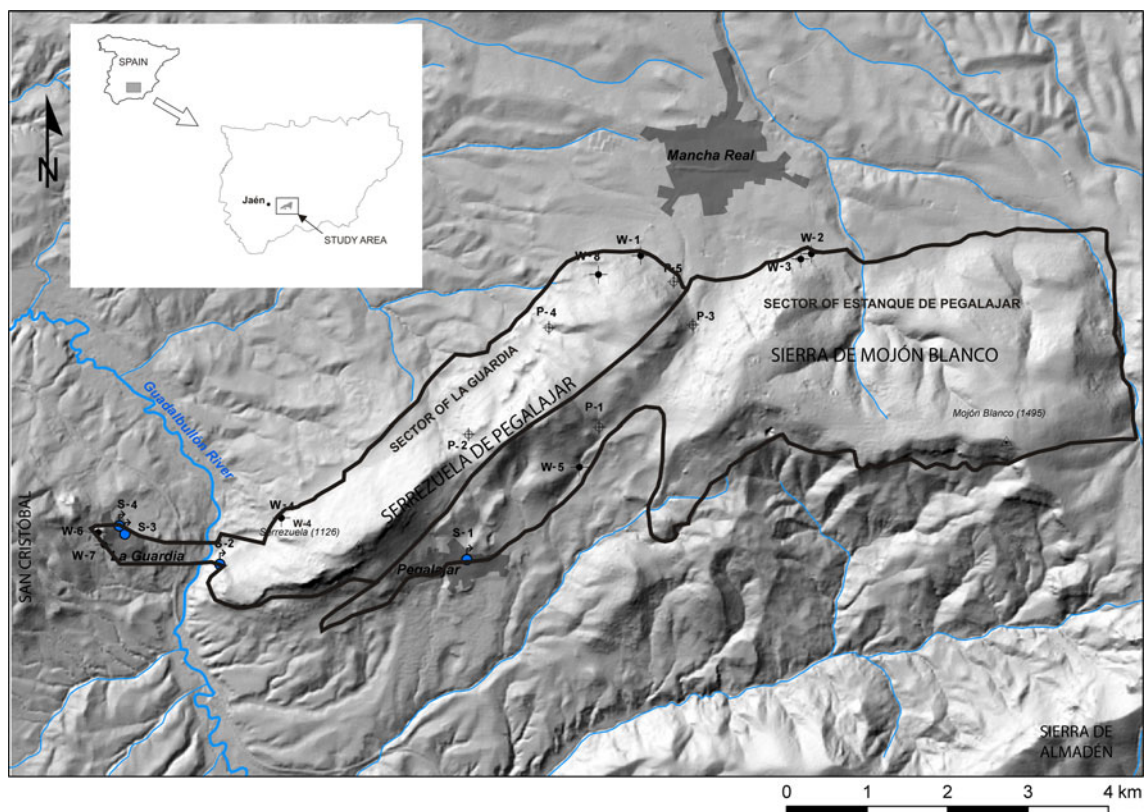

Fig. 1 Location of the study area and of the main water points (main map based on the digital elevation model of Consejería de Medio Ambiente de la Junta de Andalucía, 2005)
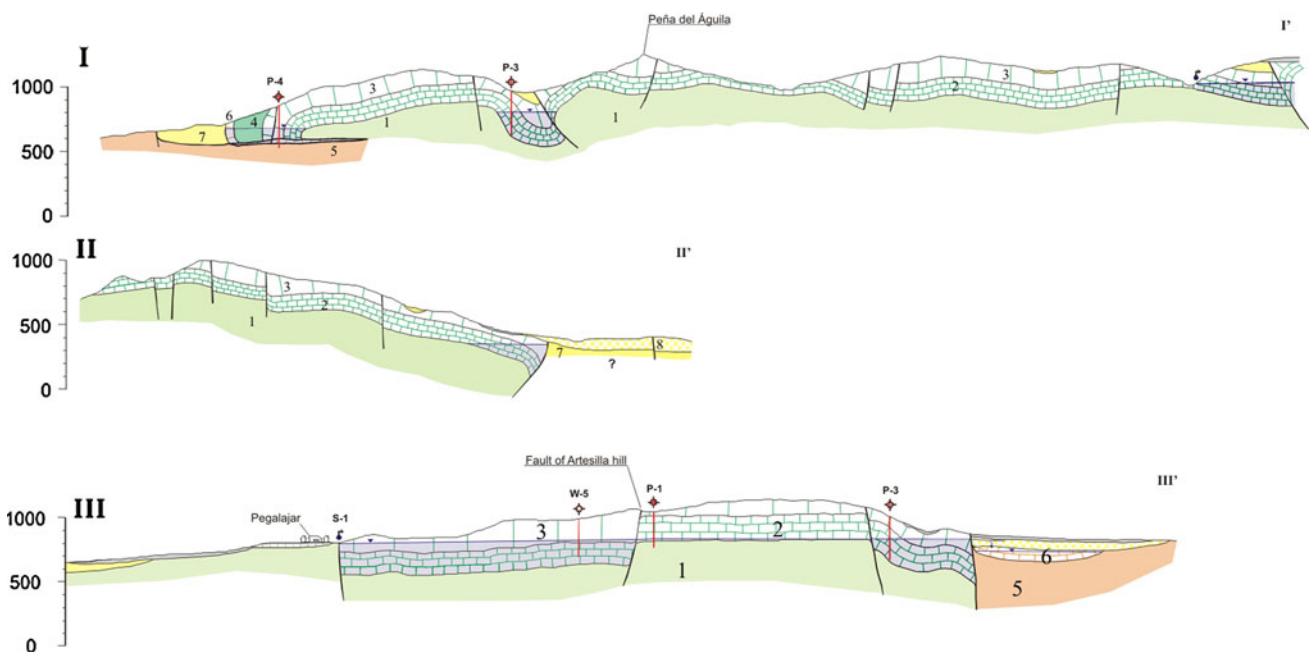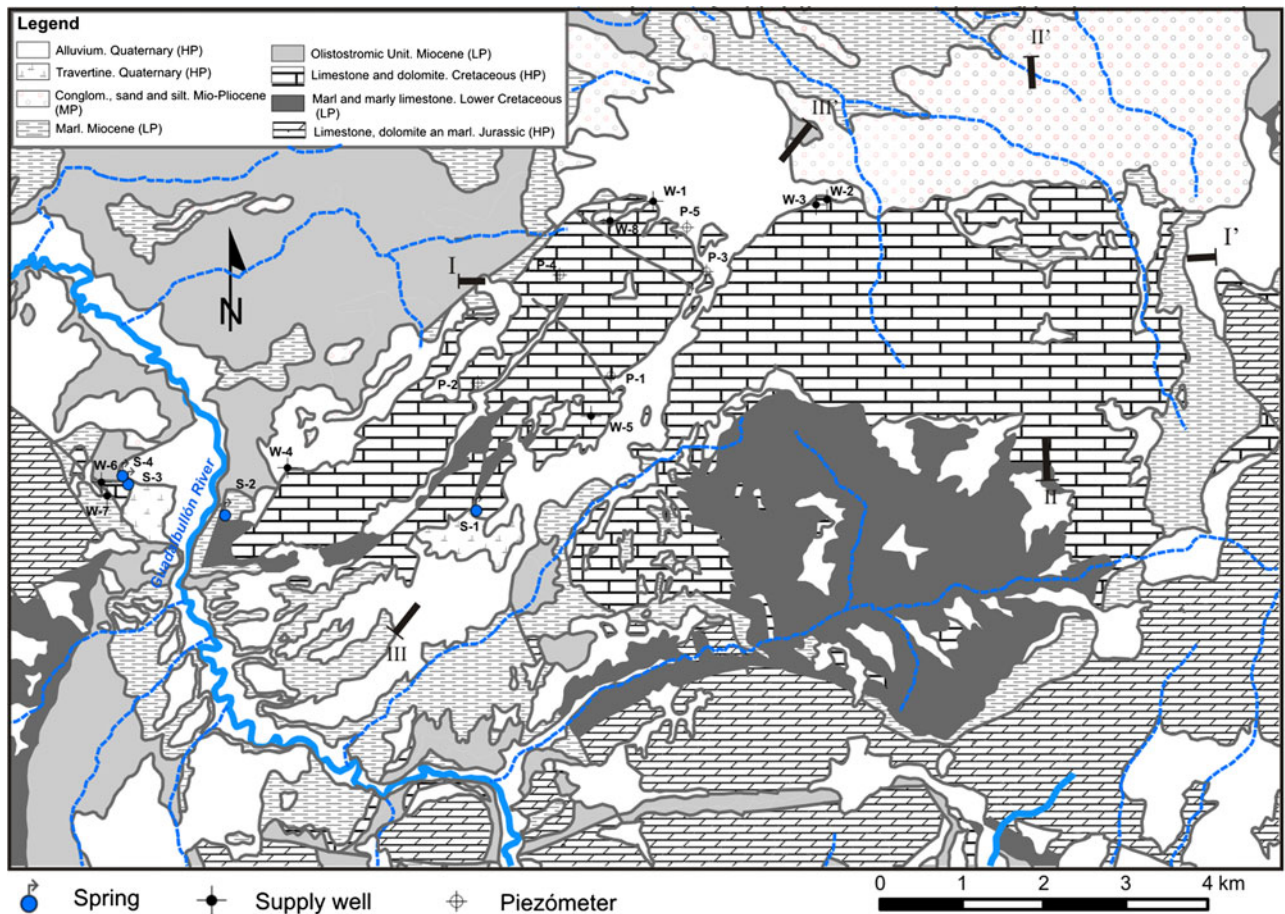
Fig. 2 Hydrogeological map of the Sierra de Pegalajar and the Mojón Blanco, and hydrogeological cross-sections. *HP* High permeability, *MP* Medium permeability, *LP* Low permeability. The legend for the cross-sections is: 1 and 4, Cretaceous marls; 2 and 3, Cretaceous limestones and dolostones; 5, Olistostrome Unit; 6, Miocene limestones and calcarenites; 7, Miocene marls; 8, Miocene conglomerates, sands and silts. (Hydrogeological map based on Roldán et al. 1991)

River is the largest in the region, passing over the aquifer with an average volume of flow of 4 m³/s (CHG 1995), although subject to extreme seasonal variations.

The zone is characterised by a continental Mediterranean climate, with dry, very hot summers and cold, relatively wet winters. The monthly precipitation regime is clearly seasonal, with winter wetter than spring, and spring wetter than autumn. July and August are the driest months, with very scarce precipitation or none at all. Average annual precipitation is on the order of 500 mm in the foothills of the sierra and may exceed 900 mm at the highest elevations. The average temperature on the aquifer boundaries is around 15°C.

The main permeable formation consists of Cenomanian limestones and dolostones. At the base there is a gradual transition to Valanginian-Albian marls (García-Hernández et al. 1979) comprising the aquifer's impermeable substrate.

The Cretaceous series is overthrust on its southeastern border by Sierra de Almadén Jurassic carbonates and, overall, the aquifer has undergone displacement and rotation on the plastic materials of the Olistostrome Unit (Roldán and García-Cortés 1988) or of the Subbetic Chaotic Complex (Arias et al. 2004), which comprise the general substrate for the entire group.

The northern boundary is covered by Pliocene and Quaternary moderately permeable detrital sediments; the southwestern boundary is the Guadalbullón River.

The Serrezuela de Pegalajar forms a N55E anticline in which the northwestern limb is steeper than the southwestern one, dotted with fractures perpendicular and subparallel to the direction of the fold. The perpendicular fractures cause displacements and sinking along the anticline axis. The largest fracture (fault of Artesilla hill; González-Ramón 2008) has been bored on both walls near its trace, thereby providing an estimate of over 200 m for its slippage. Farther north is another fault with a similar direction and with considerable slippage, so that the joint effect of the two has produced a raised, horst-like sector (Fig. 2).

The Mojón Blanco outcrop is tectonically superposed over that of Pegalajar on the western boundary, and it affects all the Miocene materials covering the valley separating the two ranges. The carbonate package comprising the Sierra de Mojón Blanco is subhorizontal, dipping gently northwards in its southern and central zones, and steeply northwards on its northern flank and steeply westwards on its western flank.

As a result of this geometrical arrangement, groundwater can only be stored on the flanks of the two outcrops: the northwestern and southeastern flanks of the anticline of Serrezuela de Pegalajar, and the northern and western flanks and part of the eastern flank of the Mojón Blanco structure.

The elevations for the piezometric levels in the groundwater reservoirs generally occur around 800 masl,

with the S-1 spring being the main visible discharge. The spring, at 796.1 masl, is related to an aquifer sector called the Estanque of Pegalajar Sector (González-Ramón 2008). This sector covers the groundwater reservoir formed by the northern and western flank of the Mojón Blanco outcrop, and the southeastern flank of the Serrezuela de Pegalajar outcrop (Figs. 1, 2). Hydraulic connectivity between the two outcrops was confirmed after the construction and subsequent monitoring of a series of piezometric boreholes (P-1 to P-5) for aquifer monitoring (González-Ramón et al. 2002).

Discharges from spring S-1 were monitored for a short period when there were yet no withdrawals from the aquifer. Data on the volume of flow discharge and calculations of the recharge volume in the permeable outcrops in the sector revealed there must be hidden discharges into other formations since the average volume of flow in the spring was plainly insufficient to account for all the infiltration (López-Geta et al. 1991).

On the NW flank of the Serrezuela de Pegalajar (La Guardia sector in Fig. 1), the water table in boreholes W-1 and W-4 and at a small spring with a discharge of less than 1 L/s associated with outcrops S-2 is at around 600 masl. The location of the water discharge from this sector was always a mystery as there are no known significant springs directly associated with the outcrop. The possibility of a diffuse discharge into the Guadalbullón River was considered, but previous data from differential flow metering caused the notion to be discarded.

On the other bank of the Guadalbullón River is a small outcrop of Cretaceous carbonates interpreted as an olistolith embedded in Subbetic Chaotic Complex materials (Roldán et al. 1991). This block contains significant springs with an average discharge of over 20 L/s (S-3 and S-4) and slight thermalism; they are currently dry due to the effect of the W-6 and W-7 wells for urban supply. Abutting the carbonate block is a travertine deposit on which part of the town core of La Guardia lies. In this zone, the water table is around 600 masl, which raises the possibility of a connection with the water stored in the NW flank of the Serrezuela de Pegalajar anticline.

Methodology

In 1992, monthly measurements began of the water tables in five piezometric boreholes (P-1 to P-5) and in three water supply wells (W-2, W-3 and W-5). A series of measurements covering 15 years is now available. During this time, the S-1 spring overflowed five times (averages of its discharge volume are also available).

Most of the points for the water table measurements and the noteworthy springs were measured for elevation with GPS with decimetric resolution.

A campaign of sample collections in the field was carried out in October of 2002, at which time the water tables were dropping, as there had been no significant rainfall throughout the summer, thereby guaranteeing a lack of recharge (low water). Between May and early June of 2003, a second campaign was held. The water tables were high and all the springs were discharging, including spring S-1 (over 50 L/s). The spring was wet and the sampling was held at a time when there was recharge in the aquifer (high water). In situ measurements were made of water temperature, electrical conductivity, pH, volume of flow, and alkalinity during the sampling for both campaigns. The alkalinity was measured by field bicarbonate analysis by volume with HCl as a titrant and methyl orange as indicator. Each sample was collected in two polyethylene double-sealing bottles, one of which was acidulated with 4 ml of HNO_3 for cation analysis.

The samples were analysed at the laboratory of the Geological Survey of Spain (IGME) in Madrid. Bicarbonate, sulphate, chloride, nitrate, nitrite, silica, ammonium, calcium and magnesium were determined by absorption spectrometry with a continuous flow autoanalyzer. The potassium and sodium were analysed by atomic emission spectrometry and the carbonates by volumetric standard.

Hydrochemical data are available for a total of nine water points directly related with the Cretaceous aquifer and with other points in peripheral geological formations or contiguous aquifers. The research was performed with the programme AquaChem (v 3.7) by Waterloo Hydrogeologic.

The saturation indices for water in different minerals (SI) were calculated with the programme PHREEQC for Windows (v.2.12.04) (Parhurst and Appelo 1999). Hydrogeochemical modelling was performed with the same programme.

Results and discussion

Piezometric evolutions and discharge status.

Figure 3 presents the most relevant piezometric data for 1992–2005. It includes data from three representative piezometers in the Estanque Sector (P-3, W-3, and W-5) that reveal the evolution in boreholes that are successively farther away from the main discharge point, spring S-1.

The piezometer closest to the spring is W-5, which is subject to daily pumping (data on water levels are always measured with the pump turned off). The borehole has very high transmissivity (around 10,000 m^2/day), and its recovery after the pump is turned off is very fast. Piezometer P-3 is near the northern boundary of the aquifer, far from the pumping points, and it best shows the piezometric evolution of the aquifer. Piezometer W-2 is located on the northern boundary of the Mojón Blanco outcrop; it

has commonly been used to supply the city of Mancha Real, and measurements are made with the pump at rest long enough to prevent any influence on the measurement.

The three piezometers show similarity in their piezometric evolutions, confirming they draw from the same groundwater reservoir. The thick horizontal line in the upper graph in Fig. 3 illustrates the moment at which spring S-1 begins to flow, just when the level of 802 masl is exceeded in borehole W-5 or in P-3. These two boreholes have almost identical water-level evolutions (0.99 correlation coefficient), with very similar elevations and no gradient between the two points. The levels evolve the same for both rising and falling phases. The level in borehole W-2 shows a similar evolution to those in P-3 and W-5, but its levels are always lower, even at its highest peaks.

Boreholes W-2 and P-3 would be expected to have higher piezometric levels than those of borehole W-5, and those of borehole W-2 should be higher than all the others since it is upstream of the main discharge point, spring S-1. However, the opposite is true. This can only be explained by invoking the existence of northward groundwater flow, which implies the existence of a groundwater divide with groundwater discharges towards that boundary.

The water table evolution is well correlated with rainfall, which is clearly the main factor controlling its rises and falls. To better understand how the aquifer recharges, Fig. 3 (top) plots the rise that occurred between the end of 1995 and early 1997, which was an extremely wet period after a long drought. Unfortunately, the data density available is insufficient to accurately describe the effects of distinct rainy episodes, for which daily piezometric readings would have been necessary. The onset of the rise in the table is not recorded in detail, but it was undoubtedly triggered by the rains of December 1995 and, particularly, the even more abundant rains of January 1996. Subsequently, the rains at the end of April and in May produced a clear increase in the slope of the curve in just a few days; however, the effect lasted until July even though there were no further rainy periods. That is, the water table continued to rise for nearly three months after the last rainfall.

The effect of summer begins to make its mark in July, ending with a significant rainfall on 11 September 1996 (85 mm in a single day), and lesser rainfalls on subsequent days. The effect of these rains is noted in a small rise in the table approximately 15 days after the main rainfall. In the first two weeks of November, there are several days of rainfall that seem to be what triggers the sharp rise in the table visible some 15 days later and augmented by the abundant rainfalls of December and January. The last day of recorded rainfall was January 23; however, the rise in the water table continued until it peaked in early March. Therefore, there is the same pattern of peaking

Fig. 3 Evolution of the water table in the Estanque of Pegalajar sector (P-3, W-3 and W-5) and La Guardia sector (P-2), volume of flow in spring S-1, and monthly rainfall. The *black horizontal line* marks the level of the water table at which spring S-1 has a discharge. Top: Detail of the rising phase of the water table in the Estanque of Pegalajar sector between the end of 1995 and early 1997, and its relation with rainfall
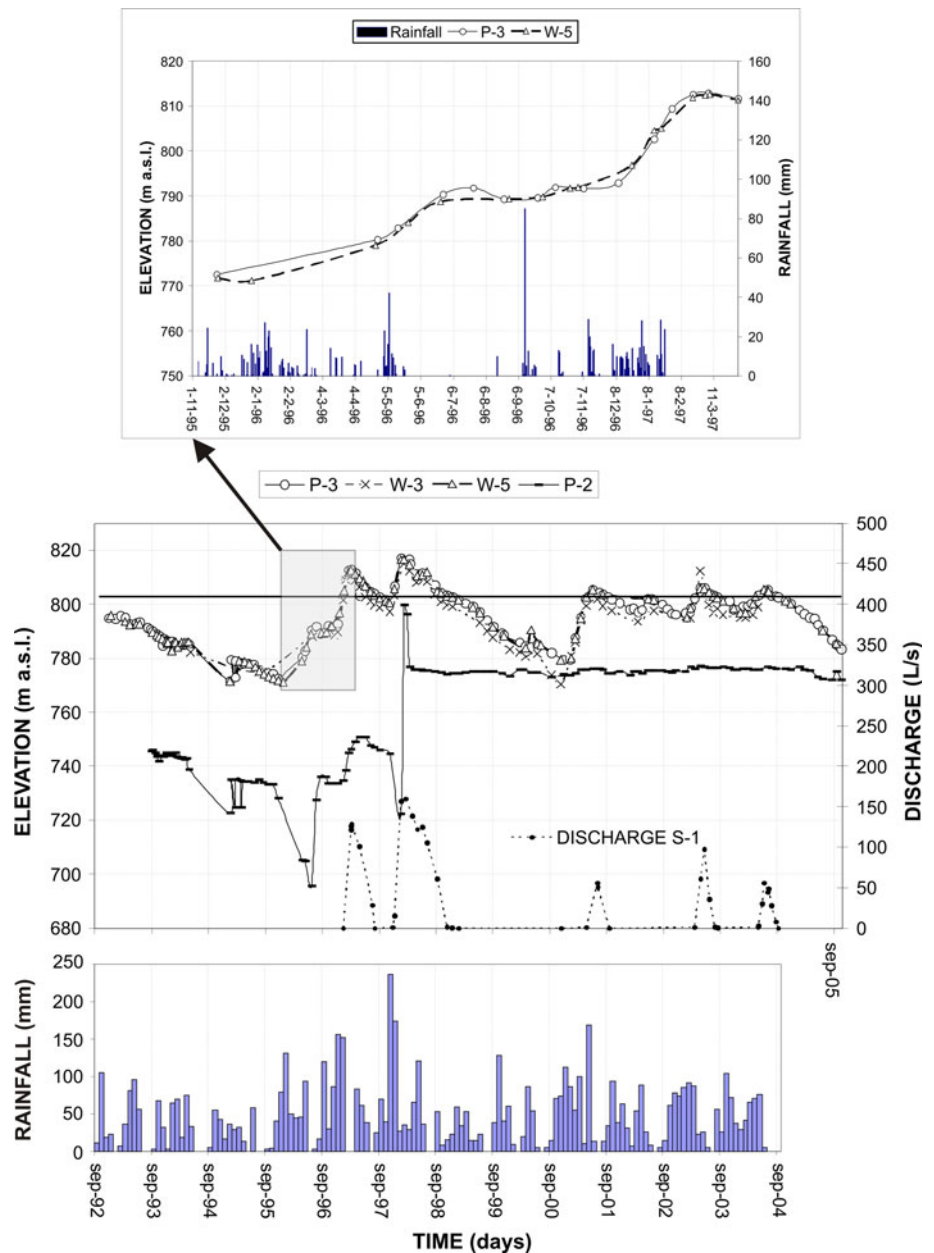
some six weeks after the last rainfall as in the rise the year before.

Note that the recharge is relatively fast, becoming noticeable 15 days after a significant rainfall, and that it continues recharging for about 6 weeks after the rainfall. These data are in contrast with readings from other aquifers of similar extension and lithology, such as the Ventós aquifer (Alicante, Spain), which records piezometric responses only hours after rainfall (Andreu et al. 2006), although that aquifer is smaller (less than 10 km^2) and has a simpler geological structure.

The effect produced by spring rains is more intense than those in the autumn and start of winter since the spring rainfall causes faster rises in the table that also continue to rise for several weeks after the rainfall.

Lee et al. (2006) studied the response times in different zones of an extensive carbonate aquifer in England based on daily piezometric readings. They conclude that the response time depends on the thickness of the unsaturated zone and on the volume of water it contains. In all the cases studied by these authors, the recharge responses are much faster both at the onset and at the end of rainfalls.

The Mancha Real-Pegalajar aquifer's main recharge area is around the Mojón Blanco Peak, which has a higher elevation and forms an extensive high plateau (Fig. 1). Most of the Sierra de Mojón Blanco is unsaturated, and water is stored on its boundaries (Fig. 3). This means that rainfall must first vertically percolate to the marly substrate through the unsaturated zone (comprising the entire aquifer

formation), and then flow towards the borders of the range before reaching the saturated zone. This flow primarily occurs through the Lower Cenomanian carbonates, which are less permeable due to marly intercalations. This long, complex journey through the unsaturated zone may account for the considerable delay in recharge, where fissures are preferential pathways for water circulation.

Once the water reaches the saturated zone, it circulates rapidly through the Upper Cenomanian carbonates (more permeable and karstified), as proven by the extremely low hydraulic gradients, particularly in the SE flank of the Serrezuela de Pegalajar.

Boreholes W-1, W-4, and W-8, representative of the NW flank (La Guardia sector), have a water table below 600 masl. Borehole P-2 broke through the water table at 777 masl, higher than expected. Its readings are compared with those of borehole P-3 on the opposite flank of the anticline (Fig. 3). Both boreholes show comparable evolution until January of 1998, when borehole P-2 was capped to prevent vertical flow that had been detected; the graph in Fig. 3 shows that the data it provides on the water table after the capping is no longer valid. The readings from August 1993 to September 1998 show a noteworthy correlation between the two piezometers, confirming the existence of hydraulic connectivity between the two flanks of the anticline. The similarity in the readings is thought to be due to discharges from the Estanque of Pegalajar sector towards the La Guardia sector. Borehole P-2 is located on the sunken block of the fault of Artesilla hill, close to the fault's trace, which is one of the zones that may allow hydraulic connectivity between the two sectors. This occurs because the impermeable substrate, consisting of Lower Cretaceous marls, is below 800 m in this zone due to the fault's activity, which allows flow from one sector to the other. Another possible connection between the two sectors lies in the periclinal closure of the fold on the northern boundary of the Serrezuela de Pegalajar.

On the left bank of the Guadalbullón River are several water points with water tables of around 600 masl (springs S-3 and S-4 and boreholes W-6 and W-7), which may be indicative of their association with the reservoir on the NW flank of the Serrezuela de Pegalajar anticline. There may be discharges of groundwater towards the Guadalbullón River through the carbonate outcrop at these points. To examine this possibility, a campaign of differential flow metering with a propeller flow metre was carried out. Results from unpublished studies had shown there were no gains in the river in the area near the aquifer from its right-hand bank. The flow metering was therefore planned for downstream of the previous study zone, where there might be discharge from the left-hand bank.

All the readings were taken on the morning of 6 February 2007. They showed a gain of 45 L/s from the left-hand bank of the river, a high enough volume to account for the discharges that should be associated with the La Guardia sector.

The piezometric observations and the location of the main discharge points indicate the hydrogeology of the aquifer may be summarised as follows: The aquifer's main recharge area must lie in the Mojón Blanco outcrop, on the high plain at its highest elevations. The water that infiltrates here circulates towards the northern and western flanks of the structure, and is stored with the water table at around 800 masl. Subsequently, the water circulates towards the SE flank of the anticline forming the Serrezuela de Pegalajar, drains through spring S-1, and feeds the NW flank of the anticline. On this flank, the water table is around 600 masl and flows south towards the course of the Guadalimar River. A small portion is discharged through spring S-2, but most flows under the riverbed towards the outcrop where the downtown centre of La Guardia lies. The water is able to flow under the river and discharge at the outcrop on the left-hand bank due to a Miocene marly cover on the permeable materials through which the water flows. A significant part of this discharge is dumped into the river's alluvium, increasing the river's volume of flow downstream.

After finishing the aquifer research, points W-7 and W-8 were included in the water table measurements. The graph in Fig. 4 shows the evolution of the table at these points (both in the La Guardia sector) from July 2007 to March 2010 and compares them with the evolution of the W-3 piezometer in the Estanque sector. Well W-8 is on the NW flank of the Serrezuela de Pegalajar anticline on the right-hand bank of the Guadalbullón River, whereas W-7 is in the outcrop on the left-hand bank of the river about 7 km away. The readings from the two wells show a total correlation ($R = 0.97$), demonstrating their hydrogeological relation. In contrast, well W-3 shows a different evolution,
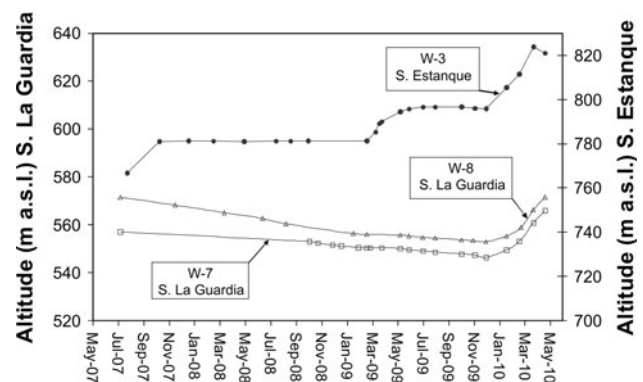

Fig. 4 Evolution of the water table in the La Guardia sector boreholes W-7 and W-8 and in borehole W-3 in the Estanque sector from 2007 to 2009

to be expected from a piezometer located in another reservoir.

Physico-chemical spatial characterization of the groundwater

Table 1 gives the results of the analyses of the two seasonal sampling campaigns in 2002 and 2003. The samples from the dry season include one taken in November 2005 from well W-7 under conditions similar to those for the 2002 samplings.

The groundwater has average salinity, with electrical conductivity (EC) ranging from 423 to 597 μS/cm and Ca-HCO$_3$ or Ca Mg-HCO$_3$ facies. Salinity varies little between low and high waters, showing similar EC for the two periods, although it is always slightly higher during low water than high. The main variation lies in the HCO$_3^-$ and NO$_3^-$ contents. The HCO$_3^-$ is systematically higher during low water (the sole exception being spring S-2).

At all the points, the NO$_3^-$ levels are double or even triple those recorded at high water, with moderate total values ranging from 3 to 17 mg/L. This scenario suggests the stored water is diluted during high-water periods due to the input of new recharge water.

The Schoeller diagram (Fig. 5) shows that the predominant ions are HCO$_3^-$ and Ca^{2+}, followed by Mg^{2+}. There is greater variability in the Cl$^-$, Na$^+$ and, to a lesser extent, SO$_4^{2-}$, both in low and high waters. In both periods, the HCO$_3^-$ and Ca^{2+} tend to decrease from the points in the Estanque sector towards those in the La Guardia sector; the other parameters show an opposite trend, with the exception of SiO$_2$, which has values that are more constant.

The Piper diagram in Fig. 6 shows the evolution from the points closest to the zone considered to be the main recharge area, in the Mojón Blanco outcrop (well W-3), towards the spring S-1, and thence towards the points in the La Guardia sector. The evolution line ends at well W-7. This is true both at low and at high waters. The evolution occurs in the sense of a gradual increase in chloride and magnesium contents. The scatter diagrams in the same figure make it even more apparent.

The moderate levels of SO$_4^{2-}$ and Cl$^-$ in the samples suggests that both ions are fundamentally meteoric in origin, from rainfall that undergoes evaporation concentration before infiltration. The Cl + SO$_4$ and Na + K scatter diagram shows a rising linear correlation in the sense of flow based on the proposed hydrogeological scheme.

The trend of a continuous increase in Cl$^-$ generally occurs in waters with longer residence times in an aquifer in the direction of flow. According to some authors (Custodio, in Custodio and Llamas 1983), the Cl$^-$ ion never reaches saturation in groundwater, and so the water increases in Cl$^-$ contents as the distance increases from the infiltration site

Table 1 Results of seasonal sampling campaigns

| Site	pH	Cond μS/cm	Temp (°C)	Volume Of Flow (L/S)	Cl$^-$ (mg/L)	SO$_4^=$ (mg/L)	HCO$_3^-$ (mg/L)	NO$_3^-$ (mg/L)	Na$^+$ (mg/L)	MG^{++} (mg/L)	CA^{++} (mg/L)	K$^+$ (mg/L)	SiO$_2$ (mg/L)	Date	Notes
W-1	7.58	517			33	6	283.65	13	17	17	71.24	0	7.3	17/10/2002	La Guardia sector
	7.51	500			33	5	274.5	5	14	16	79	0	7.4	14/05/2003	
W-2	7.59	597			23	5	393.45	13	12	10.48	106	0	8.9	17/10/2002	El Estanque sector
	7.16	585	14.8		20	4	344.65	5	11	12	104	0	9.3	14/05/2003	El Estanque sector
W-3	7.45	564	15.9		17	4	378.2	11	7	7	110	0	7.8	17/10/2002	La Guardia sector
	7.16	560	22.4		13	3	362.95	3	6	10	112	0	7.6	14/05/2003	El Estanque sector
W-7	7.90[a]	517	16.6		39	27	218	15	29	20	54	4	8.5	18/10/2005	La Guardia sector
S-1	7.34	553	17.2	50	27	6	329.4	4	11	13	102	1	7.9	15/05/2003	El Estanque sector
W-4	7.82	487	17.6		39	7	228.75	17	21	16.14	55.84	0	9.2	16/10/2002	La Guardia sector
	7.73	468			39	7	219.6	8	21	19	65	1	8.9	06/06/2003	El Estanque sector
W-5	7.56	516	15.6		15	6	350.75	9	7	11	91.24	0	7.3	17/10/2002	La Guardia sector
	7.33	505	15.5		15	3	326.35	3	6	10	94	0	7.5	15/05/2003	
S-2	7.80	427	16.4	0.5	27	9	219.6	17	17	15.82	52.92	0	8.3	16/10/2002	La Guardia sector
	7.97	423	17.2	2	23	9	244	6	13	18	56	1	8.4	14/05/2003	

[a] Laboratory value
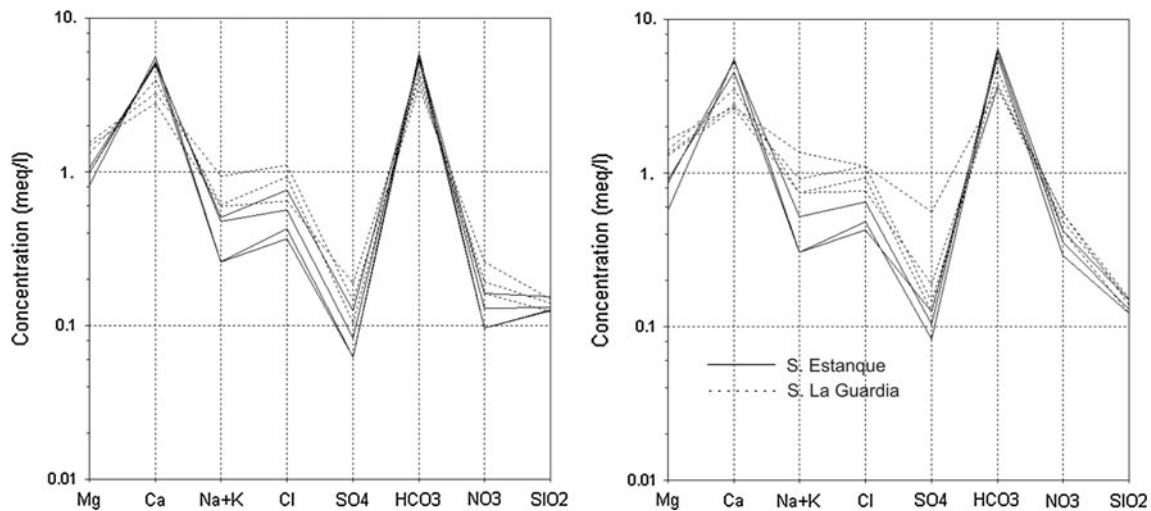
Fig. 5 Schoeller diagram. *Left* High-water conditions. *Right* Low water. The *solid lines* indicate points in the Estanque sector, and *dashed lines* of those in the La Guardia sector

simply as a result of small amounts supplied by the rock through which it circulates. The Cl^- variability is determined by elevation variations in the recharge areas and by the duration of the water–rock contact (residence time).

The correlation of the HCO_3^- with the Ca^{2+} shows an opposite trend, with a gradual decrease of both ions in the direction of flow from well W-2 to spring S-2 and to well W-7. The diagram correlating HCO_3^- with the Mg^{2+} shows a linear increase in Mg^{2+} together with a linear decrease in HCO_3^- in the direction of flow, with a significant shift between the water in the Estanque sector and that in the La Guardia sector, which is also visible in the Ca-HCO_3 correlation. This scenario implies the existence of calcium carbonate precipitation in the direction of flow; the increase in Mg^{2+} may be explained by additional supplies provided by the dissolution of dolomite.

The La Guardia borehole W-7 water follows this pattern for both low and high waters, but it does show an extra sulphate supply probably incorporated in its journey under the course of the Guadalbullón River and perhaps deriving from the Miocene marls confining the aquifer or from the gypsum-rich Subbetic Chaotic Complex clays, which bound the carbonates.

Groundwater saturation status

The study of the chemical species in the aquifer's groundwater indicates that the main hydrogeochemical processes affecting them are dissolution-precipitation of calcite and dolomite since there are no significant lithological supplies of other ions such as chloride or sulphate.

The graph A in Fig. 7 shows the correlation between the average field pH and the calculated CO_2 partial pressure logarithm. There is a steady increase in pH in the direction of flow (in accordance with the proposed hydrogeological model), and a resulting drop in CO_2, from points closest to the Sierra de Mojón Blanco (W-3) towards spring S-1 in the Serrezuela de Pegalajar, and again towards the N flank of the Serrezuela in the La Guardia sector (W-4 and S-2), where there is an abrupt jump.

At high water, the CO_2 contents range between a minimum of $10^{-2.69}$ in spring S-2 and a maximum of $10^{-1.67}$ in borehole W-3 (Table 2), with a gradual decrease in the direction of groundwater flow. At low water, the values at these same points (except for spring S-1) range from $10^{-2.52}$ in S-2 and $10^{-1.95}$ in W-3, with the same significance although with very similar values in the La Guardia sector (S-2 and W-4), which corresponds to water with a longer time of residence. The W-7 is not shown because of lack of reliable pH field data for this point.

The graph B shows the relation between water hardness (expressed in mg/L of $CaCO_3$) and CO_2 partial pressure; these parameters are very closely related, so the greater the availability of CO_2, the greater the hardness.

The graph C presents the relation of the SI in calcite and dolomite and the CO_2 partial pressure for high water; both indices show a good correlation with the CO_2 contents, having a higher saturation index the less carbon dioxide there is. This situation has also been observed by Cardenal et al. (1994) and by Moral et al. (2008) in other carbonate aquifers in southern Spain. In addition, the data plot a steeper slope for dolomite than for calcite, likely due to calcite's faster dissolution than dolomite.

According to Langmuir (1971), a solution is in equilibrium with respect to calcite if the SI is within a range of ±0.1; for dolomite, however, the range of uncertainty is ±0.5 (Plummer et al. 1990). In this light, the high waters
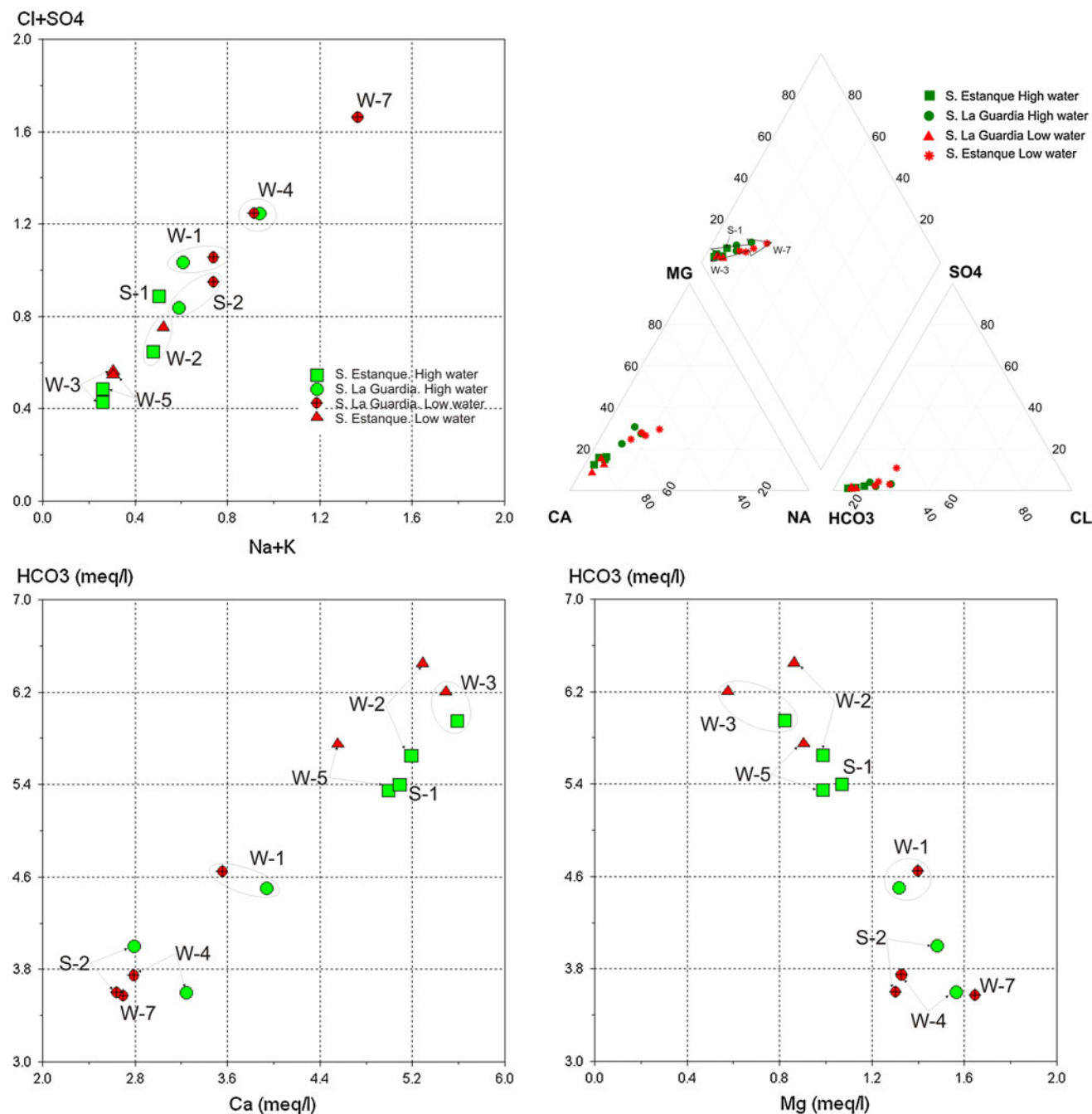
Fig. 6 Piper diagram and scatter diagrams of the points studied

of this aquifer are seen to be slightly supersaturated with respect to calcite in the Estanque sector and are clearly supersaturated in the La Guardia sector. As concerns dolomite, the waters are undersaturated in the Mojón Blanco (W-2), tend towards equilibrium in the Serrezuela (W-5 and S-1), and are oversaturated in the La Guardia sector (W-4 and S-2). These variations in the saturation indices occur as the CO_2 dissolved in the water is consumed, leading to the conclusion that the groundwater circulation in the saturated zone of the aquifer is a closed

system as regards CO_2. On the other hand, in the vicinity of the spring S-1 and, possibly, in the SE flank of the Serrezuela, the groundwater could evolve in an open system, because of the high permeability present in this area and the probable presence of well ventilated karst conduits in contact with the saturated zone. The increase in the saturation indices of calcite and dolomite between points W-5 and S-1 occurs without changes in PCO_2, suggesting the existence of external inputs to the system. In contrast, in the NW flank, CO_2 is consumed between points W-4 and
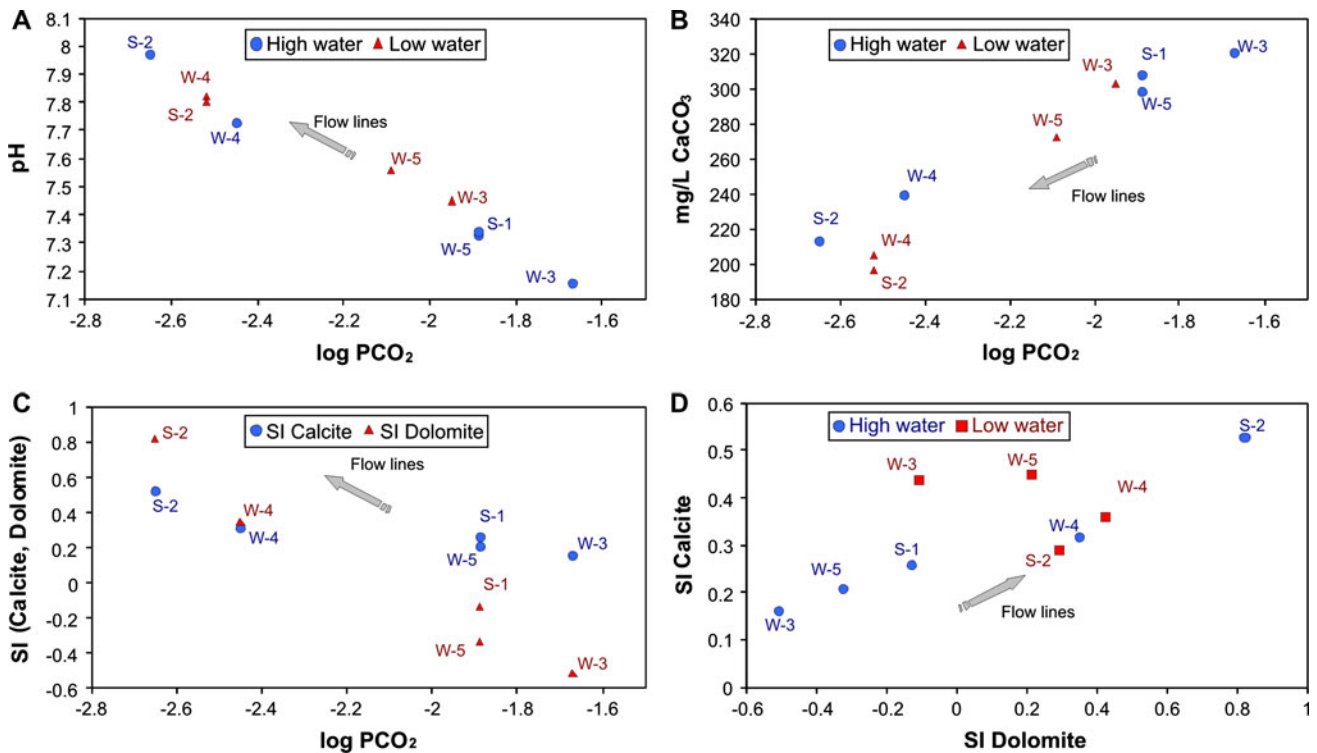
Fig. 7 Comparison of the calculated CO_2 partial pressure, the average field pH (**a**), the water hardness (**b**), and saturation indices for calcite and dolomite (**c**) and the ratio of the two saturation indices (**d**)

Table 2 Saturation indices and PCO_2 calculated for the high-water samples in May and June of 2003, for low water in October 2002, pH field data, and T

Point	pH field	T (°C)	SI calcite	SI dolomite	SI gypsum	log PCO_2	Sector
High water							
W-3	7.16	15.9	0.16	−0.51	−2.93	−1.67	El Estanque
W-5	7.33	15.5	0.21	−0.33	−2.98	−1.89	El Estanque
S-1	7.34	16.6	0.26	−0.13	−2.67	−1.89	El Estanque
W-4	7.73	17.6	0.32	0.35	−2.75	−2.45	La Guardia
S-2	7.97	17.2	0.53	0.82	−2.69	−2.65	La Guardia
Low water							
W-3	7.45	14.8	0.44	−0.11	−2.81	−1.95	El Estanque
W-5	7.56	15.6	0.45	0.21	−2.69	−2.09	El Estanque
W-4	7.82	17.2	0.36	0.42	−2.8	−2.52	La Guardia
S-2	7.8	16.4	0.29	0.29	−2.7	−2.52	La Guardia

S-2, in a similar situation, suggesting the existence of low permeability levels impeding the outflow of CO_2.

At high water, there is a gradual increase in the direction of groundwater flow in the SI of calcite and dolomite. In contrast, at low water, there is a clear drop in the calcite SI in the flow of water from the Estanque sector to La Guardia, whereas the dolomite SI continues to rise (graph D). These circumstances may be explained by the existence of processes involving incongruent dissolution of dolomite, particularly significant in the La Guardia sector where, at the same time as there is dolomite dissolution, there is also calcite precipitation.

Hydrochemical modelling

The main infiltration zone is between elevations of 1,250–1,300 masl; this elevation is that of the high plain occupying all the Mojón Blanco peaks (Fig. 1). In this zone, the average temperature is around 14°C and, although part of the carbonate outcrops are barren of soil and shaped by deep-cutting karren, other parts are covered by dense pine forests that ensure a substantial supply of CO_2 to the soil.

The Mojón Blanco outcrop comprises Cretaceous limestones containing, especially in the footwall,

Fig. 8 Scheme for modelling the flow path in the aquifer at high water
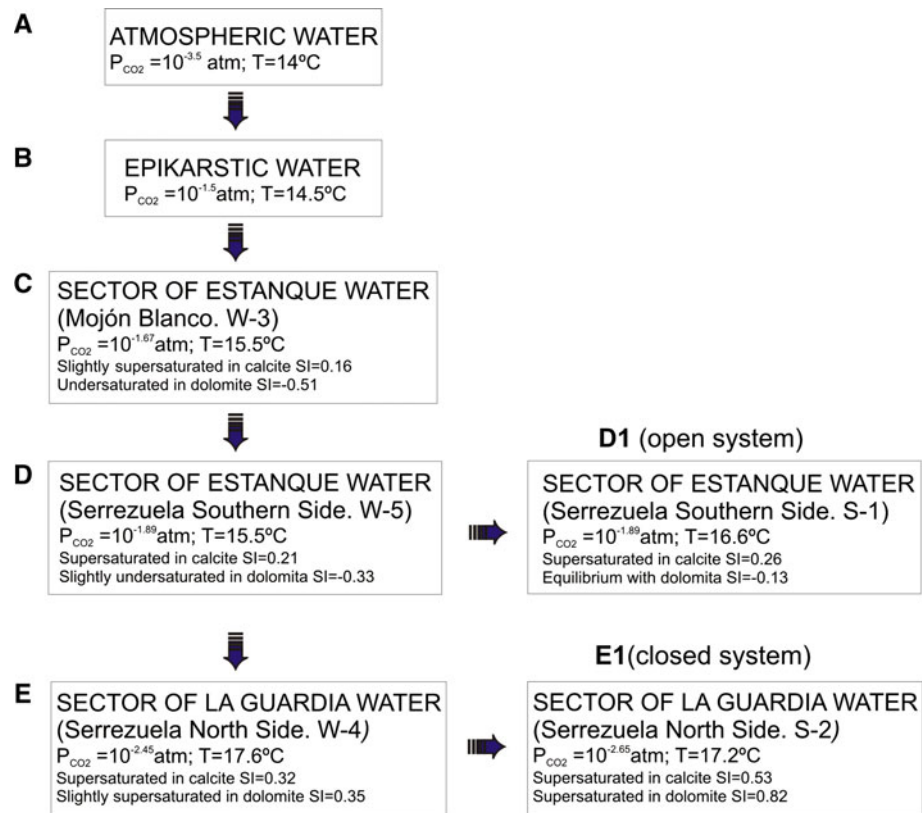
occasional thin marl intercalations. As no dolomitized outcrops have been described in this sector, dolomite is assumed to be a secondary mineral in the carbonate formation.

The piezometric and hydrochemical data collected support the existence of a hydraulic connection from this outcrop to the neighbouring outcrop of the Serrezuela de Pegalajar. A flow path between the SE and NW flanks of the anticline fold comprising the Serrezuela de Pegalajar is also deduced. The NW flank of this anticline is the only zone in the entire aquifer for which substantial dolomitized sectors have been described (Roldán et al. 1991). Finally, the existence was also determined of a hydraulic connection between the NW flank of the Serrezuela and the Cretaceous outcrop of the left-hand bank of the Guadalbullón River, on which rests the town centre of La Guardia.

A study of water saturation in the aquifer indicates that the hydrogeochemical evolution is determined, during high-water conditions, first by a fast dissolution of calcite to saturation, which must happen in the ground itself. Dolomite, however, does not reach equilibrium until the groundwater reaches nearly the NW flank of the Serrezuela, where it is supersaturated. The dolomite dissolution occurs very slowly in the first stage of the groundwater circulation between the Mojón Blanco recharge zone and the spring S-1; however, it begins to be notable in the La Guardia sector thanks to the greater prevalence of dolomite in the

rocks in the zone. The dolomite saturation entrains calcite precipitation because of a common ion when calcium and CO_3^{2-} become incorporated in the solution from the dissolved dolomite, known as incongruent dolomite dissolution. This process is observed at the points in the La Guardia sector in which there is a decrease in the bicarbonate and in the calcium associated with an increase in the magnesium ion, which implies calcite precipitation.

This entire process is also influenced by the gradual increase in the water temperature as it descends through the aquifer, from around 14°C at the main recharge area to over 17°C at spring S-2. The flow path under the Guadalbullón River towards the La Guardia outcrop involves another increase in temperature up to thermal conditions, logging 22°C at borehole W-7.

In order to discuss in detail the hydrogeochemical model described and to study its feasibility, the entire process was modelled and the results were compared to the data from the most representative points along the flow path of the groundwater. The data from boreholes W-3, W-5, and W-4 and the springs S-1 y S-2 at high water have been used as representative points. The flow path towards the La Guardia outcrop has not been modelled since there is no reliable pH field data for the points in this zone (boreholes W-6 and W-7), although temperature data is available.

The model proposed for the hydrogeochemical evolution in the aquifer starts by considering pure rainfall at a

Table 3 Values expressed in mmol/kg of the distinct elements and mineral phases showing the probable evolution of water in the Mancha Real-Pegalajar Cretaceous carbonate aquifer

Plain font shows the values measured or calculated from these measurements at the points considered, and in bold are the measurements calculated from the PHREEQC modelling. In the mineral phases, positive signs indicate dissolution and negative signs precipitation
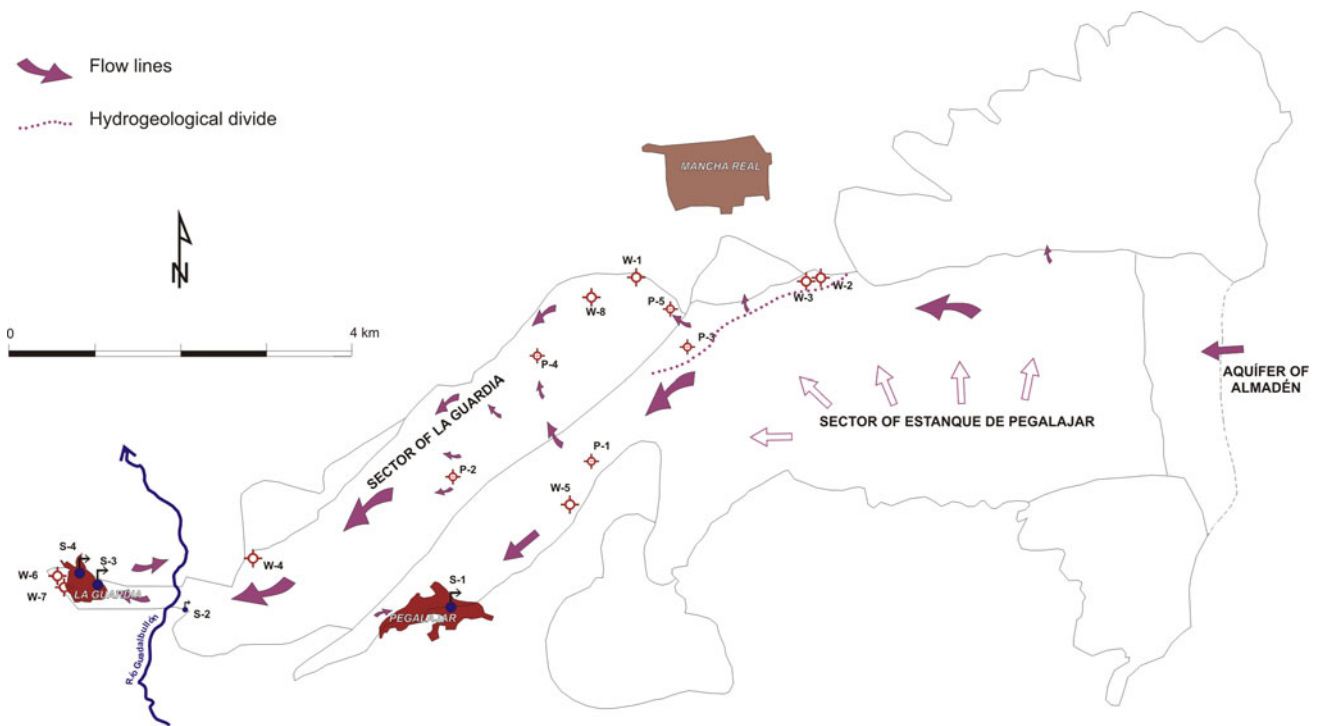
	A	B	C		D		D1 (open system)		E		E1 (closed system)	
T (°C)	14	14.5	15.5		15.5		16.6		17.6		17.2	
Log PCO_2	−3.5	−1.5	−1.67		−1.89		−1.89		−2.45		−2.65	
pH	**5.5**	**6.98**	**7.17**	7.16	**7.33**	7.33	**7.35**	7.34	**7.77**	7.73	**7.98**	7.97
Alkal. (meq/kg)	**0**	**5.98**	**6.14**	5.95	**5.37**	5.35	**5.57**	5.4	**3.88**	3.6	**4.02**	4
Ca	**0**	**2.99**	**2.68**	2.79	**2.28**	2.5	**2.29**	2.54	**1.32**	1.62	**1.31**	1.39
Mg	**0**	**0**	**0.40**	0.41	**0.41**	0.49	**0.49**	0.53	**0.63**	0.78	**0.71**	0.74
Calcite	**0**	**+2.99**	**−0.71**		**−0.41**		**+0.01**		**−1.19**		**−0.01**	
Dolomite	**0**	**0**	**+0.40**		**+0.01**		**+0.08**		**+0.22**		**+0.08**	
CO_2(gas)	**0**	**+4.43**	**−0.43**		**−0.77**		**+0.08**		**−1.19**		**0**	
SI$_{calcite}$	–	0	0.16		0.21		0.26		0.32		0.53	
SI$_{dolomite}$	–	–	−0.51		−0.33		−0.13		0.35		0.82	

Fig. 9 Sectors, associated water points, and main flow paths

temperature of 14°C and a pH of 5.5. The first step is to equilibrate this water with atmospheric conditions, using a PCO_2 of $10^{-3.5}$ atm and a PO_2 of $10^{-0.6}$ atm. In the following steps, the conditions in the topsoil and the unsaturated zone down to the saturated zone are simulated where, first, the saturation and PCO_2 conditions calculated for borehole W-3 are imposed, and then those for boreholes W-5 and W-4. The steps taken are summarised in Fig. 8. Steps A, B and D1 consider a system open to CO_2 and the others consider a closed system. Table 3 shows the values

provided by the simulation and the real values at each of the points considered.

The values yielded by the modelling programme confirm the feasibility of the hypotheses. Infiltration water reaches saturation in calcite by incorporating huge amounts of CO_2 from the topsoil; as it flows down towards the saturated zone, part of the dissolved calcite is precipitated out, probably due to the exsolution of CO_2 in karst cavities and fissures that are well connected to the outside. This process generates speleothems. In addition, dolomite

dissolution also begins to occur. The infiltrated water reaches the phreatic level saturated in calcite and undersaturated in dolomite. Along the flow path from the Sierra de Mojón Blanco to the SE flank of the Serrezuela de Pegalajar (Fig. 9), there are scarcely any changes in dolomite saturation, and there is some calcite precipitation with consumption of CO_2. In the SE flank, the permeability is very high, and is probability the presence of well ventilated karst conduits in contact with the saturated zone; specially in the vicinity of spring S-1. For this reason, the groundwater evolves to the spring without changes in PCO_2, in an open system.

In contrast, along the flow path from the SE flank towards the NW flank of the Serrezuela de Pegalajar anticline, there is incongruent dolomite precipitation together with calcite precipitation and a high loss of CO_2. Moreover, there is a significant increase in magnesium as a result of the dolomite dissolution, which is considerable in this sector of the aquifer. The groundwater evolves to spring S-2 in a closed system, without replenishment of consumed CO_2, probably due to the existence of less permeable levels that impede the ventilation near of the saturated zone.

Conclusions

For the purposes of the study, the aquifer has been divided into various sectors in accordance with the position of the phreatic level. The largest is the Estanque of Pegalajar sector, which is also where most of the groundwater infiltrates. It comprises the Sierra de Mojón Blanco and the SE flank of the Serrezuela de Pegalajar anticline.

In the southcentral zone of the Sierra de Mojón Blanco, there is a tabular structure with its strata dipping gently northwest; towards both boundaries, the carbonate package gradually increases its dip until it is nearly vertical at the edges. The central zone crops out at high elevations (1,200–1,300 masl) and is where most infiltration takes place. From this zone of preferential infiltration, the percolated water flows towards the northwest border, where it is stored.

At the northern border of the Sierra de Mojón Blanco, the stored water flows towards the west. In the SE flank of the Serrezuela de Pegalajar, the groundwater has a preferential NE-SW flow path controlled by spring S-1 and very low gradients, a reflection of the high permeability of the carbonates in this zone. However, the piezometric data for this sector indicate the presence of a piezometric threshold, which may be accounted for by the occurrence, on the northern border of the Serrezuela de Pegalajar, of discharge towards the La Guardia sector in the direction of the periclinal closure of the anticline forming this range.

This closure causes the Cretaceous carbonates to dip under the water table level of the Estanque sector over a short distance.

The La Guardia sector also receives another groundwater supply (perhaps even more substantial) from the Estanque sector, through the sunken block of the fault of Artesilla hill. In this sector, the saturated zone is found, where not subject to other influences, at elevations of 560–580 masl and with a NE–SW flow path. The groundwater reaches the right-hand bank of the Guadalbullón River and flows under it towards the Cretaceous carbonate outcrop on which lies the town centre of La Guardia. In this stage, the groundwater reaches thermal conditions (22°C). A small portion of this water emerges at spring S-2 before it passes under the Guadalbullón River. Finally, the main discharge occurs into the Guadalbullón River on its left-hand bank through the contact between the travertine created by the groundwater discharge and the river's alluvial terrace. Before the W-6 supply well was bored for La Guardia, there were also significant springs in the town centre.

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