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# Geochemical evolution of groundwater in the carbonate aquifers of Sierra de Segura (Betic Cordillera, southern Spain)

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## KEYWORDS

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Hydrochemical  
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Mg/Ca ratio;  
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**Summary** Sierra de Segura (Betic Cordillera), with a total area of over 3000 km<sup>2</sup>, is the source of the two principal rivers in southern Spain, the Guadalquivir and the Segura. Due to the orographic effect of these mountains, precipitations are considerably more abundant than in nearby lowland areas, where the climate is semi-arid. Sierra de Segura is constituted of Mesozoic and Cenozoic sedimentary rocks, among which there are thick limestone–dolomitic formations which have given rise to extensive outcrops of permeable materials. In geomorphological terms, there is a large plateau intensively karstified that constitutes the main recharge area. Discharge takes place via a large number of springs, of which the 50 most important add up to a mean spring flow of about 13,500 l/s. The active geochemical processes in aquifers of Sierra de Segura, with their corresponding time sequence, are: dissolution of CO<sub>2</sub>, dissolution of calcite, incongruent dissolution of dolomite, dedolomitization, exsolution of CO<sub>2</sub>, and precipitation of calcite. More evolved water has higher temperature, magnesium content and Mg/Ca ratio; therefore, these parameters can be utilised as indicators of the degree of hydrochemical evolution. In addition, a good correlation between water temperature and magnesium concentration (or Mg/Ca ratio) indicates that an increase in temperature accelerates the kinetics of the dissolution of dolomite. Finally, the distribution of the temperatures in the vadose zone, determined by atmospheric thermal gradient, implies an apparent stratification of the predominant hydrochemical processes and of the groundwater physical and chemical characteristics.

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## Introduction

The physical and chemical characteristics of groundwater in karstic aquifers are determined by the chemical and mineral composition of the aquifer rocks, by the predominant geochemical processes, by the residence time and by other factors inherent to the medium and the groundwater flow, such as hydraulic conductivity, the specific surface area of water–rock interface and the flow regime.

Traditionally, studies of karstic systems have addressed the above question by observing the physical, chemical and hydrodynamic characteristics of the springs flowing from the system, which in the case of unexploited aquifers are generally the only points at which access for observation of the groundwater is possible. This approach (Király, 2002) considers the behaviour of a karstic spring to represent the “global response” of the system to the input signal (infiltration episode). This response, which is relatively simple to measure, enables us to hypothesize (sometimes in various, even contradictory, ways) about processes of infiltration and groundwater flow, and about the degree of karstification.

In this respect, the temporal variability of the hydrodynamic and physico-chemical characteristics of the spring water allows to classify hydrogeological systems on the basis of the degree of karstification and the predominant type of flow. Thus, Mangin (1975) proposed a classification based mainly on the analysis of the recession curve; Shuster and White (1971, 1972) and Bakalowicz (1976) classified karstic systems in accordance with the chemical variability of groundwater, while Bonacci (1987) presented a similar proposal, based on changes in water temperature.

Nevertheless, present-day knowledge of the spatial variability of the characteristics of the karstic medium leaves many questions still unanswered. The conceptual models of karstic aquifers that are most commonly accepted today comprise a pattern of triple porosity and permeability, resulting from the existence of a matrix with primary porosity, a system of fractures and a network of conduits (White and White, 2001; White, 2002), and the presence of an epikarst, a superficial layer of high porosity and permeability, created by preferential fissuring and karstification (Gunn, 1983; Williams, 1983; Klimchouk, 2000; White, 2002). The acceptance of these concepts implies to assume the existence of a high degree of heterogeneity on the hydraulic conductivity field.

It is apparent, therefore, that karstic systems are not homogeneous: the water temperature varies, as do the predominant geochemical processes, the chemical composition of water, the degree of karstification, the predominant type of groundwater flow and the residence time of water.

In Sierra de Segura, there are numerous karstic systems, which are characteristic in that their principal recharge zone is constituted of the remains of a former karstic plateau, at an altitude ranging from 1500 to 1900 m. Scarce piezometric data and other hydrogeological, topographic, geomorphological and speleological data allow us to assert that unsaturated zone thickness is generally in the range of several hundreds of metres. So, discharge takes place at altitudes comprised between 800 and 1400 m. However, in a few places, it is known the

existence of perched water tables related to Segura plateau epikarst.

These mountains provide an essential water supply of high quality for domestic and agricultural purposes in the lowlands of Guadalquivir and Segura basins, two regions characterized by semi-arid climate with severe drought periods and a structural water deficit.

The goals of the present study are to characterize, in physical and chemical terms, the water of the springs in Sierra de Segura, to propose a model of groundwater geochemical evolution and to analyze the factors influencing the spatial variability, and particularly the vertical variability, of the physical and chemical characteristics of groundwater, together with its possible relation to other hydrogeological and environmental factors.

## Geological and hydrogeological context

Situated in the central part of Betic Cordillera (southern Spain), the Sierra de Segura (surface area of over 3000 km<sup>2</sup>) has an elongated shape (over 100 km) and is oriented approximately N30E. In these mountains, with summits over 2000 m high, is located the origin of the two main rivers of southern Spain, the Guadalquivir, which flows into the Atlantic Ocean, and the Segura, which flows towards the Mediterranean Sea.

From a geologic standpoint, the area is part of the Prebetic Zone (Fig. 1), characterized by the presence of a sequence, some 2000 m thick, of Mesozoic and Tertiary sedimentary rocks that were mainly deposited in a marine medium close to the former Iberian margin (Azema et al., 1979; Foucault, 1971; Dabrio, 1972; Rodríguez-Estrella, 1979; López-Garrido, 1971). The synthetic stratigraphic sequence of the Prebetic Zone units includes two main aquifer materials, comprised of Lias-Dogger dolomites and Upper Cretaceous dolomites and limestones, which may be superposed by Palaeogene and Miocene limestones (Pendás, 1971; Moral, 2005). Jurassic materials only outcrop, to a small extent, at the western edge of Sierra de Segura. The most important permeable outcrops are constituted of the Upper Cretaceous and Tertiary carbonate rocks.

The geological structure is of alpine age and consists of a succession of folds and fault-folds, oriented approximately N30E and with vergence towards NW, affected by dextral strike-slip faults that are perpendicular to the fold axes. In a later distensive phase, various tectonic grabens were created, these being bounded by normal faults, that were filled in by post-orogenic sediments (Azema et al., 1979; Dabrio, 1972; Rodríguez-Estrella, 1979). After the folding and emergence of the region, an erosive phase during the upper Miocene occurred, which created a smooth erosion surface. Since then, the region has been uplifted considerably, such that the former plateau is currently at an altitude of 1500–1900 m. Due to this uplifting, there has been an increase in the erosive power of the river network, which has progressively worn the Cretaceous and Tertiary rocks, breaking up the ancient plateau, although remains of the latter can still be observed, occupying a surface area of over 800 km<sup>2</sup>.

The orography of the region has led to Sierra de Segura comprising a substantial mountain barrier to humid winds

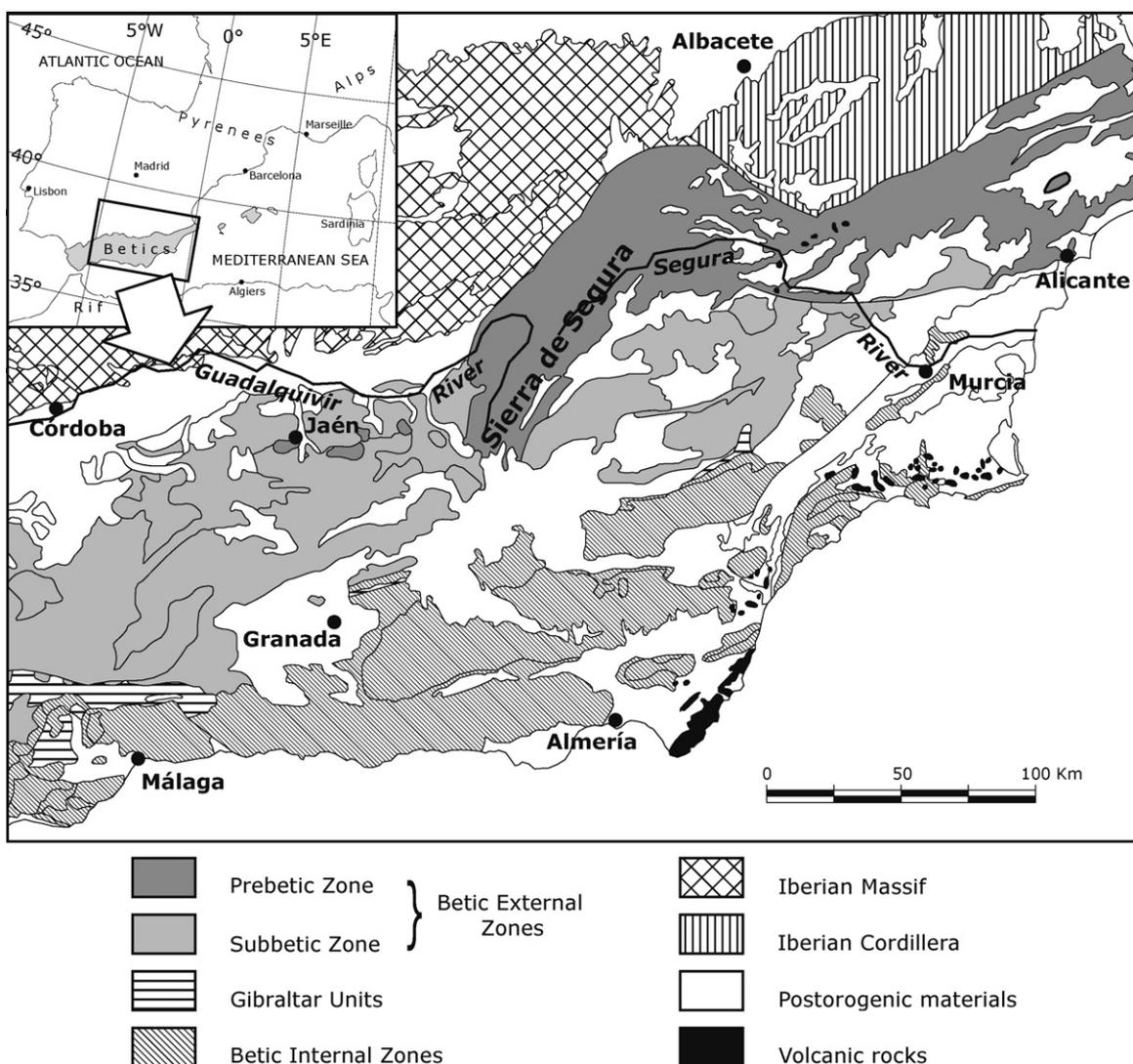


Figure 1 Regional geological setting of Sierra de Segura.

from the west, which means that precipitations are abundant (over 1000 mm annually) on the western slopes and on the summits of the mountain range, while the climate is semi-arid to the east of the mountains, with precipitations lesser than 500 mm/year.

The climate is of a Mediterranean type, with very dry summers and a rainy season extended from November to April, during which over 70% of annual precipitation occurs. Approximately 90% of surface runoff takes place from October to May.

The abundance of outcropping carbonate rocks, the relatively shallow slopes and the large volume of precipitations have favoured an extraordinary development of exokarstic forms in the remains of the plateau (López-Limía, 1987; Moral, 2005); in consequence, this is the main groundwater recharge area of Sierra de Segura.

Given the relation between the isotopic composition of the precipitation waters and the altitude, Cruz-Sanjulián et al. (1990) concluded that groundwaters infiltrate at an average altitude of around 1600 m, which is coherent with other geological and geomorphological observations.

Subterranean discharge from studied aquifers occurs in natural regime through more than 50 main springs, with a mean flow of between 40 and 1500 l/s. These springs are situated at the foot of the mountains, mainly at altitudes between 900 and 1300 m (Fig. 2 and Table 1).

In the northern sector of Sierra de Segura, fluvial erosion has individualized some twenty hydrogeological units, mainly of small surface area and with limited water resources (100 hm<sup>3</sup>/year for the whole sector). In the central and southern parts, extensive carbonate outcrops and the considerable development of the karstic morphology on the plateau created conditions enabling the infiltration of large amount of water, estimated at 330 hm<sup>3</sup>/year (Moral, 2005).

## Methods

The experimental data, corresponding to the period 1988–2004, were obtained from field trips and from chemical analyses performed in the laboratory. Portable equipment was used to obtain in situ readings of temperature, pH

and electrical conductivity. At the same time, samples of non-acidified water in 500 ml polyethylene bottles were taken. The measurement of  $\text{HCO}_3^-$  and Ca was carried out in the shortest time practicable, although the field campaigns normally took 3 or 4 days; during this period, the samples were kept at a low temperature in a portable refrigerator.

The  $\text{HCO}_3^-$  content was determined as the total alkalinity, by titration with HCl 0.05 N and methyl orange as indicator. The cations were analyzed by atomic absorption spectrometry (Ca and Mg) and by emission spectrometry (Na and K). A visible light spectrophotometer was used to analyse  $\text{SO}_4$  by turbidimetry and the  $\text{SiO}_2$ , by colorimetry. The concentrations of Cl ions were determined by argentometric titration, using  $\text{AgNO}_3$  0.01 N and 5%  $\text{K}_2\text{CrO}_4$  as indicator. Since the year 2001, all the ions, except the bicarbonates, were analysed by ionic chromatography.

The hydrochemical calculations were performed using the AQUACHEM program (Calmbach, 1997), which makes it possible, in a straightforward way, to use of PHREEQC (Park-

hurst and Appelo, 1999). The computer processing of these hydrochemical data had two main objectives: (1) to determine the saturation indexes of calcite, dolomite and gypsum, and the partial equilibrium pressure of  $\text{CO}_2$ , and (2) to calculate mass transfer along the flow path.

### Physical and chemical characteristics of groundwater

Table 1 shows the mean water temperature in the main springs; the values recorded ranged from 8.5 °C in Fuente Segura (ref. 22) to 21 °C at Los Tubos (ref. 36). The springs with the highest flows tended to drain colder waters, with temperatures ranging from 9 to 11 °C. In addition, it should be noted that there are a few weakly thermal springs (water temperature close to 20 °C), of which the most significant are Los Tubos (ref. 36), La Toba de Jartos (ref. 9) and El Nacimiento (ref. 10) springs.

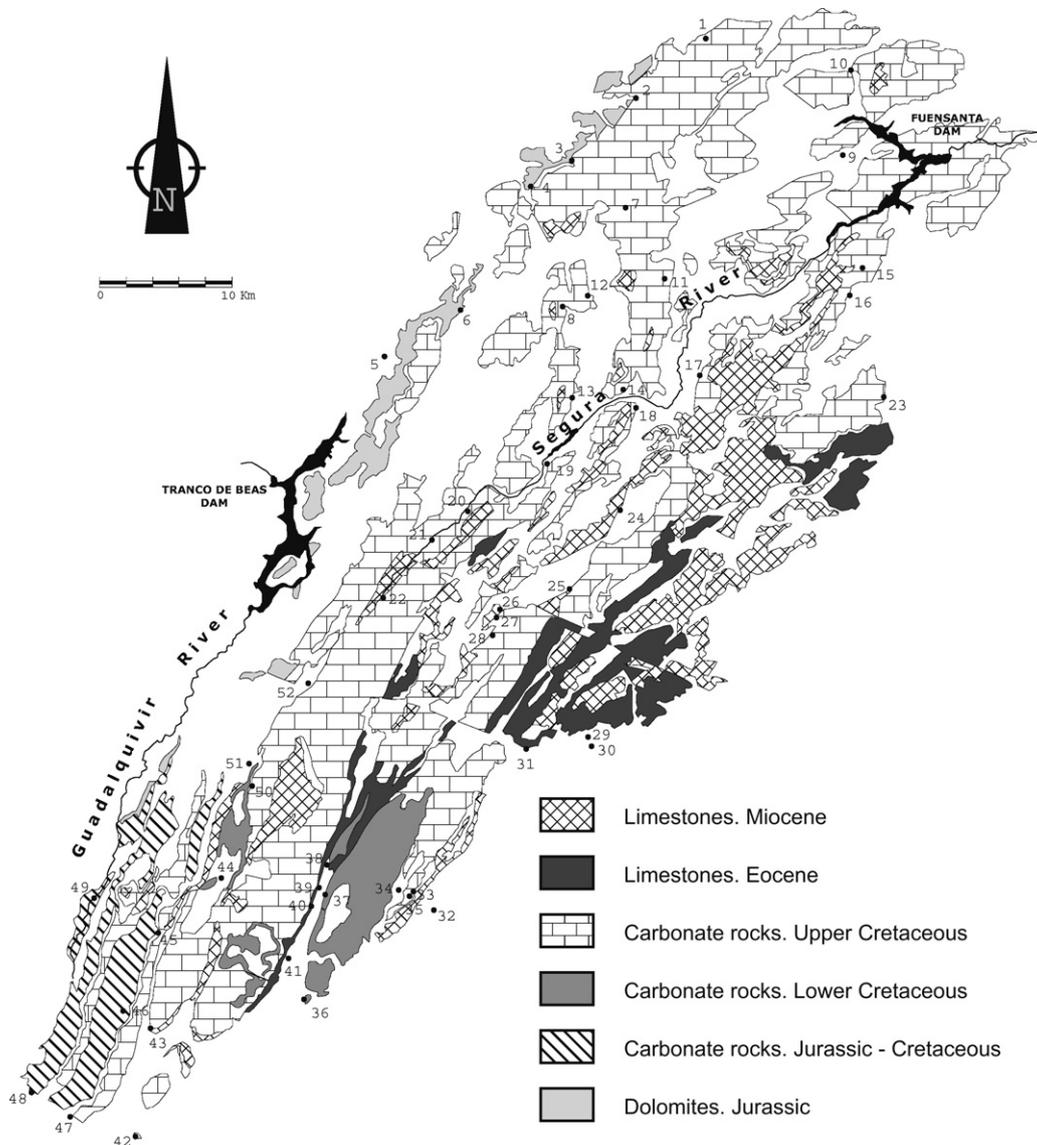


Figure 2 Carbonate outcrops in the study area and location of the main springs.

**Table 1** Physicochemical characteristics of spring waters of Sierra de Segura

Ref.	Spring	Height (m.a.s.l.)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	HCO <sub>3</sub> (mg/l)	SO <sub>4</sub> (mg/l)	Cl (mg/l)	T (°C)	EC (μS/cm)	pH	log P <sub>CO<sub>2</sub></sub>	SI <sub>calcite</sub>	SI <sub>dolomite</sub>	Mg/Ca (molar ratio)
1	El Molino	1000	36.7	11.7	0.9	184.1	3.2	2.0	10.6	253	7.93	-2.754	0.133	-0.099	0.319
2	Arroyo Frío (II)	1000	40.5	13.2	0.9	206.8	2.3	1.9	11.8	263	7.74	-2.507	0.049	-0.236	0.326
3	San Blas	980	43.9	15.5	1.1	233.8	3.7	2.1	13.0	305	8.42	-3.146	0.800	1.327	0.581
4	Era del Concejo	940	54.5	17.4	1.3	277.2	3.3	2.6	14.0	347	8.08	-2.720	0.643	0.983	0.526
5	El Ojuelo	820	63.4	16.5	2.2	272.2	16.9	4.2	13.4	414	7.36	-2.005	-0.027	-0.457	0.260
6	La Maleza	880	57.0	19.5	6.0	337.0	22.5	6.0	13.1	522	6.92	-1.474	-0.433	-1.157	0.342
7	Las Pegueras	920	37.0	10.0	3.0	191.0	4.0	4.0	11.0	272					
8	El Tejo	1320	53.4	15.1	2.0	243.6	6.2	5.7	10.0	328	7.66	-2.369	0.086	-0.182	0.282
9	La Toba de Jartos	780	69.3	30.8	54.9	347.6	65.0	89.5	20.7	762	7.27	-1.799	0.071	0.084	0.444
10	El Nacimiento	810	71.0	37.0	30.0	353.0	85.5	46.0	17.8	692	7.27	-1.789	0.044	0.057	0.521
11	Alcantarilla	880	48.0	9.4	0.9	205.4	3.6	1.6	13.4	279	8.33	-3.105	0.714	0.905	0.322
12	Santa Ana	1330	47.2	18.1	1.1	259.1	5.4	1.6		335	8.24				
13	El Gorgocín	1250	42.2	17.4	1.7	210.8	4.0	3.4	11.7	282	7.84	-2.603	0.163	0.094	0.412
14	Cuatro Caños	820	41.7	18.7	2.6	226.2	5.1	4.3	13.7	292	8.07	-2.797	0.438	0.717	0.738
15	El Arroyo	950	53.8	22.2	3.2	271.6	3.8	5.3	15.3	376	7.52	-2.157	0.094	0.017	0.413
16	Sege	950	53.8	21.9	3.2	271.0	3.2	5.3	15.2	372	7.60	-2.239	0.171	0.164	0.407
17	Torcal	1020	49.9	20.3	2.5	252.5	2.9	4.8	13.8	360	7.79	-2.467	0.281	0.361	0.407
18	Casa de Arriba	1040	50.9	12.1	1.6	219.3	3.7	3.8	12.3	321	7.79	-2.532	0.220	-0.020	0.238
19	La Toba	1010	43.9	13.1	2.0	201.4	5.5	4.4	12.7	278	7.66	-2.435	0.003	-0.350	0.302
20	Cueva del Agua	1240	43.9	10.8	1.7	185.2	3.1	3.8	10.4	228	7.88	-2.703	0.155	-0.170	0.246
21	Molino de Loreto	1280	45.0	11.8	1.8	204.8	5.1	4.9	10.0	273	7.57	-2.350	-0.109	-0.679	0.260
22	Fuente Segura	1410	45.6	5.1	1.4	168.7	3.1	4.3	8.5	224	7.64	-2.509	-0.126	-1.111	0.112
23	F. del Taibilla	Discharge into a stream channel													
24	Tobos	1110	50.9	14.7	2.4	241.3	4.8	4.5	11.6	328	7.43	-2.509	-0.112	-0.613	0.288
25	El Cerezo	1175	66.8	14.2	2.0	266.9	4.8	2.4	11.4	383					
26	El Berral	1290	48.7	11.4	1.8	217.5	5.3	5.0	9.6	300	7.55	-2.307	-0.079	-0.676	0.233
27	El Muso	1310	45.9	12.8	1.8	222.3	3.9	4.1	10.1	294	7.57	-2.315	-0.067	-0.567	0.279
28	Arroyo Frío	1350	47.4	13.3	2.0	236.4	4.0	4.5	9.6	323	7.77	-2.493	0.159	-0.120	0.281
29	Los Agujeros	1440	58.1	5.8	1.7	224.3	4.5	4.3	10.1	312					
30	El Saúco	1380	56.5	4.0	2.0	222.0	2.5	6.5	10.3	304	7.66	-2.404	0.118	-0.788	0.071
31	Montilla	1480	56.2	2.4	1.8	188.3	5.6	4.8	9.6	267	7.50	-2.317	-0.119	-1.495	0.043
32	San Clemente	1060	54.5	14.5	4.0	259.0	10.0	6.0	12.8	400					
33	La Natividad	1090	55.8	15.6	3.0	266.7	6.8	5.9	11.8	360	7.24	-1.900	-0.223	-0.847	0.301
34	Fuente Alta	1140	51.7	9.8	2.8	213.5	7.6	5.4	12.3	298	7.40	-2.151	-0.170	-0.900	0.193
35	En medio	1090	48.0	10.3	3.3	207.8	5.5	5.0	12.7	282	7.82	-2.583	0.212	-0.075	0.215
36	Los Tubos	1080	53.3	28.9	22.0	300.4	23.9	31.9	21.0	534	7.36	-1.924	0.030	0.093	0.545
37	Juan Ruiz	1170	45.2	12.9	1.8	205.1	4.8	4.3	10.2	278	7.72	-2.500	0.044	-0.333	0.285
38	Nac. Castril	1250	41.7	11.4	1.6	188.4	5.8	4.6	9.5	246	7.98	-2.802	0.223	-0.005	0.275
39	H. del Morcillo	1100	40.0	16.5	2.0	210.3	3.3	4.0	10.8	262	7.89	-2.658	0.178	0.107	0.413
40	La Magdalena	1100	39.0	18.2	1.8	216.8	3.3	4.2	10.1	271	7.73	-2.487	0.009	-0.190	0.467

(continued on next page)

Table 1 (continued)

Ref.	Spring	Height (m.a.s.l.)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	HCO <sub>3</sub> (mg/l)	SO <sub>4</sub> (mg/l)	Cl (mg/l)	T (°C)	EC (µS/cm)	pH	log P <sub>CO<sub>2</sub></sub>	SI <sub>calcite</sub>	SI <sub>dolomite</sub>	Mg/Ca (molar ratio)	
41	Lézar	980	46.8	17.1	2.3	235.9	6.7	5.3	11.6	328	7.58	-2.487	-0.009	-0.307	0.374	
42	M. de Peralta	760	44.4	19.1	16.2	226.7	8.2	22.0	16.0	368	7.72	-2.431	0.148	0.154	0.433	
43	F. Guadalentín	970	46.3	15.4	2.3	206.2	3.5	5.1	10.2	271	7.66	-2.438	-0.006	-0.366	0.333	
44	Los Chorros	1300	97.7	12.4	4.8	350.8	1.8	1.1	9.5		7.25					
45	La Canaleja	Discharge into a stream channel														
46	Guazalmanco	1170							10.5	381	7.72					
47	Siete Fuentes	900							14.0	419						
48	La Canal	760	58.1	17.0	15.4	202.9	41.9	7.0	16.4	437	7.62	-2.377	0.064	-0.130	0.482	
49	El Túnel	1050	81.4	19.2	1.2	274.5	3.6	1.4	10.2	363	7.38	-2.034	-0.064	-0.483	0.388	
50	Aguas Negras	1260	43.7	14.4	1.7	217.4	5.1	4.7	9.1	291	7.46	-2.219	-0.223	-0.824	0.331	
51	Minicentral	950	42.0	20.5	2.5	216.0	4.5	4.0	10.1	312						
52	Aguamulas	1100	41.8	6.8	1.3	166.9	5.0	4.7	9.7	230	7.70	-2.568	-0.090	-0.854	0.168	

Fig. 3 shows that there is a clear relation between the altitude of the springs and the water temperature. Comparison of the latter with the atmospheric thermal gradient reveals that most of the springs, according to Schöeller's criteria, would be classified as "cold water springs" (i.e., the water temperature is below that the mean air temperature at ground level; Schöeller, 1962).

The underground thermal gradient was found to fit the conceptual model of temperature distribution in karstic systems proposed by Luetscher and Jeannin (2004). These authors concluded that the temperature in the vadose zone is determined by the circulation of infiltration waters and, above all, by the circulation of air; therefore, within an active karstic system the temperature tends to be close to that of the mean air temperature at a point on the land surface at a similar altitude.

The water in the limestone–dolomite aquifers of Sierra de Segura is characterised as presenting low levels of mineralisation, such that the total value of dissolved solids is usually between 0.25 and 0.35 g/l, with the exception of those springs associated with thermal systems, where levels of up to 0.65 g/l have been recorded (Moral et al., 2005). Obviously, this weak mineralisation is apparent in relatively low values of electrical conductivity of the water, these generally being between 220 and 420 µS/cm, except in the case of thermal waters, where values of up to 770 µS/cm have been recorded.

As is to be expected in waters that circulate across carbonate rocks, the hydrochemical facies are calcium bicarbonate and calcium–magnesium bicarbonate, in a very pure form, such that HCO<sub>3</sub>, Ca and Mg constitute over 90% of the dissolved solids in water (Fig. 4). Once again, the exception is to be found in weakly thermal waters, where appreciable concentrations of SO<sub>4</sub>, Cl or Na can be found, although none of them exceed 100 mg/l.

Over 70% of all the water drained by the aquifers of Sierra de Segura presents a calcium content of 40–50 mg/l, a magnesium content of 10–20 mg/l and a bicarbonate content of 180–240 mg/l.

The pH values measured in situ were almost always between 7 and 8, with the exception of La Maleza spring (ref. 6), where the measured pH was 6, and some springs in the northern part of Sierra de Segura, where pH values of over 8 were recorded.

Fig. 5a and b shows calcium and magnesium concentration in the spring water related to altitude. While in the

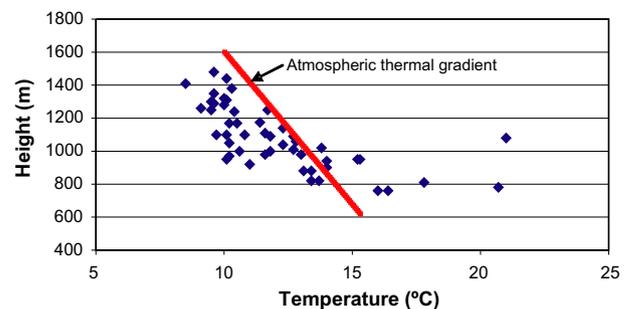


Figure 3 Plot of height above sea level versus water temperature of springs. The straight line represents the atmospheric thermal gradient.

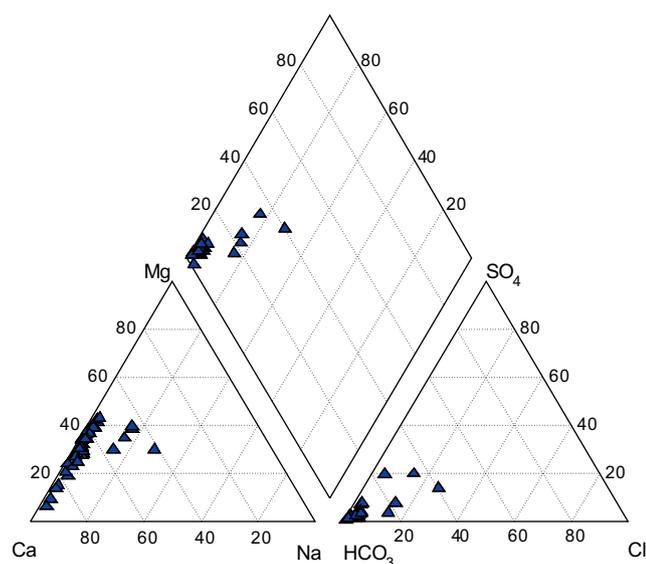
case of the former, there is no apparent relation between the two variables, in that of Mg there is, in fact, an appreciable relation, so the groundwater that emerges at lower altitudes tends to present higher contents of Mg. Obviously, water with a higher temperature tends to present a higher Mg content (Figs. 3 and 5). Finally, Fig. 5c leads us to conclude that water emerging at lower altitudes usually presents a higher Mg/Ca ratio. According to some authors, this parameter can be used as a qualitative indicator of the residence time of groundwater (Edmunds et al., 1987; Cardenal et al., 1994; Kloppmann et al., 1998; Elliott et al., 1999; Fairchild et al., 2000; Musgrove and Banner, 2004; McMahon et al., 2004).

The low temporal variability of the physical and chemical characteristics of the spring water shows that diffuse flow predominates in hydrogeological systems of Sierra de Segura (Table 2).

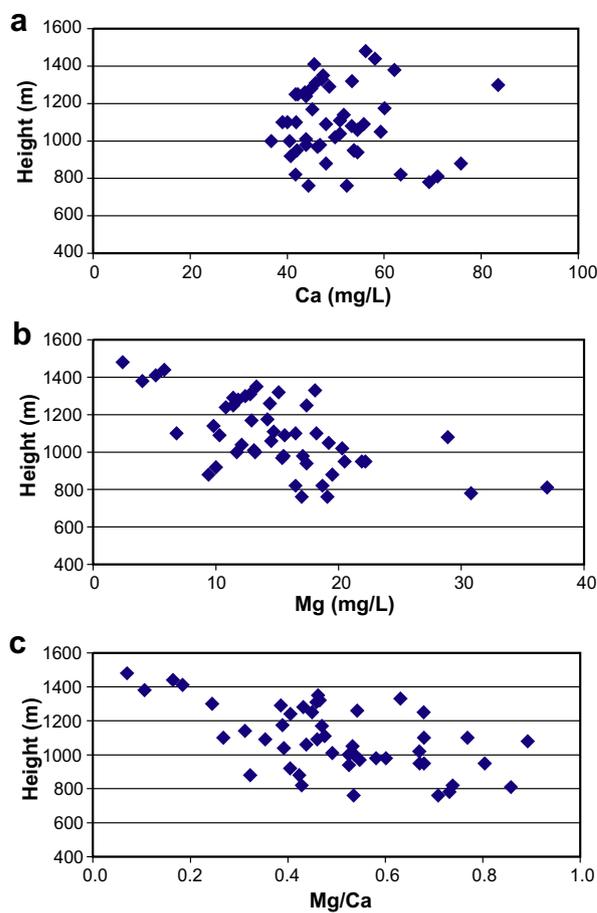
### Partial pressure of CO<sub>2</sub> and saturation indexes of calcite, dolomite and gypsum

In most of the springs, the waters were found to be in apparent equilibrium with a gaseous phase in which the partial pressure of CO<sub>2</sub> was comprised between 10<sup>-2.6</sup> and 10<sup>-2.3</sup> atm (Table 1), equivalent to a CO<sub>2</sub> content of 0.25% and 0.5% of its volume (a concentration 7–15 times greater than in the external atmosphere). Logically, there is a close relation between the pH of water and the partial equilibrium pressure of CO<sub>2</sub>; thus, the extreme values were observed in the springs where the pH value was higher than 8 (close to 10<sup>-3</sup> atm) and in La Maleza spring (10<sup>-1.48</sup> atm), which corresponded to 0.1% and 3.39%, respectively, of the volume of the gaseous phase (3–100 times greater than in the external atmosphere).

These values are similar to or slightly below those considered normal in the groundwater of carbonate aquifers: 10<sup>-2.5</sup> atm (Langmuir, 1997) and 10<sup>-2</sup> atm (Drever, 1997). In hydrogeochemical studies carried out in other sectors



**Figure 4** Piper diagram of the main spring water of Sierra de Segura.



**Figure 5** Plot of several hydrochemical parameters (Ca, Mg and molar ratio for Mg/Ca) against height of springs.

of the Betic Cordillera, such as Sierra de Lújar (Cardenal et al., 1994) and Sierra de Cabra (López-Chicano et al., 2001), mean values of 10<sup>-2.4</sup> and 10<sup>-2.3</sup> atm, respectively, have been recorded. However, in some carbonate aquifers, in the USA [Great Northern Plains (Plummer et al., 1990) and Pennsylvania (Langmuir, 1971)] and in Western Europe [Ireland (Tooth and Fairchild, 2003) and England (Heathcote, 1985)] even higher values of 10<sup>-2.1</sup>–10<sup>-1.6</sup> atm have been observed.

Langmuir (1971) proposed that a solution should be considered in equilibrium with respect to calcite if the saturation index is within the interval  $\pm 0.1$ . In accordance with this criterion, the waters of Sierra de Segura are predominantly in equilibrium or slightly oversaturated with respect to calcite. Very few springs presented waters that were highly oversaturated (San Blas, ref. 3; Era del Concejo, ref. 4; Alcantarilla, ref. 11; Santa Ana, ref. 12; Cuatro Caños, ref. 14) or subsaturated (La Maleza, ref. 6; La Natividad, ref. 33; Aguas Negras, ref. 50).

With respect to dolomite, if an uncertainty range of  $\pm 0.1$  is accepted (Langmuir, 1971), most of the springs drain subsaturated waters (La Maleza, ref. 6; Fuente Segura, ref. 22; Montilla, ref. 31; Natividad, ref. 33; Fuente Alta, ref. 34; Aguas Negras, ref. 50; Aguamulas, ref. 52), although there does exist a numerous group in which the water is in equilibrium with respect to this mineral (El Molino, ref. 1; La Toba

**Table 2** Statistical data of main studied springs (*n*: number of samples; St.D.: standard deviation; C.V.: coefficient of variation, in %)

		Q (l/s)	pH	T (°C)	EC (μS/cm)	Mg (mg/l)	Ca (mg/l)	HCO <sub>3</sub> (mg/l)
8-Tejo <i>n</i> = 35	Range	15–76	7.1–8.0	9.0–10.7	266–386	11–18	39–68	206–288
	Mean	27.8	7.66	10.0	328	15.0	53.4	243.6
	St.D.	15.4	0.24	0.3	25	1.7	6.4	25.4
	C.V.	55.2	3.14	3.9	7	11.5	12.0	10.4
19-La Toba <i>n</i> = 23	Range	147–456	7.4–7.9	12.0–13.1	254–310	10–16	35–55	175–214
	Mean	296.8	7.66	12.6	280	13.0	43.8	201.4
	St.D.	75.7	0.16	0.3	13	1.8	5.7	10.9
	C.V.	25.5	2.13	2.9	4	14.4	13.1	5.4
21-M. Loreto <i>n</i> = 22	Range	383–510	7.1–7.8	9.0–10.6	251–302	9–15	36–60	183–225
	Mean	440.6	7.57	10.0	275	11.8	45.0	204.8
	St.D.	40.7	0.20	0.4	13	1.9	5.7	11.3
	C.V.	9.2	2.66	4.0	4	16.1	12.6	5.5
26-Berral <i>n</i> = 19	Range	91–150	7.1–7.9	9.0–10.0	268–330	9–15	38–59	191–236
	Mean	113.2	7.55	9.6	303	11.3	48.6	217.4
	St.D.	14.7	0.22	0.3	15	1.8	6.7	12.9
	C.V.	13.0	2.98	3.2	5	15.9	13.7	5.9
31-Montilla <i>n</i> = 13	Range	15–93	7.0–7.8	9.0–10.3	242–276	1–4	44–61	175–198
	Mean	54.0	7.50	9.6	266	2.4	56.2	188.2
	St.D.	34.1	0.22	0.3	10	0.8	4.6	6.8
	C.V.	63.1	2.93	3.4	3	33.7	8.2	3.6
33-Natividad <i>n</i> = 38	Range	145–813	6.9–7.6	11.0–12.3	330–398	8–21	42–78	221–294
	Mean	259.9	7.26	11.8	364	15.6	55.8	266.7
	St.D.	124.2	0.21	0.3	15	3.1	10.3	19.0
	C.V.	47.7	2.96	2.9	4	19.9	18.6	7.1
34-Fuente Alta <i>n</i> = 31	Range	70–808	6.9–7.7	11.1–13.1	259–347	5–15	37–67	175–244
	Mean	209.8	7.40	12.3	301	9.7	51.7	213.5
	St.D.	197.6	0.24	0.6	23	2.4	8.6	21.6
	C.V.	94.2	3.28	5.2	7	25.2	16.7	10.1

36-Los Tubos <i>n</i> = 20	Range	65–103	7.2–7.6	20.0–21.5	503–590	20–33	35–71	249–343
	Mean	83.5	7.36	21.0	540	28.8	53.3	300.3
	St.D.	9.9	0.12	0.4	21	3.1	10.0	26.1
	C.V.	11.9	1.59	1.9	4	10.8	18.8	8.7
38-Castril <i>n</i> = 28	Range	311–5500	7.5–8.3	8.7–10.0	227–277	6–17	31–54	163–206
	Mean	1171.0	7.98	9.5	248	11.3	41.7	188.4
	St.D.	1292.9	0.18	0.3	11	2.6	4.4	11.7
	C.V.	110.4	2.30	3.5	4	23.4	10.7	6.2
41-Lézar <i>n</i> = 20	Range	146–286	7.2–7.8	10.5–12.1	312–358	14–21	31–61	206–259
	Mean	202.1	7.58	11.6	331	17.0	46.8	235.8
	St.D.	42.0	0.20	0.5	12	2.2	8.6	16.2
	C.V.	20.8	2.63	4.3	3	13.0	18.3	6.9
42-Peralta <i>n</i> = 23	Range	541–1118	6.9–8.2	15.0–17.8	286–421	15–24	35–62	183–247
	Mean	804.1	7.72	16.0	368	19.0	44.4	226.6
	St.D.	213.4	0.40	0.7	30	2.9	7.1	21.3
	C.V.	26.5	5.16	4.4	8	15.1	15.9	9.4
50-A. Negras <i>n</i> = 15	Range	105–578	7.2–7.7	8.5–9.6	255–325	7–19	38–53	191–275
	Mean	236.1	7.46	9.1	290	14.3	43.6	217.4
	St.D.	166.5	0.17	0.2	22	3.0	4.4	21.0
	C.V.	70.5	2.32	3.1	7	21.0	10.0	9.6
52-Aguamulas <i>n</i> = 20	Range	245–778	7.3–8.1	9.2–10.1	210–258	4–9	34–56	137–183
	Mean	417.4	7.73	9.6	234	6.4	42.8	168.6
	St.D.	173.2	0.22	0.2	11	1.5	5.8	11.9
	C.V.	41.5	2.79	2.7	5	23.4	13.5	7.0

de Jartos, ref. 9; Los Tubos, ref. 36) and six springs oversaturated, these being the same springs that present waters that are highly oversaturated with respect to calcite and Torcal spring (ref. 17).

In most springs, the concentrations of  $\text{SO}_4$  are very low (3–6 mg/l) and so the waters are very subsaturated with respect to gypsum ( $\text{SI}_{\text{gypsum}}$  close to  $-3$ ). Only in the systems with very deep flows, such as the thermal systems, does the index of gypsum saturation present values exceeding  $-2$  ( $-1.72$  at El Nacimiento, ref. 10;  $-1.85$  at La Toba de Jartos, ref. 9;  $-2.05$  at La Canal, ref. 48).

## Hydrochemical characteristics of the carbonate aquifers in Sierra de Segura

### Factors conditioning the hydrochemical characteristics of the carbonate aquifers

The solubility of calcite and dolomite in pure water is very low. Nevertheless, most carbonates dissolve readily in acidic solutions. The most important acid in karstic processes is carbonic acid, which is formed from the dissolution of gaseous  $\text{CO}_2$ , generally of edaphic origin (White, 1988; Drever, 1997; Parkhurst and Appelo, 1999).

The composition of water in karstic systems is the result of the dissolution of variable quantities of calcite and dolomite. Some authors have suggested that the Mg/Ca ratio in water depends on the proportion of calcite and dolomite present in the aquifer rock (White, 1988). Thus, Langmuir (1971) concluded that the low Mg/Ca ratio in the spring water in a sector of Pennsylvania is the result of the groundwater flow through limestones, while the higher value of this ratio in the water pumped from various boreholes is due to the fact that this water is obtained from dolomites. In the same sense, the calculations of Fairchild et al. (2000) suggest that the proportion of calcite and dolomite in an aquifer is, together with the transit time, one of the basic factors influencing the chemical composition of karstic waters.

However, in aquifers composed of extraordinarily pure limestone, the presence of Mg impurities in the calcite (0.2% by weight) gives rise to relatively high Mg/Ca ratios in waters with a long residence time in the aquifer (Edmunds et al., 1987). In nature, carbonate sedimentary sequences are made up of a variable proportion of limestone and dolomite layers and, as observed by Langmuir (1997), dolomites are almost always associated with limestones. In summary, available data indicate that in carbonate sequences there is a sufficient quantity of Mg to explain high Mg/Ca ratios, even when there is a predominance of very pure limestones. Thus, the proportion of calcite and dolomite in carbonate aquifers is not the only factor determining the Mg/Ca ratio of groundwater and, in certain conditions, it is not even the most significant.

In this regard, the kinetics of the dissolution of calcite and dolomite is a basic factor. Field and laboratory studies have shown that calcite dissolves more quickly than dolomite and that calcite is capable of reaching equilibrium from subsaturated fresh water in ten days or less, while dolomite may require months or even years (White, 1988).

From the model developed by Plummer et al. (1978) it can be calculated that, for a  $P_{\text{CO}_2}$  of  $10^{-1.5}$  atm and a temperature of  $10^\circ\text{C}$ , a concentration equivalent to 95% of the calcite saturation in a solution can be achieved in 10.7 h (Parkhurst and Appelo, 1999). Applying these values to different real conditions, the time needed to reach 95% calcite saturation may range from 32 min to 56 h (Dreybrodt, 1981; Buhmann and Dreybrodt, 1985). In this respect, Plummer et al. (1979) reported that an aqueous solution reaches equilibrium with respect to calcite in 16 days.

Laboratory experiments (Busenberg and Plummer, 1982) predict very low response times for the dissolution of dolomite. Appelo et al. (1984) proposed an equation to relate the dissolution rate to the index of saturation, and concluded that to achieve 95% dolomite dissolution, a much longer period (51 days) would be required than for calcite, under similar circumstances (Parkhurst and Appelo, 1999), and considerably longer periods of time to reach saturation in an aqueous solution (Busenberg and Plummer, 1982; Drever, 1997).

Thus it is explained why spring water is normally closer to equilibrium with calcite than with dolomite (Langmuir, 1997) and why it presents a more calcium hydrochemical facies in the recharge zone (Drever, 1997).

Indeed, the difference in the kinetics of the dissolution of calcite and dolomite means that downstream in the aquifer a progressive increase in the Mg/Ca ratio in the water occurs and, therefore, this ratio can be used as a qualitative indicator of the residence time of the water in the aquifer (Cardenal et al., 1994; Kloppmann et al., 1998; Elliott et al., 1999; Edmunds and Smedley, 2000; López-Chicano et al., 2001; Musgrove and Banner, 2004; McIntosh and Walter, 2006).

Another factor to be taken into account in the processes of the dissolution of calcite and dolomite is the influence of the water temperature. Carbonates present exothermal dissolution heat, i.e., their solubility decreases as the temperature increases. This reduction in solubility is magnified by the fact that the solubility of  $\text{CO}_2$  also falls as the temperature rises (Langmuir, 1997). For a  $\text{CO}_2$  pressure of  $10^{-2.5}$  atm and a pH of 7.6, typically found in groundwater, water that is saturated in calcite contains 44 mg/l of Ca at  $25^\circ\text{C}$  and 55 mg/l at  $10^\circ\text{C}$ . Palmer and Cherry (1984) reported that an increase in the temperature causes a reduction in the equilibrium concentrations of Ca, Mg and  $\text{HCO}_3$ , a reduction in the pH and a lesser transfer of mass within the system as a whole.

Furthermore, various authors have demonstrated the influence of temperature on the rates of mineral dissolution, which are significantly lower as the temperature falls (Kenoyer and Bowser, 1992). So the rate of dissolution of dolomite is reduced at lower temperatures (Herman and White, 1985).

In the study carried out by Edmunds and Smedley (2000) in the East Midlands Triassic aquifer, it was concluded that rising water temperature is an indicator of an increase in the depth of circulation, of the degree of hydrochemical evolution and of the residence time of the groundwater. In the same field, Cardenal et al. (1994) reported that, in a carbonate aquifer in the Betic Cordillera, the water temperature can be used as an indicator of the relative progres-

sion of the groundwater flow and of the hydrochemical evolution of the water.

In summary, the mineralogic and chemical composition of the rock, the residence time and the temperature are all basic factors for the understanding of the carbonate dissolution processes and the chemical composition of groundwater.

### Hydrochemical processes in the aquifers of Sierra de Segura

The lower part of the aquifer systems in Sierra de Segura contains Cenomanian–Turonian dolomites, some 300 m thick, above which there are widely varying thicknesses of Santonian, Eocene and Miocene limestone and detritic rocks. Sometimes, when the clayey detritic layers achieve an important thickness, it may be possible to distinguish an upper limestone sector within the aquifer, characterized by the lower Mg content of the groundwater.

The low variability of physical and chemical characteristics of groundwaters, the predominantly inertial hydrodynamics behaviour of springs, and the long drought period typical of Mediterranean climate let us to deduce that in most cases estimated residence times of groundwater is at least of several months.

The groundwater in the study area mainly comes from the direct infiltration of precipitation; therefore, when seeking to identify the hydrochemical processes and propose a conceptual model, it is considered that meteoric waters, in equilibrium with the partial pressure of  $\text{CO}_2$  in the open air ( $10^{-3.5}$  atm), infiltrate into the large limestone–dolomite outcrops on the plateau of Sierra de Segura.

Taking into account the meteorological data and the soil water budget, it can be stated that, in the main recharge zone, infiltration takes place from November to May, and that the mean temperature of the infiltration water is close to  $4^\circ\text{C}$ .

As the water circulates through the vadose zone, with an important downward vertical component (sometimes exceeding 700 m), it tends to reach a thermal equilibrium with the subsurface environment, which means the water temperature rises, to  $9\text{--}12^\circ\text{C}$  in the springs of the most important systems. Simultaneously,  $\text{CO}_2$  is dissolved in groundwater until equilibrium is reached with the partial pressure of the air in the unsaturated zone, which apparently in the aquifers of Sierra de Segura fluctuates with the seasons between values of around  $10^{-2.5}$  atm, in the winter and  $10^{-1.9}$  atm in the summer (Moral, 2005). This seasonal nature of the variations in  $\text{CO}_2$  content of the air in the vadose zone is indicative of the edaphic origin of the  $\text{CO}_2$ . In this region, the production of  $\text{CO}_2$  in the soil is maximum during the months of May and June, while the largest such concentrations in the subsurface are recorded during July and September, with a certain lag with respect to the production phase.

In almost all the springs, the molar ratio of the  $\text{Ca} + \text{Mg}$  to the  $\text{HCO}_3$  is close to 1:1 (Fig. 6), which reflects the predominance of the processes of dissolution and precipitation of carbonates and rules out significant cation exchange processes.

In some springs (La Canal, ref. 48; El Nacimiento, ref. 10) the  $(\text{Ca} + \text{Mg})/\text{HCO}_3$  molar ratio is somewhat higher, which is

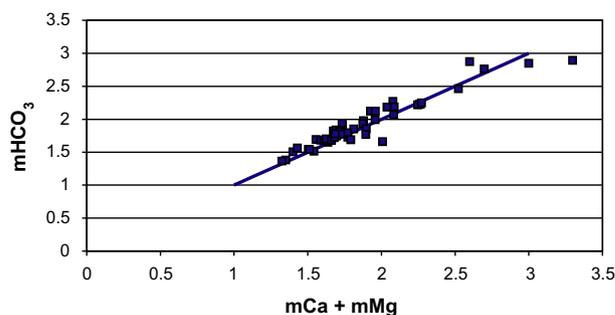
attributed to the existence of other geochemical processes, such as the dissolution of gypsum or anhydrite from evaporites of triassic rocks that constitute the regional substratum of carbonate aquifers.

The notable differences in the kinetics of the dissolution of calcite and dolomite lead us to assume that the following two processes successively occur: (1) congruent dissolution of calcite and small quantities of dolomite (until saturation with respect to calcite is achieved), and (2) incongruent dissolution of dolomite.

As commented above, the dissolution of calcite is a relatively fast reaction (Plummer et al., 1979; Palmer and Cherry, 1984). Therefore, it is to be expected that most of this dissolution will take place a few hours after the infiltration of precipitation water and mainly close to the land surface (which would explain the considerable development of exokarstic forms in Sierra de Segura and the existence of an epikarstic zone with a high degree of permeability) and, to a lesser extent, in deeper zones, within the network of karstic conduits. Consequently, the springs that drain calcite subsaturated water have been considered indicative of karstic systems where conduit flow predominates and where the groundwater has a very brief residence time within the aquifer. On the other hand, when the spring water is saturated in calcite, as in Sierra de Segura, it can be concluded that there is a predominance of diffuse flow (Shuster and White, 1971, 1972; Jacobson and Langmuir, 1974; Pitman, 1978).

Some authors have reported the generalized existence of water that is subsaturated with respect to calcite in their respective study zones (Langmuir, 1971; Shuster and White, 1972; Scanlon and Thrailkill, 1987; Hess and White, 1992). On the other hand, others have found a predominance of groundwater that is slightly oversaturated with respect to calcite (Edmunds et al., 1987; Plummer et al., 1990; Cardenal et al., 1994; Elliott et al., 1999; López-Chicano et al., 2001).

Water that has previously been saturated in calcite dissolves dolomite slowly. The addition of calcium and bicarbonate gives rises to oversaturation with respect to calcite and its subsequent precipitation. This phenomenon is known as the incongruent dissolution of dolomite, and has been described in many carbonate aquifers (Wigley, 1973; Freeze and Cherry, 1979; Palmer and Cherry, 1984; Edmunds et al., 1987; Cardenal et al., 1994; Kloppmann et al., 1998; Elliott et al., 1999). The result of this process



**Figure 6** Molar ratio for  $\text{Ca} + \text{Mg}$  versus  $\text{HCO}_3$  in groundwater. The straight line represents molar ratio 1:1.

is an increase in the concentration of bicarbonate and magnesium ions and a slight decrease in calcium.

Furthermore, we should note that during the downward groundwater flow through the unsaturated zone in Sierra de Segura aquifers, there is a progressive rise in the temperature, which causes precipitation of calcite and leads to a slight increase in the saturation index of dolomite.

In addition, some springs drain water that is oversaturated with respect to calcite (and sometimes to dolomite), which is attributed to the fact that the water has been in contact with an atmosphere that is relatively poor in  $\text{CO}_2$  near the spring (this is known as the  $\text{CO}_2$  exsolution process). This phenomenon can be related to the existence of a water flow through colluvial materials of scant thickness, or through large, karstic conduits that are partially flooded and well communicated with the external atmosphere. Due to the ventilation, there occurs a decrease in the  $\text{CO}_2$  content of the subterranean atmosphere.

On the contrary, the spring at La Maleza (ref. 6) is notable for presenting water that is very unsaturated with respect to calcite. The existence of lignite layers interbedded in the stratigraphic series near the spring and the highest value of the partial pressure of  $\text{CO}_2$  indicate a supply of  $\text{CO}_2$  of lithologic origin in this zone.

Finally, spring water whose temperature is relatively high (15–19 °C) usually is saturated with respect to dolomite and present high partial pressures of  $\text{CO}_2$ . In this case, we suppose very long residence times and, possibly, the presence of  $\text{CO}_2$  from deep origin. Some of these springs are thermal and present a particular composition that is indicative of ongoing dedolomitization. This phenomenon has been described by various authors in the Betic Cordillera (Cardenal et al., 1994; Hidalgo and Cruz-Sanjulián, 2001; López-Chicano et al., 2001) and in other regions (Plummer, 1977; Deike, 1990; Plummer et al., 1990; Capaccioni et al., 2001; McMahon et al., 2004). The process consists of the simultaneous dissolution of gypsum (or anhydrite) and dolomite, while calcite is precipitated. The supply of Ca from gypsum into the solution causes an oversaturation with respect to calcite and its subsequent precipitation, which produces a decrease in the alkalinity, an increase in the concentration of  $\text{H}^+$ , an increase in the  $P_{\text{CO}_2}$  and, finally, subsaturation with respect to dolomite. To sum up, the effect of the dedolomitization process is an increase in  $\text{SO}_4$ , Ca, Mg and  $P_{\text{CO}_2}$ , and a decrease in alkalinity and pH.

### Proposed hydrochemical model and discussion of the results

As remarked in previous sections, both the temperature and the magnesium content may be considered indicators of the geochemical evolution of groundwater. Taking these two variables into account, we have grouped the springs of Sierra de Segura from type C, corresponding to systems that drain waters that are colder and with a lower magnesium content to type G, which drain warmer and magnesium-rich waters (Fig. 7).

Table 3 describes the most significant physical and chemical characteristics of the water in each group of springs. Note that the lower the altitude of the spring, the higher the degree of hydrochemical evolution (i.e., higher temper-

ature and magnesium content). At the same time there is an increase in the Mg/Ca ratio, in the sulphate concentration and in the degree of dolomite saturation.

Fig. 8 shows the hydrochemical conceptual model proposed from the field observations and the laboratory data. In this model, it is assumed that the water acquires most of its physical and chemical characteristics in the unsaturated zone because most of the increase in water temperature, the  $\text{CO}_2$  and calcite dissolution, and, in a lesser degree, the incongruent dissolution of dolomite, take place in this zone. In the same sense, Smith and Atkinson (1976) claim that 50–80% of the dissolution that occurs within a limestone massif takes place in the first 10 m beneath the land surface.

Edmunds et al. (1987), for their part, state in their study on chalk that the water acquires its predominant chemical characteristics in the soil and in the upper vadose zone. Finally, Cardenal et al. (1994) report that in large aquifer systems, with a relatively thick vadose zone, the water can reach equilibrium with respect to calcite and dolomite in this zone.

Using the PHREEQC program we have calculated mass transfer from type A (pure water) to type G water. Fig. 9 shows that the calculated values reasonably fit the experimental values reported in Table 3. The concentration of dissolved calcium increases very quickly (from the dissolution of calcite); subsequently it tends to fall (the incongruent dissolution of dolomite) and, in the deepest-circulating systems, increases once again as a result of the rise in  $P_{\text{CO}_2}$  values and of dedolomitization processes. The magnesium content, and hence the Mg/Ca ratio, increases slowly and progressively, given the kinetics of the dissolution of the dolomite.

In almost the entire unsaturated zone the partial pressure of  $\text{CO}_2$  is high (10–15 times higher than in the external atmosphere) and so it is to be expected that most of the  $\text{CO}_2$  will be dissolved in the shallowest sectors of the system, that is, in the epikarst.

As in the case of  $\text{CO}_2$ , calcite dissolves preferentially in the upper areas of aquifers (the epikarstic zone) and, downstream, precipitates in a more or less regular manner; nevertheless, processes of dedolomitization produce an increase in the precipitation of calcite. Thus, in thermal systems the global calcite balance indicates that, as a whole,

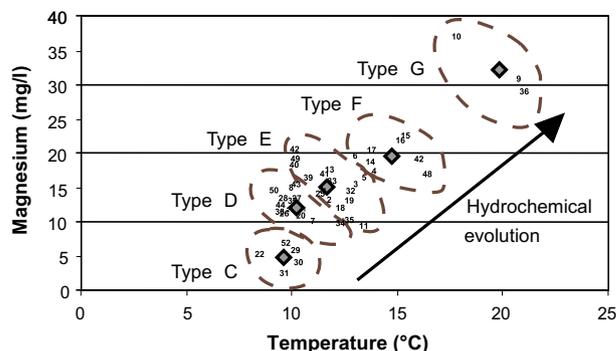
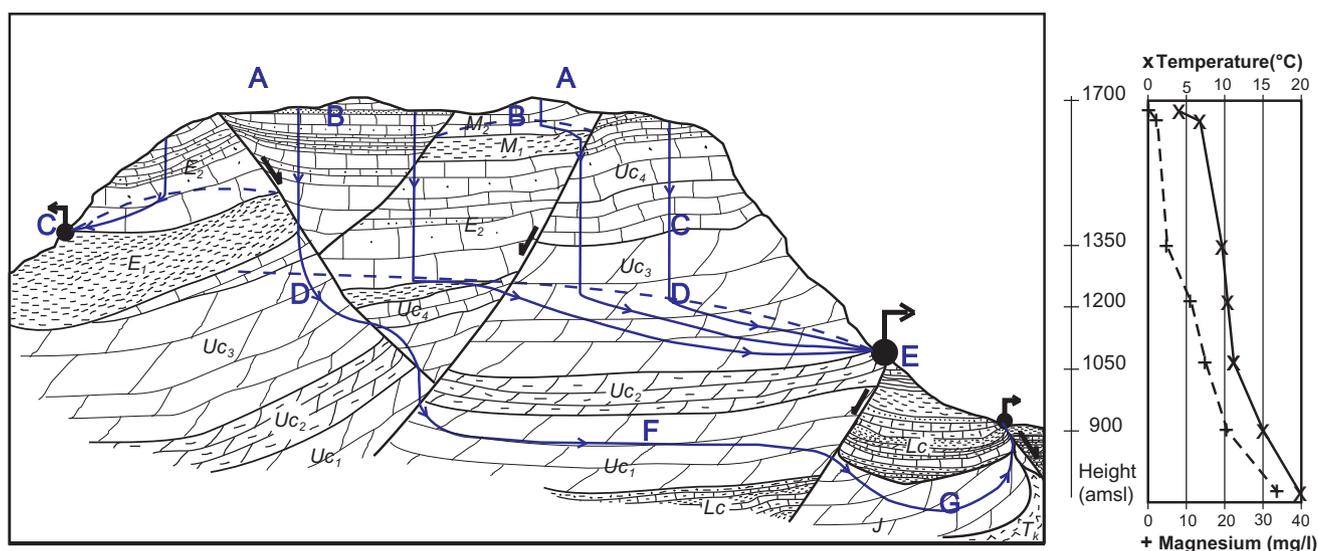


Figure 7 Plot of water temperature versus magnesium content make possible to define several groundwater types, symbolized by squares.

**Table 3** Mean measured physicochemical characteristics in the different spring water types of Sierra de Segura

Type	C	D	E	F	G
N	5	12	19	8	3
Representative springs	Fuente Segura (ref. 22), Montilla (ref. 31), Aguamulas (ref. 52)	Molino de Loreto (ref. 21), Berral (ref. 26), Nac. Castril (ref. 38)	La Toba (ref. 19), Natividad (ref. 33), Lézar (ref. 41)	Cuatro Caños (ref. 14), Sege (ref. 16), La Canal (ref. 48)	La Toba de Jartos (ref. 9), Los Tubos (ref. 36)
Height (m)	1362	1214	1033	885	890
Ca (mg/l)	52.8	48.7	48.5	53.3	64.5
Mg (mg/l)	4.8	12.0	15.2	19.5	32.2
Mg/Ca	0.150	0.406	0.516	0.602	0.822
Na (mg/l)	1.6	2.2	2.1	6.3	35.6
HCO <sub>3</sub> (mg/l)	194.0	220.2	229.3	258.1	333.7
SO <sub>4</sub> (mg/l)	4.1	4.6	5.3	11.4	58.1
Cl (mg/l)	4.9	4.1	3.9	7.2	55.8
T (°C)	9.6	10.2	11.7	14.7	19.8
pH	7.63	7.66	7.72	7.67	7.30
log P <sub>CO<sub>2</sub></sub>	-2.450	-2.414	-2.492	-2.333	-1.837
SI <sub>calcite</sub>	-0.045	-0.036	0.119	0.190	0.048
SI <sub>dolomite</sub>	-1.054	-0.400	-0.117	0.152	0.078



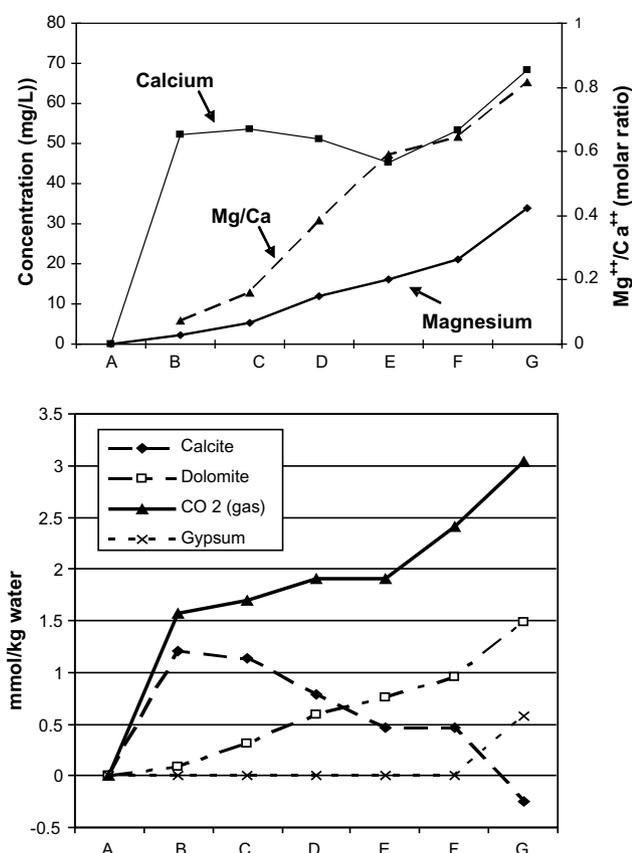
**Figure 8** Hydrogeological systems with different degrees of hydrochemical evolution of groundwater. The spring on the left emerges from a highly karstified system, with cold and calcium bicarbonate groundwater. Spring E drains an aquifer that presents a greater inertial behaviour, calcium–magnesium bicarbonate and less cold water. Finally, spring on the right is fed by a weakly thermal system, with calcium–magnesium bicarbonate water, which contains significant amounts of ions from evaporite dissolution (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, etc.). Lithologies: T<sub>k</sub>, Triassic lutites and evaporites; J, Jurassic dolomites; L<sub>c</sub>, Lower Cretaceous marls, marly limestones, and sandstones; U<sub>c1</sub>, Upper Cretaceous dolomites; U<sub>c2</sub>, Upper Cretaceous marly dolomites; U<sub>c3</sub>, Upper Cretaceous dolomites; U<sub>c4</sub>, Upper Cretaceous limestones; E<sub>1</sub>, Eocene marls; E<sub>2</sub>, Eocene limestones, and sandy limestones; M<sub>1</sub>, Miocene marls; M<sub>2</sub>, Miocene limestones.

the water precipitates more calcite than had previously been dissolved.

On the contrary, the dissolution of dolomite takes place in a much more steady manner throughout the aquifer system.

Finally, the dissolution of gypsum, and if there is any, of halite, only occurs in systems where the groundwater flow is deepest, and which are fundamentally of a thermal nature.

Thus, the waters in the springs of Sierra de Segura represent different stages of a general evolutive model. Logically, the springs that are representative of each stage, in turn, present a certain degree of heterogeneity that can be related to variations in the partial pressure of CO<sub>2</sub> in the atmosphere of the unsaturated zone, the residence time of the water, the groundwater flow velocity, the amount of recharge, etc.



**Figure 9** Theoretical mass-transfer evolution from pure water (Type A) to weakly thermal water (Type G). Calculations made with PHREEQC: (a) concentration of solutes; (b) dissolution–precipitation of solid phases and dissolution of CO<sub>2</sub>.

In fact, when the evolution of the water characteristics in relation to the altitude of the spring is observed, it can be concluded that, as the latter diminishes, the water is less cold, presents a higher Mg content and a higher Mg/Ca ratio, i.e., it presents a higher degree of geochemical evolution.

It seems evident that the residence time is not the only factor that influences the degree of saturation with respect to dolomite; in addition, higher temperatures tend to accelerate the kinetics of the dolomite dissolution reaction.

As remarked above, the water temperatures in the unsaturated zone of a carbonate massif are related to the dynamics of the air and the water, and tend to approach the average temperature of the external atmosphere, which gives rise to a thermal stratification that, to a certain degree, reproduces the mean temperature distribution at different altitudes in the external atmosphere. The vertical variation of water temperatures can be translated into a stratification of the predominant hydrochemical characteristics and geochemical processes. This particular distribution of physical and chemical characteristics of groundwater can be related to the heterogeneous distribution of the network of karstic conduits, which are much more abundant in the epikarstic zone.

In consequence, the springs that are located at very high altitudes, such as Montilla (ref. 31) and Fuente Segura (ref. 22), drain cold, highly calcic waters and frequently repre-

sent the discharge of systems with a more highly developed karstic network. On the other hand, those springs that are at lower altitudes, such as La Toba (ref. 19) and La Canal (ref. 48) present warmer, more magnesium-rich waters, and drain systems with a higher regulatory capacity, the result of the predominance of diffuse flow.

## Conclusions

The more important processes in aquifers of Sierra de Segura are the dissolution of CO<sub>2</sub>, the dissolution of calcite, the incongruent dissolution of dolomite and, to a lesser extent, the dedolomitization and the exsolution of CO<sub>2</sub>.

The kinetics of the dissolution of calcite and dolomite, much faster in the case of the former, means that the chemical facies of the water evolves from calcium bicarbonate to calcium–magnesium bicarbonate.

The degree of hydrochemical evolution is largely determined by the residence time of the water within the aquifer, i.e., by the duration of the water–rock interaction. Nevertheless, it is not the only factor, as there exists a marked positive relation between the water temperature and other parameters such as the Mg content, the Mg/Ca ratio and the index of dolomite saturation, which leads us to conclude that an increase in water temperature accelerates the kinetics of the dissolution of dolomite.

In turn, the distribution of the temperature in the unsaturated zone of a karstic system is clearly influenced by the dynamics of the air and of the water, and so a vertical thermal gradient resembling thermal gradient of the external atmosphere is observed. In carbonate aquifers where the unsaturated zone is thick and where there is a significant diffuse flow, as is the case in Sierra de Segura, there is seen to be a thermal ‘stratification’ in the karstic systems, on a regional scale, which is apparent as hydrochemical ‘stratification’. Thus, in zones that are topographically higher, the water is colder and less evolved (calcium bicarbonate facies), while at lower altitudes, the spring waters are warmer and more highly evolved, with respect to their hydrochemical characteristics (calcium–magnesium bicarbonate facies).

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