Hydrochemical characteristics of an overexploited karstic aquifer: the case of the Cabeçó d'Or (SE Spain)

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ABSTRACT

The karstic system of the Cabeçó d'Or is a small overexploited aquifer where water level declined by more than 200 m from the early sixties to 1987. After this year the water level has recovered 20 m and it has been almost stabilized. The waters of this aquifer are calcium-sulphate type and show a clear thermal positive anomaly. Mineralization has been related to the presence at depth of evaporite deposits (Keuper facies) rich in gypsum. The processes occurring in the aquifer include the dissolution of gypsum, calcite and dolomite, and the precipitation of calcite. Lower concentration in sodium than chloride shows a cation exchange processes between water and clay minerals. These processes could be favoured by the input of CO_2. The content of carbon-13 could be related to the deep CO_2 inputs. Fractures within the study area appear to be responsible for the temperature and CO_2 anomalies, as well as for the elevated concentrations of radon and radium encountered in these waters. Oxygen-18 and carbon-13 have remained relatively constant, reflecting the relatively stable hydrogeochemical conditions. This hydrogeochemical stability over time is interpreted as an indication that overexploitation of the aquifer has not induced any significant deterioration in water quality. The thermal anomaly of groundwater can be responsible of a mixing processes what prevent a vertical hydrogeochemical zoning.

Key words: CO_2, dedolomitization, hydrogeochemistry, karst, overexploitation

Características hidroquímicas de un acuífero kárstico sobreexplotado: el caso del Cabeçó d'Or (SE de España)

RESUMEN

El sistema kárstico del Cabeçó d'Or es un pequeño acuífero sobreexplotado donde los niveles han descendido más de 200 m entre los años 60 y 1987. Después de ese año los niveles han recuperado 20 m y se han estabilizado. Las aguas de este acuífero son sulfatadas cálcicas y presentan un claro carácter termal. Su mineralización ha sido relacionada con la presencia de rocas evaporíticas (facies Keuper rica en yesos) en profundidad. Algunos de los procesos que tienen lugar en el seno del acuífero son la disolución de yeso, calcita, dolomita y precipitación de calcita. Las menores concentraciones de sodio que de cloruro apuntan a procesos de intercambio iónico entre el agua con minerales de la arcilla. Estos procesos podrían estar favorecidos por la entrada de CO_2. Los contenidos de carbono-13 parecen estar relacionados con la existencia de aportes de CO_2 de origen profundo. Las fracturas de gran envergadura existentes en el área de estudio parecen ser las responsables del ascenso calorífico, del CO_2, así como de las elevadas concentraciones de radón y radio encontradas en estas aguas. Los contenidos de oxígeno-18 y carbono-13 han permanecido relativamente constantes, lo que manifiesta unas condiciones hidrogeológicas e hidrogeoquímicas bastante estables. La relativa estabilidad hidrogeoquímica a lo largo del tiempo se manifiesta como un indicador de que la sobreexplotación del acuífero no ha originado cambios significativos en el deterioro de la calidad del agua. La anomalía termal del agua subterránea de este acuífero puede ser responsable de los procesos de mezcla, lo que dificulta la existencia de una zonación hidrogeoquímica en la vertical.

Palabras clave: CO_2, dedolomitización, hidrogeoquímica, karst, sobreexplotación

Introduction

The Cabeçó d'Or aquifer is a small karstic aquifer occupying a surface area of approximately 15 km² in the Alicante province in south-eastern Spain (Figure 1). Due to the thermal nature of its waters, a spa was

built near to the main springs to exploit their therapeutic qualities. In the early sixties a phase of intensive exploitation began to meet the large increase in water demand in the region. As a consequence of heavy pumping the springs ran dry and the spa was abandoned. Overexploitation continued for over twenty years, leading to a fall in water levels of more than 200 m. Most of the wells were abandoned after 1985 and pump abstractions were much-reduced. The piezometric level was monitored between 1990 and 1994, and water samples taken from the few boreholes that were still being pumped.

The aim of the present study was to characterize the hydrochemistry of the water abstractions pumped from over 200 m depth. It also aimed to establish some of the processes taking place within the aquifer, including the possible influence of the intensive abstractions on mineralization of the groundwater.

The Cabeçó d'Or aquifer

Geological setting

From a geological point of view, the aquifer lies within the domain of the Southern Prebetic of the External Zones of the Betic Cordillera (Azema, 1977; Granier, 1987). Jurassic and Lower Cretaceous limestones outcrop in the Cabeçó d'Or area (Figure 1). Overlying these formations is an alternating sequence of marls and marly limestones, which include reef constructions and calcarenite episodes. This sequence exceeds 600 m and dates from the Upper Valanginian-Hauterivian to Upper Albian-Cenomanian. The series continues with limestones, which towards their upper margin present intercalations of marly layers, ending with marls from the Upper Cretaceous (Azema, 1977). Above lie alternating layers of marls with intercalations of bioclastic calcarenites, reaching an estimated thickness of 300 m and dating from the Palaeocene-Lower Miocene. Lastly, there are Quaternary slope or piedmont deposits and some travertine outcrops related to the former thermal springs that formed the natural discharge of the aquifer.

The general tectonic situation of the region, and in particular of this system, point to compression over the last few millions of years (De Ruig *et al.,* 1987). According to De Ruig (1992), the region is a fold-and-thrust belt composed of a deformed sedimentary cover, detached from its basement along Triassic lutites and evaporites (Keuper facies). NNW-verging folds and thrusts, along with normal and strike-slip faults dominate the structure of this sedimentary

cover. The Cabeçó d'Or mountain forms an asymmetric anticline, which is aligned approximately N-S (Figure 1). Its eastern flank dips in the region of 45-50°, whilst the western flank is more disposed towards the vertical, and is even inverted in some places. In the central part there are outcrops of Jurassic limestones, which give way to Cretaceous series on either flank. The intense tectonic has provoked numerous fractures. Whilst there are no outcrops of Keuper facies gypsums in the Sierra of Cabeçó d'Or or in the surrounding area, we cannot reject the possibility that these materials are present at depth.

Hydrogeological features

The Cabeçó d'Or aquifer comprises the Jurassic-Cretaceous limestone series. The other Cretaceous limestones and Quaternary deposits that outcrop in the study area are largely devoid of hydrogeological significance. The structure of the Jurassic-Cretaceous carbonate series and the rest of the Cretaceous marly formations isolates the system from a hydrogeological point of view. The geometry of the impermeable substrate is difficult to establish, given that the existing boreholes do not penetrate the carbonate series. Based on regional studies, one possibility is that an Upper Kimmeridge marl formation acts as the impermeable base of the aquifer (IGME, 1987). Nevertheless, the possibility of a Keuper facies basement cannot be rejected.

With respect to the hydraulic functioning of the aquifer, various pumping tests have yielded transmissivity values between 160 and 2400 m^2/day, and a storage between 1.7 and 3% (Andreu, 1997). This value was determined from the ratio between the volume of water abstracted and the volume of desaturated rock, measured during a dry period when inputs to the aquifer were nil.

Recharge of this aquifer derives solely from direct infiltration over the approximately 11 km^2 of permeable Jurassic materials that outcrop in the zone (Figure 1). Estimates of the mean input to the aquifer according to Kessler method range from 1 to 1.4 hm^3/year, although there is wide variation according to the annual climatic variation. A mean of 412 mm/year precipitation has been calculated for the period 1977-1994 (Andreu, 1997). The standard deviation (STD) of 137 and variation coefficient (CV) of 34 show that annual rainfall is highly variable. During this period there were differences of approximately 500 mm between wet and dry years (Figure 2). Autumn is the season which receives the major precipitation being close to 31% of the annual rainfall. An analysis of
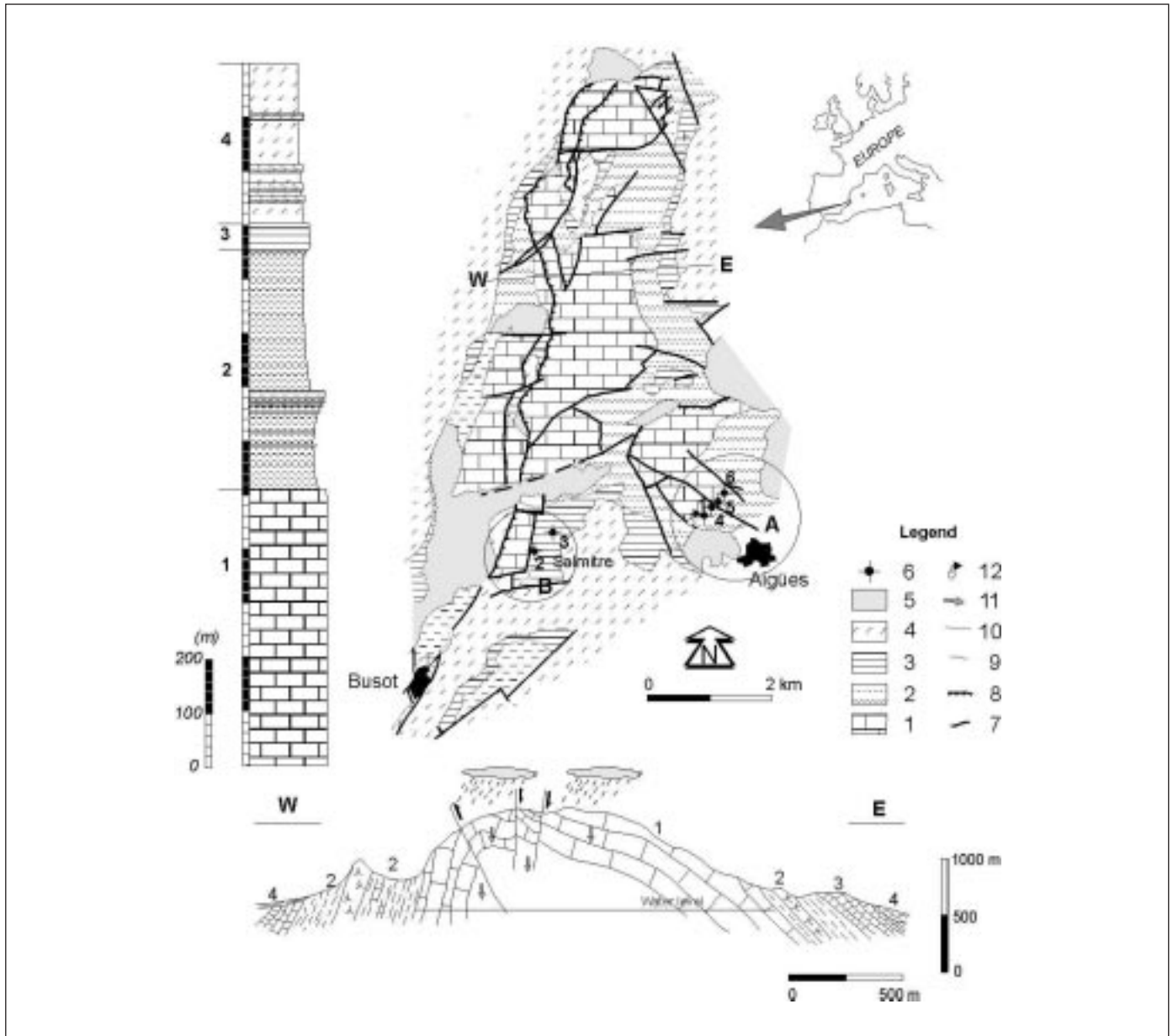
Fig. 1. Hydrogeological map, stratigraphic log and cross section of the study area. Legend: 1. Limestones and sandy limestones (Jurassic-Lower Cretaceous) 2. Marl and calcarenites (Lower Cretaceous) 3. White limestones (Upper Cretaceous) 4. Marl and marly limestones (Tertiary) 5. Undiferenciated Quaternary deposits 6. Well 7. Normal fault 8. Reverse faul 9. Unconform contact 10. Groundwater flow 11 Dry springs: A. Aigües sector. B. Salmitre sector
Fig. 1. Mapa hidrogeológico, columna estratigráfica y corte geológico del área de estudio. Leyenda: 1. Calizas y calizas arenosas (Jurásico-Cretácico Inferior) 2. Margas y calcarenitas (Cretácico Inferior) 3. Calizas blancas (Cretácico Superior) 4. Margas y calizas margosas (Terciario) 5. Depósitos cuatrenarios indiferenciados 6. Pozo 7. Falla normal 8. Falla inversa 9. Contacto discordante 10. Flujo subterráneo 11. Manantiales secos: A. Sector de Aigües. B. Sector de Salmitre

temperature gives an annual mean of 15.1ºC. Highest temperatures are recorded in the summer months, with absolute maxima in July and August (mean values of 25ºC). Minimum temperatures are recorded in January with a mean of 7.7ºC, falling to below 0ºC only very infrequently.

Changes in water level through time

Although pumping from the aquifer started in the early sixties, no piezometric measurements were made for more than a decade and so the changes in water level are not known with any precision. The
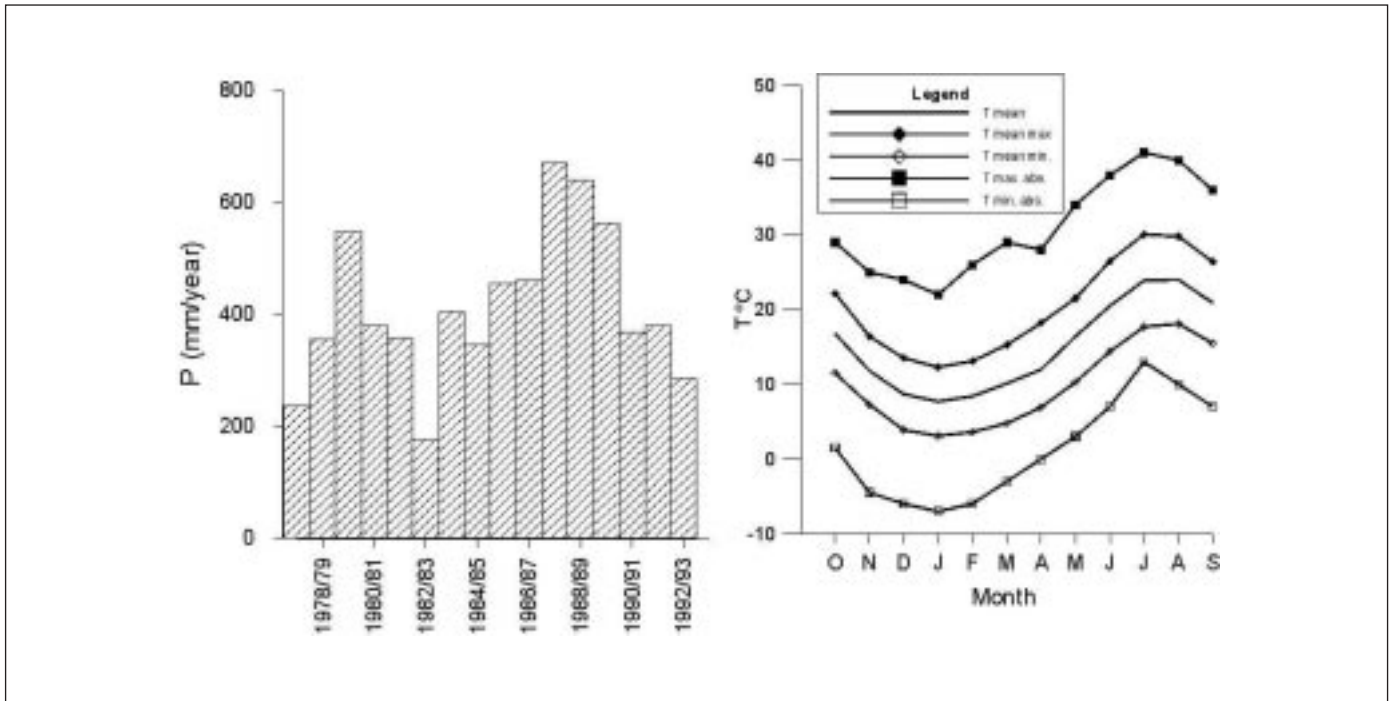
Fig. 2. Annual rainfall from 1977/78 to 1992/93 (left). Temperature chart (right). T mean: mean temperature: T mean max: mean maxima temperature. T mean min: mean minimun temperature. T max abs: absolute maximum temperature. T min abs: absolute minimun temperature

Fig. 2. Precipitación anual desde 1977/78 a 1992/93 (izquierda). Diagrama de temperaturas (derecha). T mean: temperatura media. T mean max: temperatura máxima media. T mean min: temperatura mínima media. T max abso: temperatura máxima absoluta. T min abs: temperatura mínima absoluta

first piezometric records correspond to 1977 (Figure 3). At this time the water level was already more than 200 m deep with regard to the height above sea level of the old spring which drained the system before the begin of abstraction. This means that until that moment there was a relative decline of 19 m/year. Abstractions from the aquifer during this period are not known with any certainty but estimates of more than 10 hm³/year have been made (IGME, 1987). The decreasing trend persisted until the middle of 1987. The water level recovered during occasional wet periods and the fall in levels slowed over time. This slowing-down has been attributed to the reduced abstractions resulting from the almost total abandonment of the boreholes as they ran dry, as well as to an increase in abstraction costs and the changeover of abstractions to other aquifers in the region (IGME, 1987). By the early nineties the decreased pumping (less than 1 hm³/year), together with an increase in rainfall provoked a reversal in the trend and a period of clear recovery began. Over the last few years abstractions must have been similar to inputs in the aquifer, this is the reason why water levels have been practically stabilized.

Methodology

Between 1991 and 1994 ninety water samples were taken from boreholes tapping the aquifer, for physico-chemical characterization. All the samples were taken after several hours pumping. When the samples were taken the water depth was placed between 260 and 270 m below surface. Temperature, pH and electrical conductivity were measured directly in the well using Hanna instruments. The following parameters were determined in the laboratory: chloride by titration with silver nitrate, bicarbonate by titration with hydrochloric acid, sulphate and nitrate by ionic chromatography. Calcium, magnesium, sodium, potassium, strontium, boron and silica, as well as the trace elements lithium, copper, iron, zinc, cadmium, barium, aluminium, nickel, cobalt, chromium and lead were analysed using inductively-coupled plasma spectrometry (ICP).

A study of the isotopic composition was mainly based on data from monthly samples taken between September 1993 and May 1994 in borehole n° 1. Isotopic determinations were made in the Laboratory of Environmental Studies at the Hungarian Academy

of Sciences (Debrecen) and in the Stable Isotope Geochemical Laboratory at the Zaidin Experimental Station (CSIC, Granada, Spain), following the classical methods of Epstein and Mayeda (1953). The samples were determined by mass spectrometry with a measurement error of < 0.2 per mille.

Ten litre samples were collected in clean polypropylene bottles, to provide sufficient carbon for carbon-13 analysis. Dissolved inorganic carbon was converted to carbonate by raising the pH (> 12) with high-purity sodium hydroxide. The carbonate generated was then precipitated by reaction with high-purity barium chloride. Carbon isotope ratios were identified using standard techniques (Kendall and McDonnell, 1998).

Results

A statistical summary of the principal hydrochemical variables is presented in Table 1. The main characteristic of the waters in this aquifer is their thermal nature. Temperatures range between 25.4 and 39.5ºC. In terms of their mineralization, conductivity ranges from 1381 to 2260 μS/cm, with sulphate and calcium the most abundant ions. With the exception of iron, the remaining trace elements analysed are present at concentrations of less than 20 μg/L. There is a difference between the points around Aigües (sector A) and those around Salmitre (sector B). Waters from the former are more thermal and more highly-mineralized. Nevertheless, all the water samples analysed are (Figure 4) of calcium-sulphate type.

Sulphate and calcium ions and, to a lesser extent chloride, magnesium and sodium, are responsible for the elevated salinity. Table 2 shows the correlation coefficients between the various ions. Sulphate is strongly correlated with calcium, magnesium and sodium, and also with chloride. This close correlation points to a common origin. This might be attributable to the dissolution of Triassic evaporite rocks occurring at depth, or to tectonic events. The moderate increase in water temperature, particularly in the immediate vicinity of Aigües, would facilitate the dissolution of such rocks, producing the close correlation observed between temperature and many of the ions. Gypsum is most soluble at temperatures of above 40ºC, close to the temperature measured in the boreholes around Aigües (Catalán, 1981). However, it is not certainly known whether such deposits are in contact with the aquifer or not.

To establish the origin of the elevated sulphate content of these waters the sulphur-34 content was determined. Two samples of solid gypsum had pre-
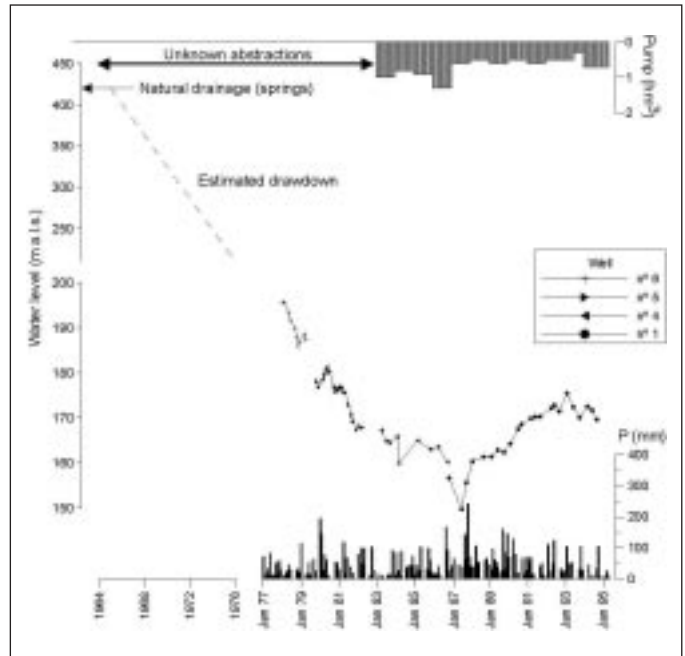

Fig. 3. Representative piezometric evolution in the Cabeçó d'Or aquifer
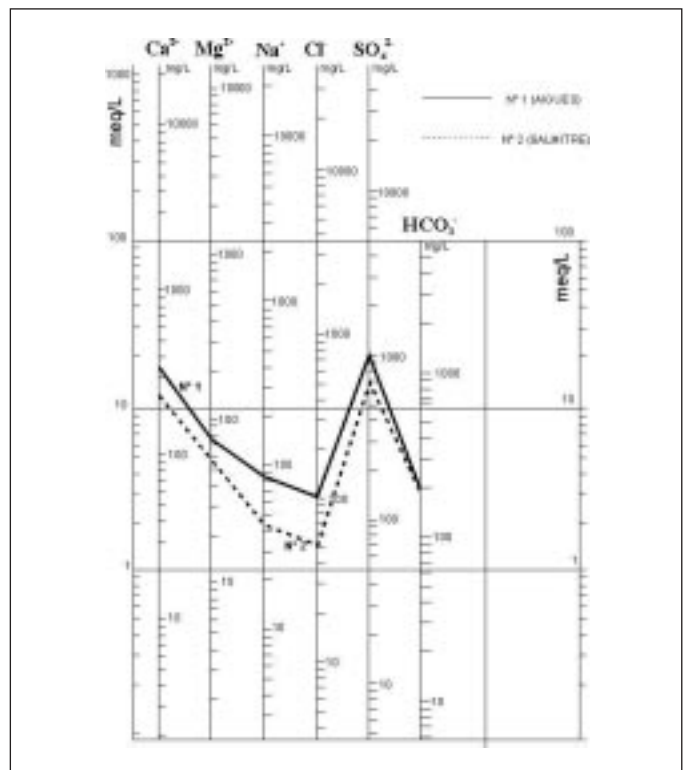*Fig. 3. Evolución piezométrica representativa en el acuífero del Cabeçó d'Or*

Fig. 4. Columnar logarithmic diagram of water quality from Aigües sector (nº 1) and Salmitre sector (nº 2)
Fig. 4. Diagrama logarítmico columnar de la calidad del agua de los sectores de Aigües (nº 1) y de Salmitre (nº 2)

Parameter	Mean	Maximum	Minimum	STD
Conductivity	1724	2260	1381	289
pH	7.2	7.7	6.5	0.2
T	31.4	39.5	25.4	5
Ca^{2+}	269	215	355	50
Mg^{2+}	70	87	56	8.6
Na^+	70	113	48	22
K^+	2.9	4	2	0.5
HCO_3^-	189	205	183	4
SO_4^{2-}	816	1069	580	167
Cl^-	74	128	50	22
NO_3^-	0.4	2.7	0	0.5
Sr^{2+}	13.9	15.5	10.1	1.2
SiO_2	19.6	25	15	2.5
Boron	0.15	0.27	0.01	0.05
Iron	0.1	1.2	0.003	0.21

Table 1. Main hydrochemical data of the ninety samples taken at different times in the aquifer (STD: standard deviation; Conductivity: $\mu S/cm$; Temperature: °C; ions: mg/L)
Table 1. Principales datos hidroquímicos de las noventa muestras tomadas en diferentes fechas en el acuífero (STD: desviación están-dar; conductividad, en $\mu S/cm$; Temperatura, en °C; iones, en mg/L)

viously been taken from the Triassic Keuper outcrops in other parts of the same region. The values obtained for these solid samples were 11.4 and 12.9‰, quantities similar to those reported by other authors for this facies (Pilot *et al.,* 1972; Claypool, 1980). Similarly, samples from borehole 1 in the present study yielded values of sulphur-34 between 10.6 and 16.0‰. We can therefore conclude that the sulphate in the water may derive from dissolution of gypsum from the Keuper facies (Krothe, 1988; Urilla, 1989; Balderer *et al.*, 1991). The water must have contact with these facies at depth. Other possible sources of sulphur in the water in this region are Messinian marls but they are not present around Sierra del Cabeçó d'Or and their values of sulphur-34 (between 20-23‰) are very different of groundwater from this aquifer.

Another feature to highlight is the weak correlation between bicarbonate and calcium. There is also less calcium than sulphate (Figure 5) and this points to calcite precipitation as a possibility, occurring due to the addition of a common ion from the dissolution of gypsum in water already saturated in both calcite and dolomite. Calcite precipitation causes depletion of the bicarbonate ions in solution and, to compensate this imbalance, there is a tendency for further dissolution of carbonate, in this case coming from the dolomite (Hanshaw and Back, 1979; Plummer *et al.*, 1990; Calaforra and Pulido Bosch, 1993). As a result, the magnesium content becomes relatively high, although the Mg^{2+}/Ca^{2+} ratio remains low because of the amount of gypsum dissolution. The pH of less than 7 could be another consequence of the same process (Appelo and Postma, 1993).

Finally, the Na^+/Cl^- ratio of greater than 1 (Figure 5) may indicate some interaction with clay minerals (ion exchange), probably with clays from the same Keuper facies, or with marly limestones deeper in the Jurassic carbonate series. In this process Ca^{2+} ions present in water could be exchanged against Na^+ ions adsorbed on the clays.

A study of the thermodynamic equilibrium for the principal minerals present in this type of aquifer was undertaken using the SOLUTEQ code (a modification of the WATSPEC code by Bakalowicz and D'Hultz, CNRS, unpublished). In general, the water was saturated with respect to calcite (SI calcite between 0.10 and 0.63), but subsaturated with respect to dolomite in some samples (SI dolomite between -0.59 and 0.70). The values of the gypsum saturation index were close to equilibrium (SI between -0.37 and -0.60), whilst halite saturation indexes showed clear subsaturation (SI between -7.24 and -7.76). This reflects greater dissolution of gypsum compared to halite. This finding, together with the low chloride content of the water, are explained since the Keuper facies are composed mainly of gypsum.

The carbon dioxide partial pressure calculated using the same code ranged from 0.6 to 2.5%. Although these values are not high, this represents a slight anomaly with respect to other karstic aquifers in the same region (Andreu, 1997). Over most of the permeable outcrops there is no soil cover and this suggests that some other CO_2 input exists. The dedolomitization process described above could be responsible for the increase in CO_2 (Appelo and Postma, 1993). Nevertheless, one cannot disregard the possibility of a deep CO_2 intrusion into the aquifer (Pulido Bosch *et al.*, 1995). The carbon-13 values obtained from borehole n° 1 (-2.53 to -4.1‰), indicate enrichment in the heavy isotope. In accordance with other authors, enrichment in carbon-13 suggests an input of CO_2 from depth (Maisonneuve and Risler, 1979; Blavoux *et al.*, 1982; Wexteen *et. al.*, 1988). The presence of endogenous CO_2 has been recorded relatively nearby (Cerón *et al.*, 1998; Cerón *et al.*, 2000).

The levels of radon in this aquifer reach 96 Bq/L, whilst ^{226}Ra reaches 0.0399 Bq/L, both relatively high

	C	pH	T	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	HCO$_3$	SO$_4^{2-}$	Cl$^-$	NO$_3^-$	Sr^{2+}	SiO$_2$
C	1.00												
pH	-0.80	1.00											
T	0.97	-0.87	1.00										
Ca^{2+}	0.98	-0.81	0.97	1.00									
Mg^{2+}	0.94	-0.73	0.91	0.95	1.00								
Na$^+$	0.96	-0.83	0.97	0.97	0.94	1.00							
K$^+$	0.98	-0.80	0.96	0.97	0.93	0.96	1.00						
HCO$_3$	0.15	-0.21	0.18	0.15	0.13	0.15	0.09	1.00					
SO$_4^{2-}$	0.98	-0.80	0.97	0.99	0.97	0.98	0.97	0.14	1.00				
Cl$^-$	0.95	-0.83	0.96	0.95	0.91	0.94	0.94	0.16	0.95	1.00			
NO$_3$	-0.58	0.35	-0.57	-0.60	-0.64	-0.57	-0.55	0.02	-0.60	-0.58	1.00		
Sr^{2+}	0.32	-0.36	0.31	0.32	0.25	0.30	0.31	0.08	0.30	0.27	0.06	1.00	
SiO$_2$	0.86	-0.79	0.87	0.87	0.84	0.88	0.7	0.10	0.88	0.83	-0.45	0.45	1.00

Table 2. Correlation matrix between the main hydrochemical parameters
Table 2. Matriz de correlación entre los principales parámetros
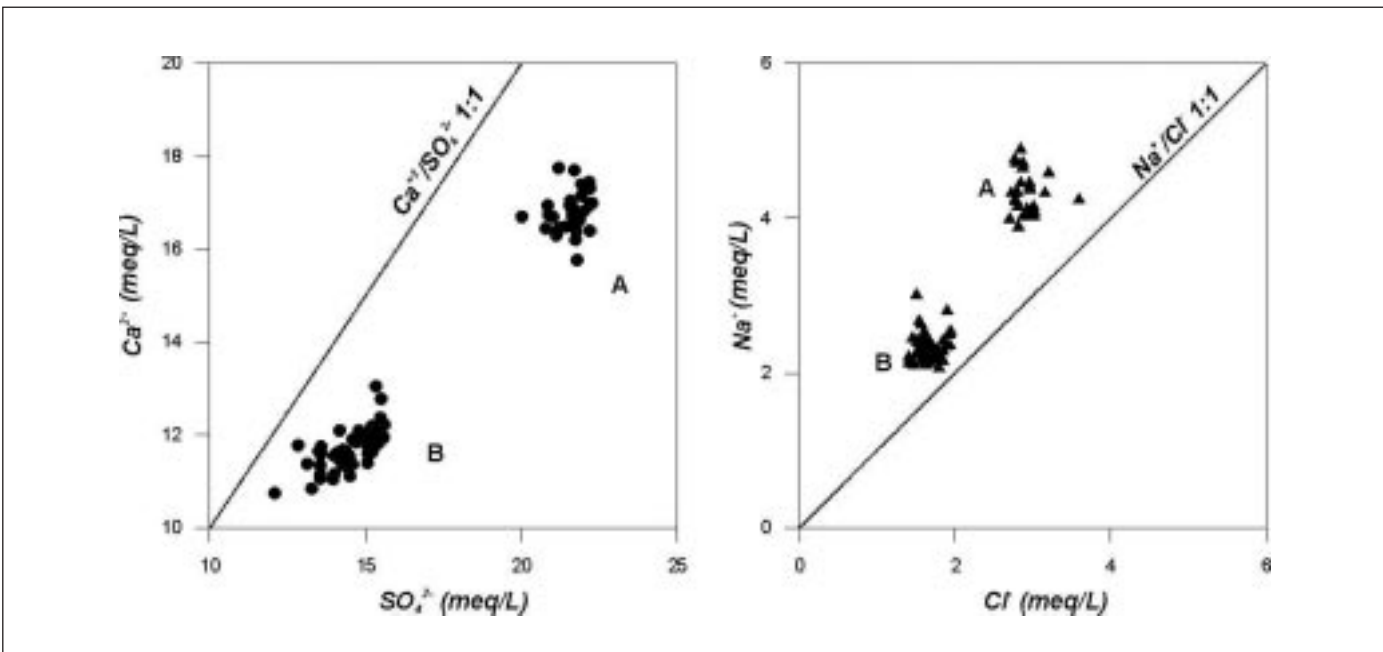

Fig. 5. Relationship between calcium-sulphate and sodium-choride in groundwaters. A: Aigües sector. B: Salmitre sector
Fig. 5. Relaciones entre Ca^{2+} y SO$_4^{2-}$ y Na$^+$ y Cl$^-$ en las aguas subterráneas. A: Sectoir de Aigües. B: Sector de Salmitre

values for this type of carbonate formation, although characteristic of thermal reservoirs (Polhl-Rüling, 1982; Wilkening, 1990; Soto *et al.*, 1995). Given the thermal character and the depth of the water table, an exogenous origin can be discarded. The radon must have an endogenous source, probably related to the tectonic activity. Thus, the faults and fractures could act as conduits along which deep, radon-rich waters could ascend (Lorenz *et al.*, 1961; Varley, 1993; Gall *et al.*, 1995). Moreover, it is known that aquifers subjec-

ted to compressive forces can emanate radon (Harvey, 1981; Smith, 1988). The Cabeçó d'Or aquifer has a complex structure and fractures reach considerable depths. The area is seismically active (López Casado *et al.*, 1987) and is characterized by the occurrence of mainly low-magnitude earthquakes, though occasionally earthquakes have reached intensity VIII (M.S.K. scale -Medvedev Sponhauer Karnik-). This seismic activity is related to the collision of the African and Eurasian plates, which are converging at a rate of approximately 5 mm/y (Argus *et al.*, 1989). This suggests that the tectonic factor is principally responsible for the high radon concentrations encountered.

The oxygen-18 and deuterium content were determined in January 1993 at points n° 1 and 2. Values of -7.4 and -7.1‰ for oxygen-18 and -43.1 and -43.3‰ for deuterium were obtained. As there are no isotopic data for precipitation in this area, the samples are compared with different metoric water lines. In January 1999 a survey to determine the isotopic gradient with altitude was conducted within a 20 km radius of the Cabeçó aquifer. Rain gauges were installed at 90, 300, 600, 800 and 1150 m altitude. A plot of $\delta^{18}O$ vs. δD (Figure 6) shows the groundwater samples situation (1 and 2 square) close to the Mediterranean Meteoric Water Line, suggesting a meteoric origin for the groundwater in the aquifer.

Figure 7 shows $\delta^{18}O$, $\delta^{13}C$, $\delta^{34}S$, electrical conductivity, piezometric level and rainfall plotted against temperature for the period September 1993 to May 1994 in borehole n° 1. ^{18}O values fall in the range -7.11 to -7.65‰, with a mean of -7.39‰. The monthly differences are not very pronounced and there is poor correlation with piezometric level. The values of carbon-13 and sulphur-34 over the monitoring period also remain relatively stabile. Changes in isotopic values and electric conductivity indicate that the inflow is relatively small in comparison with the volume of water held within the aquifer. Water reaching the saturated zone does not reflect seasonal variation clearly. This suggests that a residence time in the aquifer of several years. Likewise, the only record of tritium in the waters of this aquifer, at point 1, is less than 1 TU and this confirms that all the water pumped from the aquifer is at least several decades old.

The hydrogeochemistry of this aquifer is stable over time. It seems the overexploitation of the aquifer did not provoke any change in water quality. Thus, the 1876-1877 Official Yearbook of the Mineral Waters of Spain classified waters from this aquifer as calcium and magnesium sulphate type. The restitution of some analyses from the XIX century and early XX show sulphates of greater than 1.1 g/L and calcium
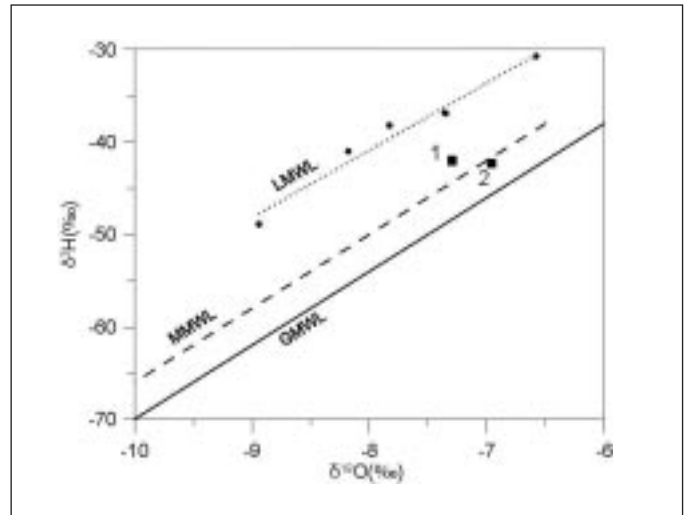

Fig. 6. Position of the groundwater samples in relationship to the MMWL (Mediterranean Meteoric Water Line), GMWL (Global Meteoric Water Line) and LMWL (Local Meteoric Water Line). Local Meteoric Water Line was established from January 1999 rainfall. Numbrers 1 and 2 are the samples of groundwater from Cabeçó d'Or
Fig. 6. Posición de las muestras de agua en relación con la línea meteórica mediterránea (MMWL), la línea meteórica global (GMWL) y la línea meteórica local (LMWL). La línea meteórica local fue establecida a partir de la lluvia de enero de 1999. Los números 1 y 2 son muestras de agua subterránea del Cabeçó d'Or
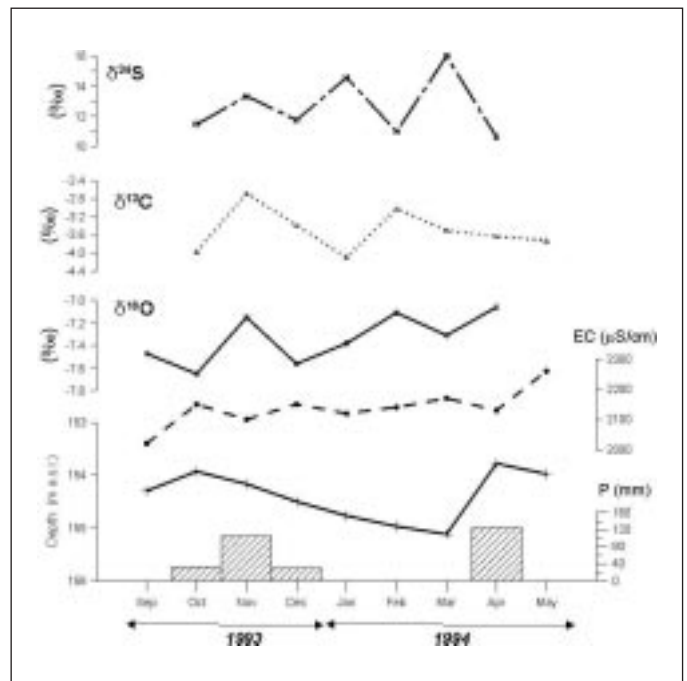

Fig. 7. Monthly variation of the $\delta^{18}O$, $\delta^{13}C$ and $\delta^{34}S$ with respect to conductivity, water level and rainfall (bars) during September 1993-May 1994
Fig. 7. Variación mensual del $\delta^{18}O$, $\delta^{13}C$ y $\delta^{34}S$ con respecto a la conductividad, nivel freático y lluvia (barras) durante el período comprendido entre septiembre de 1993 y mayo de 1994

above 200 mg/L (Gascon, 1992). The first modern determinations were made in 1974 (Figure 8). By this time, the aquifer was already overexploited, although the parameters analysed are not much different from the values found in recent years, despite a fall in water level of some 50 m in the interim. This homogeneity over time is mirrored by vertical homogeneity in the saturated zone. An electrical conductivity log made shows that the mineralization is almost constant over the depth of the water column (Figure 9). This means that there is vertical mixing in the aquifer, and no vertical salinity gradient exists. This is the reason why overexploitation did not induce changes in the hydrochemistry of the aquifer, in contrast to what has happened in other aquifers of the region (Pulido Bosch, 1991; Pulido Bosch *et al.*, 1996). The major hydrogeological difference between this aquifer and the other ones in this region is the thermal anomaly of groundwater in the Cabeçó d'Or aquifer. In this way the existence of "convective flows" could be responsible for the mixing between the bottom and top waters inside this aquifer. On the other hand the existence of elevated degree of fracturing can facilitate the hydraulic continuity and mixing processes of the waters.

Final considerations

The water of the karstic aquifer of Cabeçó d'Or is cha-

racterized by its positive thermal anomaly, with temperatures of between 25.4 and 39.5°C. The waters are mainly of calcium sulphate type, with sulphate content higher than 1 g/L.

In our opinion the high calcium and sulphate concentrations, the small positive SI with respect to calcite and dolomite, and the sulphur-34 content can be explained by the presence of evaporite facies (Keuper) at depth. However, the gypsum dissolution seems not to be the only process occurring in the aquifer. The fact that the concentration of calcium is lower than the sulphate concentration, together with the poor correlation between calcium and bicarbonate are evidence that calcite precipitation also occurs. This withdrawal of bicarbonate is compensated by the dissolution of dolomite, which in turn is favoured by inputs of carbon dioxide. Further interactions between the water and clay minerals (ion exchange) could also take place in the aquifer and may be responsible for the higher sodium concentrations compared to chloride.

The carbon-13 content in the groundwaters could be related to inputs of CO_2 at depth. The extensive fractures may act as conduits for the ascent of CO_2, and may also account for the elevated radon and radium concentrations and the thermal nature of the aquifer. The content of oxygen-18 and carbon-13 over the monitoring period showed only slight variation, and this is interpreted as being due to the large volume of reserves in the aquifer compared to the volume
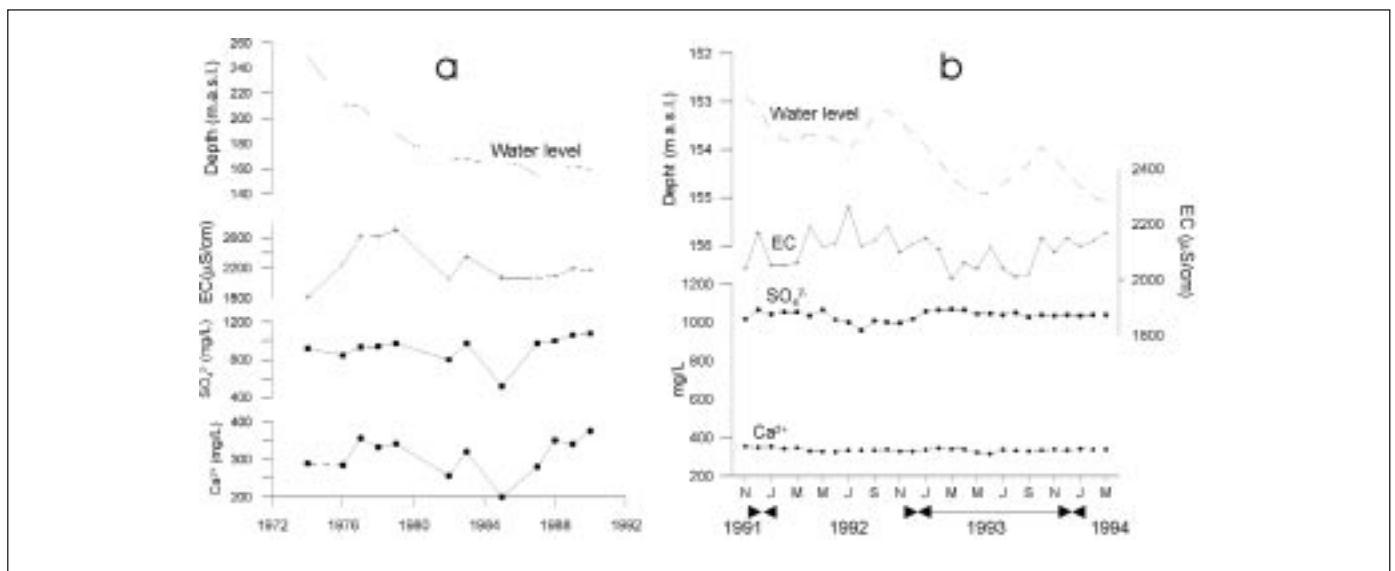

Fig. 8. Calcium (mg/L), sulphate (mg/L), electrical conductivity (μS/cm) and water level vs. time during 1974-1990 (a) and from Novembre 1991-March 1994 (b)
Fig. 8. Evolución de la conductividad eléctrica (μS/cm), el calcio (mg/L) y el sulfato (mg/L) y la piezometría durante el período 1974-1990 (a) y de noviembre de 1991 a marzo de 1994 (b)
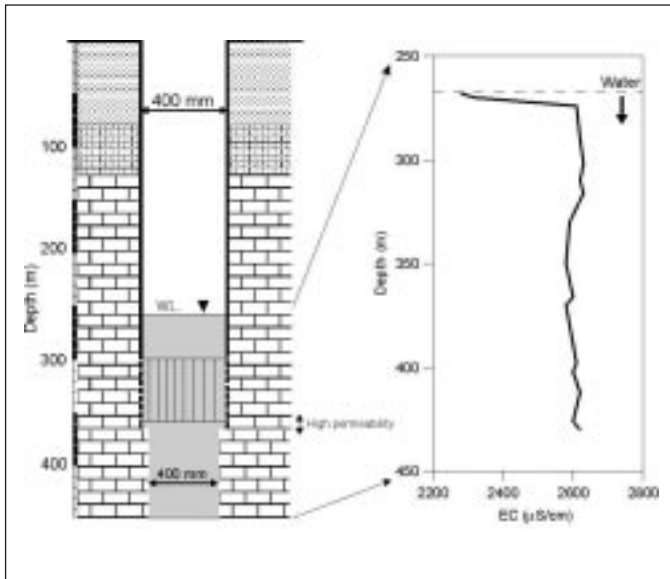
Fig. 9. Variations of conductivity with depth in well nº 1
Fig. 9. Variaciones de la conductividad con la profundidad en el sondeo nº 1

of infiltration. This interpretation can be confirmed by the low tritium content of the groundwater (less than 1 TU).

Hydrogeochemical data suggest that overexploitation has not caused any change in the chemical characteristics of these waters. Mixing processes within the aquifer mean that water pumped from different depth shares the same chemistry. The thermal anomaly of groundwater could be driving force for the mixing, which has been facilitated by the intense fracturing.

Acknowledgements

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