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Factors which determine the hydrogeochemical behaviour of karstic springs. A case study from the Betic Cordilleras, Spain

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Abstract

The Cabra-Alcaide karstic massif situated in the south of Spain constitutes an important part of the so-called Natural Park of the Subbetic Sierras. This aquifer system is drained by various springs which supply a population of some 100,000 inhabitants. The feed areas of these springs show very different characteristics with respect to their geological structure, size of the drainage area, thickness of the vadose zone, elevation and degree of karstification. In addition, the carbonate rocks lie over a clayey substratum which contains large masses of intercalated evaporites. Due to these conditions, the hydrochemical composition of the springs is relatively variable. In this study a hydrogeochemical characterization of the aquifer in both space and time is undertaken and the factors that determine it are discussed. To achieve this, 19 monthly samples were taken from the 6 most significant springs of the hydrogeological system. The commencement of sampling coincided with the transition from a period of several years of severe drought and a very wet two-year period, which amplified considerably the hydrochemical and hydrodynamic response of the springs to the recharge. Identification of hydrogeochemical processes was performed by studying hydrographs, the temporal evolution of physico-chemical parameters, ionic ratios (mainly Mg/Ca) and by means of simple and multivariate statistical analyses. The saturation status was established using the WATEQF program and the mass transfer was quantified using PHREEQC. With the exception of the epikarstic subsystem (i.e. the Zarza spring), the majority of the results indicate that the aquifer exhibits a diffuse flow model, in which *piston flow* phenomena are seen, closely linked to the most intense precipitation. Along the direction of flow hydrochemical trends are seen as the water type changes from Ca–HCO₃ to Ca–Mg–HCO₃; at the same time enrichment in some ions, derived from the dissolution of evaporitic minerals of the impermeable substratum, and dedolomitization processes occur. In this way, almost 90% of the water samples were oversaturated in calcite, the majority of cases being a consequence of the dissolution of the gypsum of the substratum. Only in the epikarstic springs can it be considered that the oversaturation in calcite is due to loss of CO₂ from the emerging groundwater. It is concluded that hydrodynamic aspects together with hydrogeochemical characteristics need to be taken into account to correctly explain the hydrochemical evolution of the karstic springs. Moreover, the use of both approaches permits a more accurate establishment of the degree of aquifer karstification, which in turn needs to be known in order to assess its vulnerability to contamination and to protect recharge zones.

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1. Introduction

In karstic aquifers, temporal variations in the chemistry of the springs are often related to the physical characteristics and permeability of the carbonates, and this has led to the use of these characteristics to differentiate between different types of hydrodynamic behaviour of the karstic systems drained. Thus, Garrels and Christ (1965) defined two flow mechanisms (diffuse and conduit flow) and concluded that the variation in water hardness is a good criterion to differentiate between the two types of hydrodynamic operation. Shuster and White (1971, 1972), studying carbonate aquifers in Nittany Valley (central Pennsylvania, USA), noted the same thing and considered that the coefficient of variation of groundwater hardness in these springs provides a useful tool in the interpretation of the hydrodynamic behaviour of karstic aquifers. Likewise, Ternan (1972) concluded that the chemical behaviour of groundwaters in Yorkshire (UK) depends upon the physical characteristics of the springs. Jacobson and Langmuir (1974) in central Pennsylvania (USA) used other criteria, such as the type of recharge, electrical conductivity and the coefficient of variation of the discharge, and proposed 4 mechanisms of flow in karst. Ede (1972) and Cowell and Ford (1983) related the large temporal variations in groundwater temperature with conduit flow whilst the small variations were taken as indicative of diffuse karstic flow. Atkinson (1977), in a study on limestone terrain in the Mendip Hills (UK), established a formal classification of karstic aquifers in the two models already noted by the majority of authors cited above; these conceptual models have been widely used in the scientific literature.

Consideration of only one or just a few of the physico-chemical parameters that characterize groundwater can lead to an erroneous interpretation of the hydrodynamics of the karstic catchment draining to the spring. Thus, as the peculiarities of a large number of karstic-carbonate aquifers have become known, it becomes clearer that their interpretation is not straightforward, and that it is usually necessary to bear in mind all possible hydrodynamic, lithological, geometrical and hydrogeochemical aspects.

The physico-chemical characteristics of groundwaters in karstic systems are determined by the lithology of the rocks that they cross, the physico-chemical processes that predominate, the residence time of water and the various conditions and modes of circulation that coexist within them. Bakalowicz (1977) demonstrated that the coefficient of variation of the chemical components of karstic waters from southern France, if the distribution is multimodal, does not enable the definition of the karstic aquifer. On the other hand, Scanlon and Thrailkill (1987) rejected the classification criteria established by previous authors and showed that the hydrogeochemical variability of the springs, in the case of the karstic aquifer of Inner Bluegrass (Kentucky), did not allow the structural

characteristics of the aquifers that fed them to be distinguished, because different flow path lengths counteracted the effect of varying conduit size between two different types of springs. Recently, Raeisi and Karami (1996) suggested assessing all the factors that determine the geochemistry of the Sheshpeer spring waters (Iran), including factors external to the karst system such as type of recharge (point or diffuse), soil type and thickness, as well as internal factors such as flow mechanism, lithology and dimensions of the aquifer systems.

With an aim similar to these latter studies, the present study effects a comparative analysis of some of the physico-chemical parameters of the groundwaters drained by the main karstic springs of the Cabra-Alcaide aquifer. These springs are situated at different elevations, they drain waters with different transit times from the areas of recharge, they show significant divergence in their discharge and their supply catchments are affected to a greater or lesser extent by the existence of evaporite substrata (perhaps the most novel aspect). The principal aim is to analyse the influence of all possible factors, including the degree of karstification, on the temporal hydrogeochemical behaviour of the springs. In this way, a correct interpretation of the spatial and temporal hydrochemical variations of the karstic springs enables a better understanding not only of the geochemical processes that take place in the aquifer, but also of their physical characteristics. Both factors determine the intrinsic vulnerability of the aquifer system in the face of possible contamination of the groundwaters.

2. Hydrogeological setting

The Cabra-Alcaide massif is situated within the external zone of the Betic Cordilleras, in the south of the province of Cordoba (Fig. 1). From a geological point of view, this massif comprises two stratigraphically and tectonically distinct units: the Cabra and Gaena units. Both are characterized by Triassic detritic-evaporite rocks at the base of the lithological series and, above this, by 10 m of rauhewackes or cavernous dolomites (Felgueroso and Coma, 1964) and a thick (up to 300 m) bed of dolomites and limestones, dating from Lower to Middle Lias. In the Cabra unit, the carbonate series is overlain by white Dogger oolitic limestones, up to 300 m thick (Molina, 1987; Vera et al., 1988). The remainder of the lithological series, up to the Middle Miocene, is composed of low-permeability materials.

Within the study area, the Gaena unit is superimposed tectonically over the Cabra unit, with the Triassic rocks acting as the level of detachment. Locally, the Gaena unit outcrops in the form of tectonic klippen comprised almost exclusively of limestones and dolomites in the highest parts of the mountain range. So, in these sectors there are 3 superimposed carbonate entities,

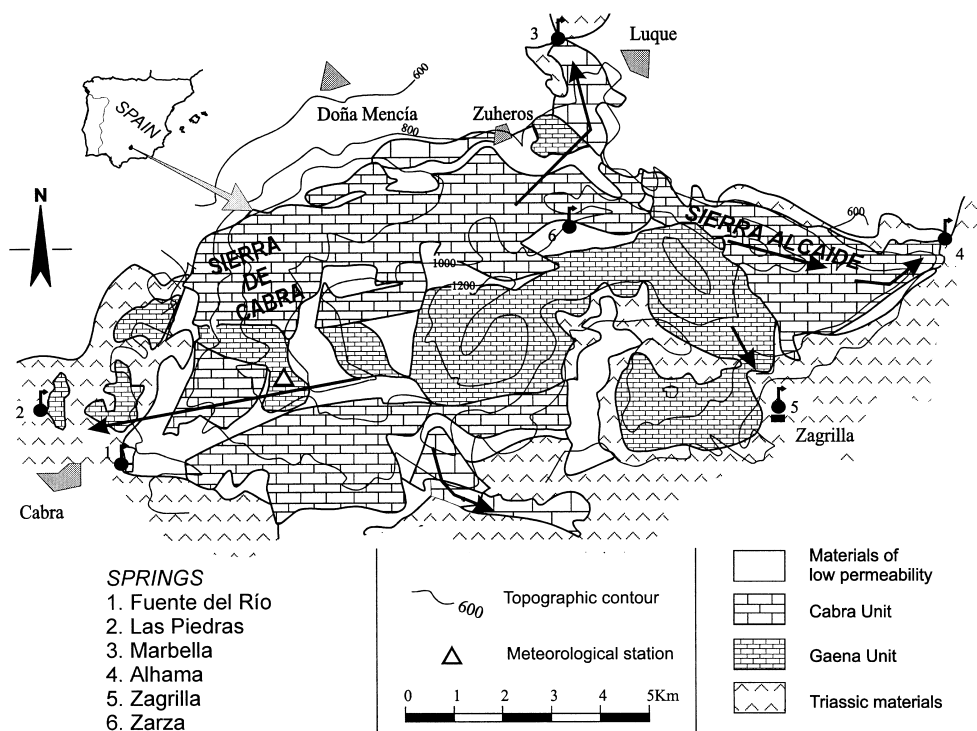


Fig. 1. Hydrogeological map of the Cabra-Alcaide aquifer. The arrows indicate the approximate direction of groundwater flow.

sometimes with hydraulic connection between them, thanks to the narrowness or lamination of the intercalations of the low-permeability rocks.

On a regional scale, the impermeable substratum of the aquifer series corresponds to detritic (mainly clayey) materials and evaporites (gypsum and halites) of Triassic age. However, in several sectors these rocks have been heavily laminated by tectonics, and in their place appear Cretaceous marls and marly limestones or other Tertiary rocks of low permeability that correspond to the parautochthonous units (Felgueroso and Coma, 1964).

To the north and east of the aquifer the substratum outcrops to form its impermeable border, whilst in the southern and western sectors the aquifer is confined below the Cretaceous materials of the Cabra unit or the Triassic basal materials of the thrust unit (Gaena unit).

The aquifer is fed mainly from infiltration of rain-water that falls over the carbonate outcrops (105 km² of total surface area). In addition, there is a small indirect recharge from infiltration of surface waters and from re-infiltration of water flowing from the small epikarstic springs, sometimes situated at the base of tectonic klippen of the Gaena unit, as is the case of the Zarza spring (Fig. 1). The main aquifer discharge occurs from various springs located in the lower parts of the massif, at elevations between 460 and 570 m a.s.l. Table 1 presents the mean discharges of these springs for the period October 1995 to April 1997.

3. Sampling and analytical methods

Sampling runs were undertaken at the end of every month from October 1995 to April 1997, in the 6 main springs of the aquifer. In spite of there being a relatively small number of samples (19) for each sampling point, the survey period was quite long and included nearly two complete hydrogeological cycles, and at least two periods of intense recharge following a long drought; it is during the transition between such extreme situations that the most radical hydrochemical changes take place. The flow of each spring was gauged, and one or more direct flow measurements were carried out by means of a micro-flowmeter. Field measurements of electrical conductivity (using a portable 524 Crison conductivity meter), pH and temperature (both using a portable 507 Crison pHmeter) were made in the field. HCO₃ was also determined in the field by titration with HCl 0.05N, with an error lower than 2%. The accuracy of pH measurement was ±0.05 pH units.

In the laboratory, SO₄ was determined by turbidometric spectrophotometry with barium sulphate (Spectronic 501, Milton Roy Company, USA) and Cl was determined by titration with 0.02 N silver nitrate. Ca, Na, Mg and potassium were determined by flame spectrophotometry (ICP, Leeman Labs Inc., USA), on samples previously conserved in 2 ml 65% nitric acid (Appelo and Postma, 1993). The accuracy of the analysis was

Table 1

Hydrodynamic and hydrogeochemical data from the main springs that drain the Cabra-Alcaide aquifer. October 1995 to April 1997. (CV: coefficient of variation, in %; EC: electrical conductivity, in mS/m; SI: saturation index)

	Zarza	Fuente del Río	Zagrilla	Alhama	Marbella	Piedras
Altitude (m)	980	485	570	470	480	460
Mean discharge (l/s)	3	470	100	360	100	40
<i>Ca (mmol/kg)</i>						
Range	1.37–2.39	1.62–1.92	1.12–2.07	1.87–2.47	1.72–2.29	2.15–2.64
Mean	1.88	1.72	1.75	2.15	1.97	6
CV	14	5	14	7	9	6
<i>Mg (mmol/kg)</i>						
Range	0.08–0.25	0.33–0.62	0.53–0.66	0.53–0.66	0.66–0.82	0.62–0.99
Mean	0.16	0.41	0.62	0.58	0.80	24.3
CV	31	15	8	5	9	12
<i>Na (mmol/kg)</i>						
Range	0–0.26	0.17–0.35	0.04–0.22	0.17–0.43	0.70–2.00	1.13–1.74
Mean	0.09	0.30	0.13	0.30	1.35	1.43
CV	63	18	37	20	32	11
<i>Cl (mmol/kg)</i>						
Range	0.14–0.34	0.31–0.51	0.20–0.31	0.39–0.65	0.65–2.20	1.41–1.86
Mean	0.23	0.42	0.25	0.48	1.52	1.73
CV	23	14	17	12	31	8
<i>SO₄ (mmol/kg)</i>						
Range	0.006–0.14	0.16–0.25	0.44–1.06	0.59–0.91	0.49–1.00	0.51–0.94
Mean	0.07	0.22	0.69	0.79	0.74	0.70
CV	61	10	32	9	17	16
<i>HCO₃ (mmol/kg)</i>						
Range	2.75–4.61	3.25–3.75	2.85–3.38	3.51–3.87	3.38–3.75	4.34–4.80
Mean	3.75	3.67	3.00	3.64	3.57	4.57
CV	13	4	5	3	4	3
<i>EC (25°C)</i>						
Range	23.4–45.8	38.6–53.0	36.4–46.2	45.4–56.6	45.4–78.0	63.0–79.7
Mean	36.8	41.9	43.5	51.2	63.3	72.5
CV	14	6	10	6	14	6
<i>Temperature (°C)</i>						
Range	11.8–17.5	14.5–16.3	15.1–16.3	15.3–16.1	15.1–16.7	16.3–19.2
Mean	14.0	15.7	15.5	15.8	16.4	18.2
CV	13.5	2.3	1.6	1.1	2.2	3.0
<i>pH</i>						
Range	7.48–8.39	7.38–7.86	7.13–8.04	6.98–8.03	7.13–7.80	7.25–7.68
Mean	7.89	7.61	7.70	7.60	7.58	7.40
<i>SI_{Calcite}</i>						
Range	0.06–0.99	–0.02 to 0.43	–0.40 to 0.48	–0.34 to 0.60	0.02–0.50	0.07–0.46
Mean	0.59	0.19	0.18	0.23	0.21	0.21
<i>SI_{Dolomite}</i>						
Range	–1.08 to 0.87	–0.62 to 0.24	–1.30 to 0.56	–0.30 to 0.80	–0.95 to 0.50	–0.30 to 0.42
Mean	0.60	–0.22	–0.08	–0.06	–0.04	–0.11
<i>SI_{Gypsum}</i>						
Range	–3.77 to –2.36	–2.39 to –2.15	–1.96 to –1.52	–1.70 to –1.50	–1.90 to –1.60	–1.85 to –1.54
Mean	–2.76	–2.21	–1.75	–1.62	–1.70	–1.60
<i>logP_{CO₂}</i>						
Range	–3.18 to –2.21	–2.59 to –2.09	–2.86 to –1.94	–2.70 to –1.70	–2.50 to –1.85	–2.31 to –1.86
Mean	–2.71	–2.32	–2.52	–2.33	–2.30	–2.00
<i>Mg/Ca</i>						
Range	0.14–0.04	0.37–0.2	0.42–0.31	0.34–0.26	0.43–0.36	0.45–0.24
Mean	0.08	0.24	0.34	0.29	0.38	0.30

estimated from the electro neutrality (E.N.) condition: $E.N. (\%) = \frac{(\text{sum cations} + \text{sum anions})}{(\text{sum cations} - \text{sum anions})} \times 100$, where cations and anions are expressed as meq/l. These errors were less than 5% in all samples. The saturation indices for the different mineral species and the partial pressure of CO_2 were calculated using WATEQF (Plummer et al., 1984).

4. Results and discussion

4.1. Water discharge and temperature

In general, there are no marked differences between the flow hydrograph of the studied springs (Fig. 2), except for the Zarza spring. In this case, the response to rainfall events seems to be very fast and partly independent of the other springs, as occurred in August 1996 when a spike in the discharge was observed due to a local, short and

intense rainfall event not recorded in the other springs. Therefore, the rough pattern observed at Zarza may reflect a weak power of control on infiltration, which is explained by the high degree of karstification of the carbonate rocks, the small area of the aquifer drained by this spring and with the existence of a thin vadose zone. The lag observed between the hydrographs of the Marbella spring and those of the Zagrilla and Alhama springs implies that the karstification of the aquifer is less developed in the catchment drained by the former spring than in those drained by the latter two (Bouamama et al., 1996). Something similar can be observed in the western part of the aquifer, between the hydrographs of Piedras and Fuente del Río springs. However, given that the groundwater flow in this sector is from east to west and that both springs have approximately the same recharge area, the flow path is longer in the former. This circumstance could contribute to producing this lag.

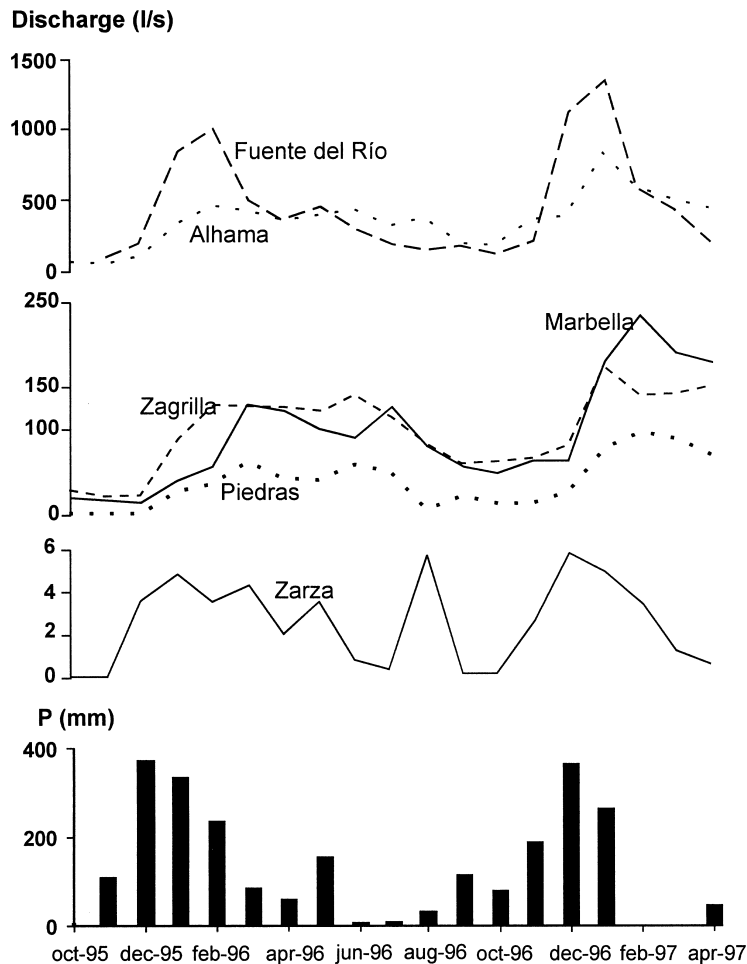


Fig. 2. Hydrographs of the springs studied in the Cabra-Alcaide aquifer, obtained during the period October 1995 to April 1997. Discharge in l/s; P: precipitation in mm.

The close statistical correlation between the Alhama and Zagrilla discharges ($r^2=0.82$, probability of F -value less than 0.05 significance level) accords with their geographical proximity (Fig. 1), in that both drain a portion of the aquifer with relatively homogenous characteristics, in spite of a difference in elevation of more than 100 m (Table 1).

A high coefficient of correlation ($r^2=0.88$, probability of F -value less than 0.05 significance level) is also seen in the case of the Piedras and Marbella springs, suggesting that both have similar hydrodynamic regimes, although in this case the criterion of proximity cannot be argued. The hydrographs of both springs show the largest lag between rainfall and discharge; thus, a priori, their recharge areas must be the least transmissive and least karstified within the Cabra-Alcaide aquifer. Bouamama et al. (1996), on examining the response to rainfall events and the recession, deduced that the Fuente del Rio drains areas that are relatively more karstified.

As regards groundwater temperature measurements in the studied springs, temporal trends are seen that differ markedly. The only exception is the case of the Fuente del Rio and Piedras springs, which showed very similar trends ($r^2=0.82$, probability of F -value less than 0.05 significance level), though the difference in their mean temperature is nearly 2.5°C (Table 1 and Fig. 3). An inverse relationship exists between the mean temperature of spring water and its emergence altitude; nevertheless, the high water temperature values recorded at Piedras spring, greater than the mean air temperature (which never exceeds 17°C), are likely to be the consequence of the relatively deep flow system that feeds this spring. This, together with the confined nature of the aquifer and the geological position of the spring, provides an explanation for other peculiarities in the chemical and physical characteristics of its water. Variations in temperature are very marked in the epikarstic Zarza spring (Fig. 3), with a difference of 5.7°C between the maximum recorded in August 1996 and the minimum obtained in November 1995, the month in which the most intense recharge began. In broad terms, the temporal fluctuations

in all sampled springs follow the seasonal changes in ambient temperature, according to the characteristics deduced above for their recharge area.

4.2. Groundwater chemistry

The Piper diagram of Fig. 4 — plotting the proportions in meq/l of the major cations and anions — shows the main hydrogeochemical features, as well as their temporal evolution. In general, the Ca–Mg–HCO₃ facies predominates in the water sampled, although the springs of the Sierra Alcaide sector (Alhama and Zagrilla springs) show a tendency towards higher SO₄ content, and those of Marbella and Piedras towards a more marked Cl–SO₄ composition. Both trends are the consequence of processes that change the chemistry of water along the direction of flow and, more importantly, of the lithology of the Triassic substratum in each drainage sector, be it purely detritic, gypsiferous or with halites disseminated within it.

Within the main group of groundwater in the Cabra-Alcaide aquifer we can distinguish two subtypes by examining the value of the ratio Mg/Ca (Scanlon, 1989). Values of this index greater than 0.17 define a subtype of Ca–Mg waters, whilst smaller values are attributable to a Ca subtype (Fig. 4). This last subgroup includes the waters emerging from the epikarstic Zarza spring (Mg/Ca=0.08), whose values on the graph are situated very close to the lower left origin of the cation triangle (Fig. 4). Waters from the remainder of the springs belong to the Ca–Mg subtype, with values of the index ranging between 0.38 (Marbella) and 0.24 (Fuente del Rio), as can be observed in Table 1.

Fig. 5 shows the temporal evolution of electrical conductivity of water (at 25°C) measured at 4 of the springs studied. The mean values indicate very different levels of water mineralization (Table 1), which oscillate between low values (36.8 mS/m at Zarza spring) and relatively high values (72.5 mS/m at Piedras spring). In contrast, the temporal trends are similar, although in some cases divergences were observed which are difficult to explain.

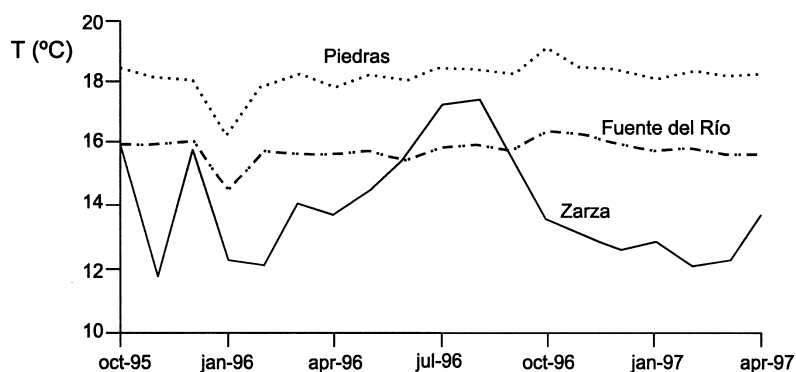


Fig. 3. Seasonal variation of temperature for some spring waters, from October 1995 to April 1997.

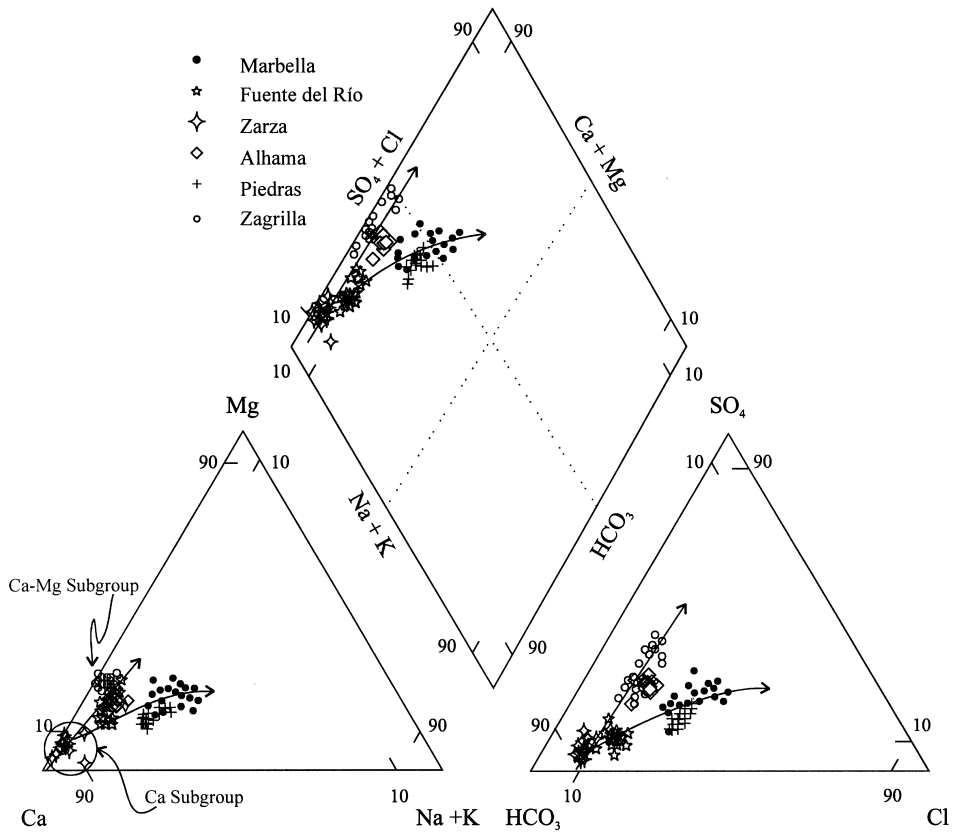


Fig. 4. Piper diagram of the sampled groundwaters. Arrows indicate the evolution and trends in water chemistry on both a spatial and a temporal basis.

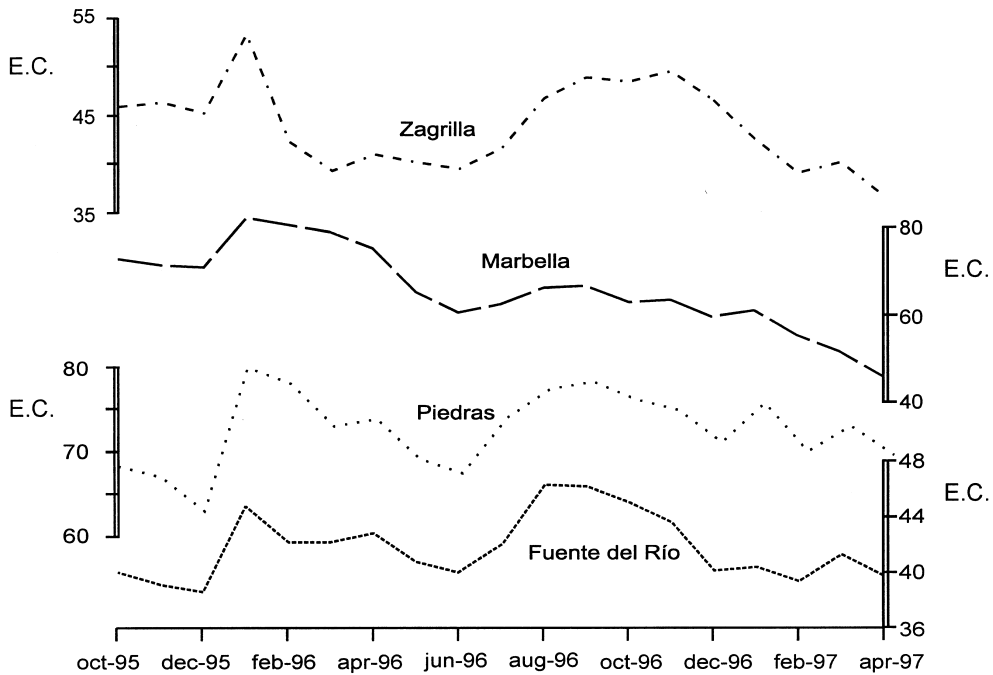


Fig. 5. Temporal variation of values of electrical conductivity (in mS/m) measured in 4 of the springs studied.

For example, the similarity of this parameter between the Fuente del Rio and Piedras springs would seem obvious bearing in mind their geographical proximity. However, as noted above, the lack of correlation between the flow values at these two springs ($r^2=0.12$) suggests that their hydrodynamic behaviour is independent. The explanation of this phenomenon requires serious reflection about the factors that affect each of the two parameters considered — flow and conductivity — with those determining the mineralization being larger in number and more difficult to interpret. What is clear is that, considered in isolation, the results lead to different interpretations.

Electrical conductivity of water at Zagrilla follows a similar temporal pattern to that of the two springs mentioned above with only small differences. In contrast, the time series at Marbella on changing from the dry years (1994–1995 and the 4 previous years) to the wetter ones (1995–1996 to 1996–1997), shows that an intense and slow process of dilution and some renovation of the phreatic storage waters (mainly indicated by a decrease in the concentration of SO_4 and Cl; Fig. 6) occurs in this part of the aquifer. Thus, there seems to be an inverse correlation between the temporal evolution of conductivity values and that of water flow at this spring. This phenomenon relates to an initial rapid expulsion by piston displacement of more mineralized waters during January 1996, as discussed below.

Almost all of the springs studied show a relative maximum conductivity between January and April 1996, roughly coinciding with the maximum discharge of the 1995–1996 hydrological cycle. The increased mineralization corresponds, in the majority of cases, to an increase in the concentration of SO_4 and Ca although, as occurs in the Piedras spring, increases are also observed in the HCO_3 and Cl concentrations. If we were dealing solely with an increase in Cl, we would have to conclude that

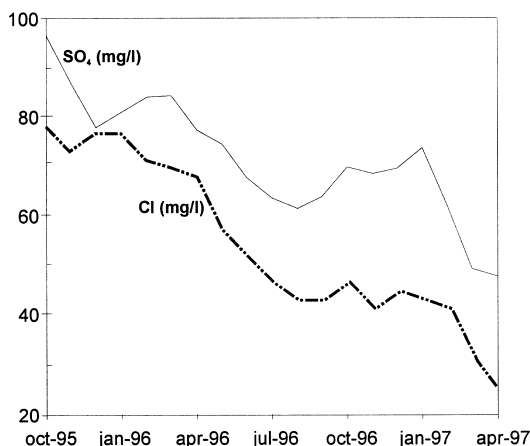


Fig. 6. Monthly evolution of SO_4^{2-} and Cl of groundwaters from Marbella spring.

the increased conductivity is due to the rapid leaching of Cl (reconcentrated by evaporation during the previous drought) from the subcutaneous part of the aquifer, a feature described by Blavoux and Mudry (1986) in other karstic aquifers. In the case of the Cabra-Alcaide aquifer, and given that the increased mineralization is due to the dissolution of the limestone and dolomites of the aquifer and of the evaporitic substrate, the only explanation is that there is apparently a *piston effect* during the transition between extremely dry periods and periods of intense rainfall recharge. This situation is what occurred at the end of 1995: the year 1994–1995 was 50% drier than the average annual rainfall (and the previous 5a had also been relatively dry), whilst 1995–1996 was 40% rainier than this average.

The *piston effect* means that the intense rainfall recharge that started at the end of 1995 caused a displacement of more mineralized groundwaters towards the spring. These waters, rich in SO_4 , Ca and other ions from the host rock, had spent a relative long time in contact with the rock of the aquifer and the evaporite substratum, and were probably waters from deeper within the saturated zone. Although it may be debatable, to suppose a mechanism of diffuse flow in the aquifer seems most reasonable in order to explain this piston effect, on the understanding that, at all times, the water that emerges from the springs is a mixture in variable proportion of relatively old waters and renewed waters. Really, a dominantly diffuse flow in the aquifer is compatible with a greater verticality and deepening of the flow lines as the hydraulic gradient increases due to the intense recharge. Thus, expulsion of the oldest and most mineralized waters is favoured and the fact that this effect lasts several months is explained as well. The phenomenon was not repeated in the following rainy season (November 1996 to January 1997), when there was a decrease in the water conductivity of the springs as the flow increased. Therefore, it appears that this phenomenon is a sporadic one that occurs only in extreme hydrological situations.

In the case of the Marbella spring, the hydrodynamic and hydrochemical data agree with the theory described above of a low degree of karstification in this part of the aquifer. However, the coefficient of variation of conductivity has a relatively high value (14%) which, for some authors (Shuster and White, 1971), would indicate the opposite. The degree of chemical variability cannot be used to assess the degree of karstification because the system memory extends beyond one year.

In the Zarza spring, the coefficient of variation for electrical conductivity is also high, but in this case it is justified by the local high degree of karstification. Nonetheless, as discussed above, it seems clear that the role played by the small drainage area and the narrowness of the unsaturated zone is the determinant in the hydrological behaviour of this spring.

4.3. Saturation state

The WATEQF program was used to calculate the saturation indices. This makes corrections to the total ionic concentrations for the effect of electrostatic shielding and for the presence of aqueous complexes or ion pairs. The field pH and temperature measurements were taken into account in the calculation of solubility and saturation state. Under these conditions and given that the analytical and pH errors are no greater than those obtained by Langmuir (1971), the imprecision in the calculation of the saturation index with respect to calcite is similar to that established by this author, that is, between -0.1 and $+0.1$. Thus, using this range of uncertainty, all the groundwaters studied are on average oversaturated in calcite (Table 1), which, according to Shuster and White (1972), suggests a mechanism of diffuse flow, not conduit flow. On first inspection it seems surprising that, of all the sampled springs, it is Zarza that shows the highest mean degree of calcite saturation. In fact, according to the previous section, this can not be explained by a prolonged water-rock contact time, as the authors cited would argue, but to a loss of CO_2 from the groundwater due to a high degree of karstification of the unsaturated zone and a shallow water level. The Zarza spring subsystem can be considered open with respect to CO_2 , but the input of this gas from the soil is low because at the present time it is poorly developed and has a low content of organic matter and sparse vegetation. For this reason, water becomes oversaturated in calcite in spite of its low mineralization (Table 1). Thus, the criteria of Shuster and White (1972) must be used with some caution.

Fig. 7 shows the relationship between the saturation indices for calcite against the total SO_4 content. It can be seen that only two samples were undersaturated and 12 were in equilibrium for this mineral. The remainder were oversaturated which suggests a potential for precipitation of calcite, though the degree of oversaturation

required for this to occur is not known for the area under study. The high indices of saturation encountered in the Cabra-Alcaide groundwaters contrast with those observed in the study areas of other authors, such as Langmuir (1971), Shuster and White (1972), Scanlon and Thrailkill (1987), and Hess and White (1992), who found a generalized undersaturation in calcite. In contrast, Plummer et al. (1990) and Cardenal et al. (1994) found that the majority of the groundwaters in their respective study areas were slightly oversaturated. In the same way as in these latter studies, the groundwaters of the Cabra-Alcaide aquifer become oversaturated with respect to calcite through solution of more soluble minerals containing Ca (gypsum from the evaporite substratum), as will be demonstrated below. The Zarza spring is an exception, and its saturation state has been explained above.

The only two water samples which were undersaturated in calcite were taken from two springs very close to each other: Fuente Alhama and Zagrilla- during February 1996, coincident with large discharges. Bouamama et al. (1996) considered that in the eastern part of the Cabra-Alcaide aquifer there exist some very transmissive karstic structures, of the overflow type, which become operative when the recharge to the aquifer is very intense. These structures could allow a very fast evacuation of recently infiltrated, aggressive waters.

Values of the saturation index for dolomite in the range -0.5 to $+0.5$ indicate that water is in equilibrium with respect to this mineral (Plummer et al., 1990); the majority of the waters studied yielded values of this index within this range (Table 1). However, all the springs are permanently undersaturated with respect to gypsum.

4.4. Hydrogeochemical processes

The karstic Cabra-Alcaide aquifer, despite its moderate extent, shows a large degree of hydrogeochemical variability that results from its marked hydrogeochemical

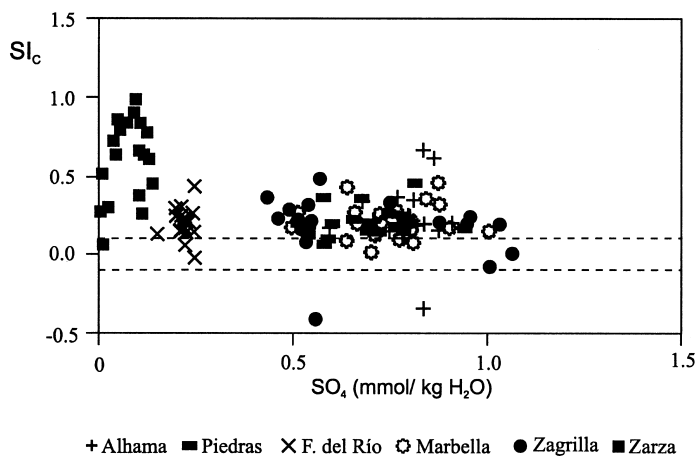


Fig. 7. Plot of dissolved SO_4^{2-} concentration vs. the saturation index for calcite. Equilibrium fields are also indicated.

and lithological complexity. In general, since we are dealing principally with a carbonate aquifer, the most common chemical reactions along the flow lines are those of calcite and dolomite dissolution, ultimately responsible for the Ca–Mg–HCO₃ facies that predominates here. Nevertheless, the lithology of the carbonate aquifer substratum favours the occurrence of gypsum and halite dissolution processes by the groundwater. The existence of these main processes has already been highlighted in the interpretation of the Piper diagram (Fig. 4).

Fig. 8 shows a graph derived from the Principal Components Analysis (PCA) applied to the 8 most important hydrochemical variables determined in the 123 samples of groundwater springs. Principal components I and II explain 75% of the total variance of the data population. This statistical treatment assists in understanding the origin of the hydrochemistry and in inferring the existence of certain hydrogeochemical processes which have affected it, in both space and time (Melloul and Collin, 1992). Thus, all the variables which determine the mineralization of the water, together with the $p\text{CO}_2$, are found to be inversely correlated to pH, indicating that the most mineralized waters — or at least some of the most saline springs — tend to be less alkaline, and rich in dissolved CO₂. This may seem strange but, as will be demonstrated below, there are hydrochemical processes of dedolomitization which affect the most mineralized waters (e.g. Marbella spring) and which can explain this fact.

The closest correlations are between Na and Cl and between Mg and SO₄. To begin with, it seems obvious to explain the relationships and the enrichment in these ions by the dissolution of the evaporite minerals that comprise the substratum of the aquifer, being halite in

the first case and sulphate minerals rich in Mg in the second. However, sedimentary magnesium sulphate minerals are not found in the Triassic lithofacies in Spain, although Mg may be present as a minor impurity of gypsum (Marfil-Perez, 1970), where Mg comes from the weathering of clays and dolomitic rocks close to the gypsum layers.

The different position occupied by Cl with respect to SO₄ on the PCA graph (Fig. 8) indicates that, although there is some relationship between the two, they are not always supplied simultaneously by the evaporite substratum, but that their abundance in the groundwater depends on the basic composition of this substratum at any location (be it halite and gypsiferous as in the Marbella and Piedras springs, or solely gypsiferous as occurs in the Zagrilla and Alhama springs), according to the trends seen from the Figs. 4 (Piper diagram) and 9.

The lack of correlation between Mg–SO₄ and HCO₃ suggests both a different lithologic origin (dissolution of gypsum for SO₄ and limestones-dolomites for HCO₃) and the existence of hydrogeochemical processes of dedolomitization that selectively modify the concentrations of Mg and HCO₃ in the flow path (e.g. in the flow line of Zarza-Fuente del Rio-Piedras).

Lastly, Ca is near equidistant between HCO₃ and SO₄ on the PCA graph. This indicates that, for some springs or at various times during the study period, the Ca is derived both from the dissolution of limestones and dolomites as well as from the dissolution of the gypsum substratum.

In the Ca subgroup of water, to which Zarza belongs, calcite dissolution is more intense than that of dolomite (as deduced by a very low Mg/Ca ratio), because the kinetics of dissolution in the latter are considerably slower than that of calcite (Plummer et al., 1978; Busenberg and Plummer, 1982). The increase in the Mg content in the other spring waters (the Ca–Mg subgroup) is mainly a result of the higher rate of dolomite dissolution, given the longer flow path, and hence the longer residence time and greater water-rock interaction. On a temporal basis, this process appears to be dominant in some of the springs studied, such as Fuente del Rio and Piedras, where there is good correlation between HCO₃ and Mg. Nevertheless, the hydrochemical influence of the Triassic detritic-evaporite substratum is a factor to take into account in order to fully interpret the chemical equilibria of these Mg-rich groundwaters. So the dissolution of gypsum from the substratum may provoke the incongruent dissolution of dolomite in the aquifer rock and a tendency for precipitation of calcite. The increase in Ca concentration in the water, caused by gypsum dissolution, provokes calcite precipitation by the *common ion* effect. As a consequence, the concentration of HCO₃ in the water diminishes and decreases the pH, producing undersaturation in dolomite, so contributing to an additional

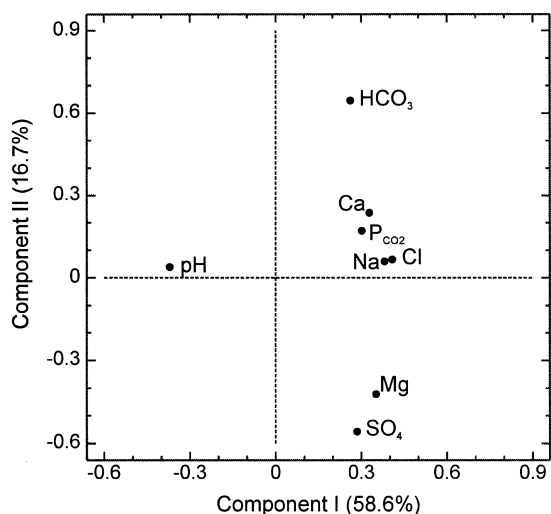


Fig. 8. Distribution of variables as given by Principal Components Analysis. Weight of the components in parentheses.

dissolution of dolomite as well as the increase in the Mg concentration in water.

The dedolomitization mechanism in the presence of Ca–SO₄-rich solutions, i.e. from dissolution of evaporite minerals, has been widely described (Back et al., 1983; Plummer et al., 1990; Sacks et al., 1995). This is an important process in the temporal chemical evolution of the waters of the Alhama, Zagrilla and Marbella springs, though to a varying degree. In Fig. 9 one can see that in these spring waters an increase in SO₄ content is accompanied by an increase in Ca and Mg, together with a slight decrease in pH. The same decreasing trend should be seen with the HCO₃ ion, but in this case it is

not evident because of other possible hydrogeochemical processes (Plummer et al., 1990; Cardenal et al., 1994). With the sole exception of the Zarza spring subsystem, the Cabra-Alcaide aquifer is considered as a closed system with respect to CO₂ gas, because of the great thickness of the vadose zone and the confined nature of the aquifer in some sectors. As a result, the enrichment in HCO₃ may be due to an additional input of CO₂ produced by decomposition of organic matter located at depth. In this respect, it is known that an oil well more than 5000 m deep drilled between Luque village and Fuente Alhama spring (Fig. 1) yielded relatively large quantities of natural gaseous hydrocarbons. On the

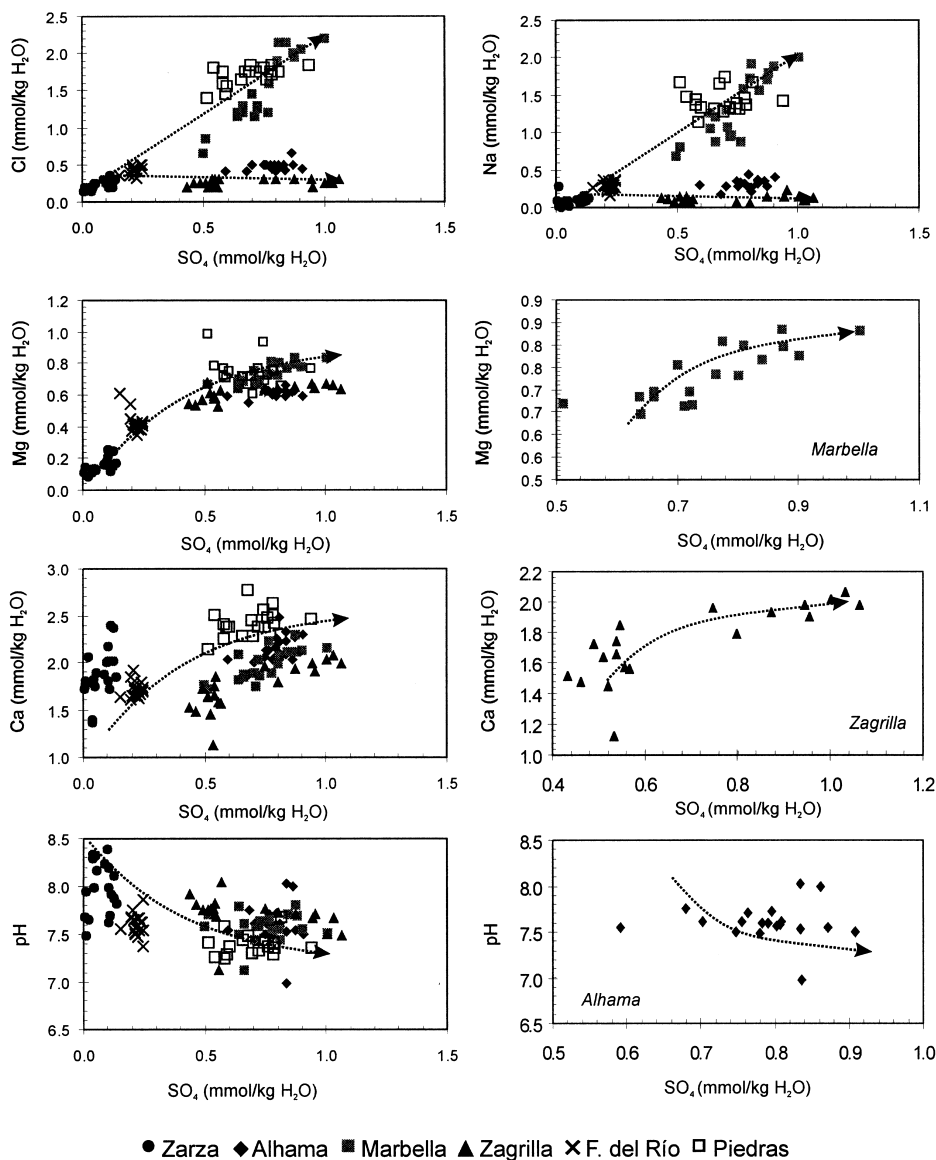


Fig. 9. Sulphate concentration plotted against various hydrochemical parameters.

other hand, the occurrence of groundwaters heavily enriched with CO_2 are not uncommon in the Betic Cordilleras (Ceron et al., 1998), being related to large-scale faulting and seismic instability in the region. Thus, in some of the springs like Piedras a certain input of CO_2 originating at depth could provide the explanation of the enrichment in HCO_3^- .

On a spatial basis, a comparison of the chemical data from all the springs (Fig. 9), does not clearly indicate the existence of dedolomitization. This is due to the concurrence of other hydrogeochemical processes, but above all to the fact that not all of the springs are strictly situated on the same line of flow. In spite of all this, there is lithological evidence that dedolomitization acts or has acted as an extremely belated diagenetic process (Martin, 1980), acting preferentially at the base of the carbonate aquifer. Effectively, a layer of rauhewackes of variable thickness lies beneath the basal Liassic dolomites and over the Triassic detritic-evaporite materials. These diagenetic dedolomites have a limestone-dolomite composition and a brechoid and/or cavernous structure (Fairbridge and Bourgeois, 1978); they are usually traversed by numerous veins of white calcite (Molina, 1987). Under the microscope, frequent pseudomorphs of calcite after dolomite are seen, indicating a mineral replacement (Martin, 1980). According to Felgueroso and Coma (1964), these rauhewackes or “cornieules” are the most porous and permeable rocks within the study area, and many of the springs are linked to them (Alhama, Zagrilla, Marbella and Piedras springs). The field investigation by Schaad (1995) showed that the dissolution of dolomite-bearing gypsum or gypsum-bearing dolomite leads to the formation of rauhewackes.

4.5. Hydrogeochemical modelling

To illustrate the chemical changes in the water that take place along the flow path towards one of the most important springs (Marbella spring), inverse hydrogeochemical modelling was applied in two stages, using PHREEQC (Parkhurst, 1995). In the first stage, modelling began with the entry of water from precipitation into the aquifer, the characteristics of which were determined in the laboratory from various samples taken over the study period. A value for pH in rainwater was not available and so this was calculated assuming it was in equilibrium with the atmosphere ($p\text{CO}_2 = 10^{-3.5}$ atm). In this way the original pH of the rainwater was estimated as 5.66 (Drever, 1997). Since the Zarza spring is epikarstic, and the flow path within the aquifer is very short, its chemical composition was used as the input end-member to the second stage of modelling, i.e. as recharge water that reaches the saturated zone of the aquifer.

The quantity of calcite precipitated from the moment that the rainwater penetrates the aquifer until it emerges via the Marbella spring is in the order of 1.5 mmol/kg

H_2O , and the amount of dolomite and gypsum dissolved is 0.8 and 0.85 mmol/kg H_2O , respectively. These transferred mineral masses are similar to those estimated by a thermodynamic simulation of isothermic dedolomitization for a hypothetical aquifer with similar lithological characteristics as the Cabra-Alcaide one. In order that the conditions were as similar as possible to actual conditions, up to 2 mmol/kg H_2O of CaSO_4 were added to the system, and up to 3 mmol/kg H_2O of NaCl .

5. Conclusions

The results obtained during the present study show that the hydrogeochemical variability of karstic springs in many cases does not allow the structural characteristics of the aquifer to be established. The chemical composition of groundwaters in karst does not depend solely on the local hydrogeological characteristics or, in other words, on the type of groundwater flow (diffuse or conduit). Nevertheless the present study does not rule out the influence of the degree of karstification as an additional factor that may control the quality of groundwater.

Given that karstic systems tend to be highly vulnerable to contamination, due mainly to their great permeability, and given that these systems are highly complex, both from a physical point of view as well as because of the hydrogeochemical processes that can take place within them, a correct evaluation of the predisposition of such systems to contamination and of their response to this can only be made by applying as many approaches as possible to their study and understanding.

The hydrogeochemical behaviour of the springs that drain the aquifer is seen to be influenced by the hydrodynamic characteristics of its supply areas, and this in turn by the extent of the catchment which serves them, the thickness of the infiltration zone, the geometry of the aquifer and its fissure and karstic structure. The hydrodynamic features can profoundly affect the transit time of water and the water-rock interaction and, in the case of the Cabra-Alcaide aquifer, allow a segregation of the hydrochemical facies along the direction of water flow. A transition is seen from Ca-HCO_3 to Ca-Mg-HCO_3 type, a process that, in principle, is independent of lithology and has to do only with the kinetics of dissolution both of calcite and dolomite.

Other trends observed along the direction of flow, towards Ca-SO_4 or Na-Cl waters, are the consequence of the influence of the Triassic substratum of the aquifer, in principle of low permeability, although not so low, judging from the karstic forms which develop in the evaporites and the yield at certain pumping wells. The input of SO_4 from these basal rocks also induces a degree of dedolomitization which has considerable repercussions on the chemical composition of some groundwater springs.

The use of diverse hydrochemical and hydrodynamic methods in an attempt to establish the type of dominant flow in this aquifer, sometimes leads to contradictory results, some of which are easily explained and others not. Thus, the criterion of saturation or undersaturation in mineral species does not appear to have an application in this region, because of the loss of CO₂ from the epikarstic springs, the scarcity and variability of precipitation and the dissolution of gypsum.

Acknowledgements

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