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# Hydrogeochemical effects of groundwater mining of the Sierra de Crevillente Aquifer (Alicante, Spain)

**Abstract** The groundwater mining of the Crevillente aquifer (southeastern Spain) has resulted in the progressive deterioration of water quality, with particularly significant increases in chloride, sulfate, and sodium. The possibility of a vertical hydrochemical zoning is deduced that would require examining the importance of the geometry and lithology (evaporitic materials) in the salinization process. The time of water–rock contact (residence time) and dilution by infiltration of rainwater also influences the hydrogeochemistry of the aquifer. The hydrochemical data are useful in defining the conceptual model of the aquifer, completely karstified with relative homogeneity.

**Key words** Overexploitation · Hydrochemistry · Karstic aquifer · Conceptual model

## Introduction

Groundwater mining is practiced in many areas, for example in Phoenix (Arizona, USA), Kern County (California, USA), Riyadh (Saudi Arabia), and in areas of India, Jordan, and Cyprus (Navarro 1989). The aim of this practice is to take advantage of stored groundwater. However, there are two basic approaches: exploitation can proceed in accordance with a plan for reasonable management that can satisfy economic and/or social needs. The other approach is controlled exploitation that not only can seriously degrade water quality but also deplete the aquifer.

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jeopardizing the activities dependent upon that water supply. The most typical examples are coastal aquifers in which a decline in the piezometric level invites saltwater intrusion.

The aquifer of Crevillente is currently under intense exploitation, with annual pumping exceeding 20 hm³, while the mean annual recharge is estimated at 6–10 hm³. The piezometric level has declined as much as 40 m yr⁻¹ and progressive salinization is detectable.

Some 84% of the pumping is directed to irrigating roughly 9000 ha devoted mostly to the cultivation of table grapes, a highly profitable crop. However, the steady deterioration of the water quality, as well as the rising costs of pumping, is now threatening the economic feasibility of growing this crop.

## The Crevillente aquifer

### Geology

The Sierra of the Crevillente aquifer system has an area of 87 km², located within the Subbetic zone of the Betic Cordilleras (Fig. 1). The hydrogeological features have been described in previous work (Pulido-Bosch and Fernandez-Rubio 1981; Pulido-Bosch and others 1982; Pulido-Bosch 1985, 1988, 1991).

The oldest outcropping materials are clay and gypsum, from the Upper Triassic (Keuper facies), overthrusted by Subbetic materials. The Jurassic materials occupy the largest part of the area (Sierras of Crevillente, Ofra, Argallet, Rollo, Pelada, and Reclot), with lateral changes of facies, interruptions in the deposit, nonsedimentary fractures, and palaeokarstification (García Hernández and others 1989). The four sets that can be differentiated are, from bottom to top: grey dolomite with dolomitic limestone on top, exceeding 500 m in thickness (Lower Liassic); 150 m of white, pink, and oolithic limestone; marl, limestone with silex, and red nodular limestone (Upper Liassic-
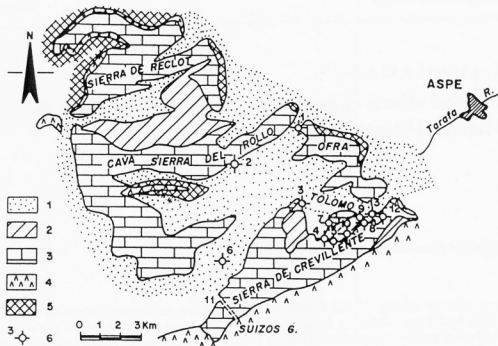
Fig. 1 Hydrogeological setting of the Sierra of Crevillente aquifer and its surroundings. *1*: Quaternary sediments; *2*: Cretaceous marls; *3*: Jurassic carbonate materials; *4*: Triassic materials; *5*: Prebetic terrains; *6*: wells and their numbers

Dogger); and about 30 m of limestone with some beds of marl (Malm).

Cretaceous materials occupy synclines separating anticline ridges formed by limestone and dolomite, with white marl as much as 400 m thick. Eocene materials appear only in the southern part of the Sierra of Crevillente, composed of green marl and limestone with silex, some 25 m thick. Miocene materials are local (Abanilla-Monte Alto), but the Quaternary deposits occupy large areas with glacis and alluvial sediments between La Romana and Aspe. The underlying Prebetic materials are composed of limestone, calcarenite, marl, and marly limestone from the Eocene and Miocene (Azema 1977).

## Hydrogeology

The hydrogeological setting consists of fissured and karstified Liassic limestones, which constitute the most important water-bearing formation; the impervious bottom and both the northern and southern boundaries are composed of Triassic materials and/or Prebetic marl. There is good hydraulic connection between all the carbonate outcrops.

The hydraulic parameters of existing wells differ in specific capacity, between 1 and more than 100 l s$^{-1}$ m$^{-1}$. The results of pumping tests indicate a transmissivity that ranges from 3000 (Sierra del Rollo) to 50,000 m$^2$ d$^{-1}$. The effective porosity is an estimated at 2.2% (Pulido-Bosch and Fernandez-Rubio 1981).

The system lacks streams or springs with perennial flow, so that the recharge corresponds exclusively to rain infiltration and discharge to pumping. The rainfall constitutes an estimated 6–10 hm$^3$ for an average year and 16 hm$^3$ for a wet year.

Pumpage is from 25 wells distributed in the following sectors: (1) Suizos Gallery (SW area), 16 hm$^3$ yr$^{-1}$; (2) Tolomo (SE area), 10 hm$^3$ yr$^{-1}$; (3) south of the Sierras del Rollo and la Cava, 1 hm$^3$ yr$^{-1}$; and (4) area between Suizos Gallery and Tolomo, 1 hm$^3$ yr$^{-1}$.

The Suizos Gallery is 2300 m long; the first 700 m penetrate marl and clay to horizontally penetrating the aquifer. The gallery was built between 1962 and 1966, when the piezometric level was 100 m above the gallery; the absolute altitude at the surface is 250 m. The initial flow produced by the gallery was more than 1 m$^3$ s$^{-1}$, decreasing to depletion two years after completion. Over the length of the gallery there are 12 wells with a total pumpage of about 400 l s$^{-1}$, with specific capacities of 45–75 l s$^{-1}$ m$^{-1}$ and transmissivity of roughly 7500 m$^2$/day. The effective porosity is an estimated 5.5%. The total decline in the piezometric level has been 200 m, a decline of more than 8 m yr$^{-1}$.

In the sector of Tolomo from 1962 to 1994 the piezometric level has plummeted 290 m, averaging a decline of 11 m yr$^{-1}$ (Fig. 2). In the last few years, the rate of decline has slowed and a rise of 15 m yr$^{-1}$ has been recorded (Fig. 3); this reversal is due to higher rainfall than average and a notable decline in pumping as a consequence of the rules imposed when the administration declared the aquifer overexploited.

This sharp piezometric decline caused the comparmentalization of the aquifer into two subsystems separated by a SW–NE line coinciding approximately with the anti-
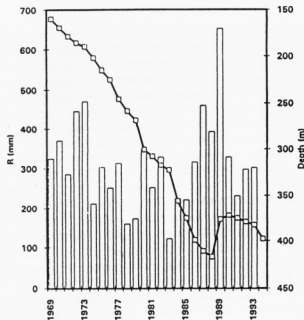
Fig. 2 Piezometric hydrograph in a representative well in the Tolomo area (corresponding to January each year). Annual rainfall is superimposed

**Table 1** Changes in physical and chemical parameters during the period 1975 to 1990[*]

| Year | Suizos area | | | | Tolomó area | | | |
|---|---|---|---|---|---|---|---|---|
| | 1975 | 1980 | 1985 | 1990 | 1975 | 1980 | 1985 | 1990 |
| Conductivity | 1800 | 2350 | 2710 | 2700 | 1240 | 1400 | 2370 | 2750 |
| Cl | 426 | 450 | 570 | 550 | 230 | 260 | 520 | 620 |
| SO$_4$ | 390 | 360 | 350 | 510 | 320 | 260 | 270 | 440 |

[*]Conductivity in $\mu$S cm$^{-1}$; Cl and SO$_4$ in ppm.

## Hydrochemical evolution

The progressive exploitation of the reserves has led to consistently more saline water, evolving from a calcium-bicarbonate to a sodium-chloride type, with the notable presence of sulfates as a consequence of the dissolution of highly soluble materials (gypsum and halite) and the pumping of water from greater depths.

Table 1 shows data from certain points that reflect the progressive increase in salinity, although with fluctuations. For example, during the period 1986 to 1989, which was relatively wet, there were pronounced reductions in pumping, increased recharge, and thus a piezometric recovery of about 7 m in the Suizos area and almost 40 m in the Tolomo area (Fig. 2). This situation translates as a temporary improvement in the water quality, which was not sustained in 1990.

The exploitation has not affected the entire aquifer uniformly, but rather zoning can be established, essentially due to the spatial distribution of the pumping, although other important aspects are involved, including geometry, proximity of the evaporitic salts to the substrate and Trassic boundaries, etc. For the study of the hydrogeochemical differences within the aquifer, which must follow hydrodynamic principles, a collection of water samples was made (Table 2) in July 1990.

The least saline waters (900–1000 $\mu$S cm$^{-1}$) were in the area of the Sierra del Rollo, and the most saline (1500–4000 $\mu$S cm$^{-1}$) in the Tolomo-Suizos area, where the pumping is more intense and the evaporitic materials are closer in proximity to pumping. The freshest water was determined to be the calcium-bicarbonate-chloride type and the most saline the calcium-sodium-chloride type.

Chloride ion is the principal ion responsible for the increased salinity (Fig. 4), although the sulfate ion is also significant. Nevertheless, the relationship between conductivity and the sulfate ion (Fig. 4b) shows a notable dispersion attributable to a less homogeneous distribution of sulfate content in the sector. In fact, in the area of the Suizos Gallery, the sulfate concentration is relatively higher than in the rest of the aquifer, but appreciably lower in the western sector (Fig. 5).

Figure 6 represents the changes of the saturation indices for calcite (SIc), dolomite (SId), and gypsum (SIg), calculated by the program WATEQB (Arikan 1988). The most

clinal axis of the Sierra de Crevillente. The altitude of the piezometric surface is at 64 m asl in the western sector, at 61 m in the northern zone of the eastern sector, and at −25 m in the southern zone of the eastern sector. As a result, the general direction of the flow is from west to east, reversing the flow direction that existed prior to 1981. In the eastern sector, the flow direction caused by the exploitation is N–S with a gradient of around 1.6%.
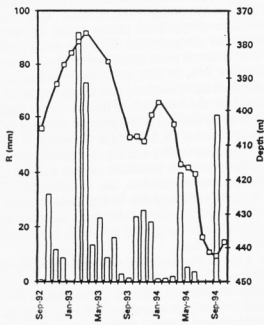


Fig. 3 Detail of the monthly piezometric hydrograph in the same well from September 1992 to September 1994

**Table 2** Physical and chemical parameters of samples analyzed

| | Sample | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| Temp (°C) | 23.8 | 22.4 | 24.4 | 25.3 | 25.4 | | 24.0 | 24.0 | 24.4 | 25.3 | 25.7 | 23.9 | 24.8 |
| pH | 7.78 | 7.24 | | 7.22 | 7.26 | 7.17 | 7.28 | 7.10 | 7.20 | 7.15 | 7.45 | 7.23 | 7.20 |
| Cond (µS/cm) | 912 | 1005 | 1454 | 1462 | 1800 | 1860 | 2010 | 2200 | 2400 | 2550 | 2700 | 2970 | 3960 |
| TDS (mg l$^{-1}$) | 679 | 739 | 1015 | 1126 | 1399 | 1358 | 1224 | 1592 | 1562 | 1700 | 1754 | 1977 | 2487 |
| Cl (mg l$^{-1}$) | 168 | 176 | 273 | 354 | 392 | 441 | 449 | 504 | 545 | 582 | 553 | 690 | 1008 |
| SO$_4$ (mg l$^{-1}$) | 76 | 95 | 207 | 207 | 270 | 290 | 238 | 380 | 322 | 354 | 511 | 493 | 483 |
| HCO$_3$ (mg l$^{-1}$) | 252 | 252 | 248 | 238 | 253 | 252 | 238 | 280 | 305 | 242 | 230 | 216 | 223 |
| Ca (mg l$^{-1}$) | 83 | 113 | 112 | 113 | 126 | 121 | 112 | 119 | 133 | 138 | 151 | 144 | 134 |
| Na (mg l$^{-1}$) | 74 | 79 | 140 | 171 | 223 | 212 | 220 | 292 | 268 | 337 | 252 | 370 | 574 |
| Mg (mg l$^{-1}$) | 24 | 24 | 36 | 40 | 47 | 43 | 39 | 58 | 51 | 51 | 52 | 69 | 59 |
| K (mg l$^{-1}$) | 0.5 | 0.6 | 1.1 | 1.4 | 2 | 4.5 | 4 | 2.1 | 1.9 | 6 | 5.5 | 5.5 | 9 |
| Sr (mg l$^{-1}$) | | | | | | 1.6 | | | | | 2.5 | 2.6 | 2.6 |
| SIcalc (dimensionless) | 0.546 | 0.112 | -0.003 | 0.043 | 0.131 | 0.020 | 0.077 | -0.143 | 0.029 | -0.004 | 0.274 | -0.004 | -0.058 |
| SIdol (dimensionless) | 0.896 | -0.125 | -0.152 | -0.001 | 0.200 | -0.040 | 0.044 | -0.246 | -0.003 | -0.067 | 0.459 | 0.026 | -0.060 |
| SIgyp (dimensionless) | -1.701 | -1.512 | -1.252 | -1.260 | -1.150 | -1.136 | -1.305 | -1.063 | -1.077 | -1.056 | -0.131 | -0.936 | -1.011 |

outstanding feature is that only two samples were clearly oversaturated with respect to calcite and dolomite: sample 1 (Rollo sector), which corresponds to a water low in salinity, and sample 11 (Suizos Gallery), relatively enriched in sulfates and, simultaneously, calcium. With regard to saturation in relation to gypsum, all samples were clearly undersaturated, although there was an appreciable decrease in the index with salinity (except in sample 7).

There is a noteworthy correspondence between the sulfate, magnesium, and strontium ions (Fig. 7), possibly influenced by their common origin linked to the underlying evaporitic sediments, since strontium can appear as celestine (SrSO$_4$) in these deposits. In addition, there may be an origin related to the dissolution of the dolomite present in the aquifer matrix. The dissolution reaction of dolomite by water enriched in sulfate, and the subsequent precipitation of calcite, which reaches saturation rapidly, leads to an enrichment parallel to the magnesium ion, according to the classical model proposed by Hanshaw and others (1971), Plummer (1977), Wigley and others (1978), Fidelibus and others (1992), and Giménez (1994).

Strontium may have a similar origin: the dissolution-precipitation processes of the carbonates has been suggested by a number of authors to explain the presence of high concentrations of strontium in certain waters (Harris and Matthews 1968; Plummer and others 1976; Fidelibus and Tulipano 1986; Arad 1988; Moldovani and others 1990; Vacher and others 1990; Fidelibus, unpublished data; Tulipano and Fidelibus 1991). The strontium enrichment may be related with the residence time of the water in the aquifer and, consequently, can be an environmental tracer (Mazor and Mero 1969; Lloyd and others 1982; Brondi and others 1983; Heathcote and Lloyd 1984).

The dissolution of carbonate rocks enriches the water with calcium, magnesium, and strontium; over the evolutionary process, the precipitation of calcite, after successive dissolution–precipitation phases, causes an increase in the strontium concentration (Tulipano and Fidelibus 1991). These residence times can be explained also in terms of relative flow rate, so that the longer residence times must be attributable to relatively slow circulation, as might be assumed from the deep levels of the Crevillente aquifer.

Tulipano and Fidelibus (1991) propose choosing reference concentrations of Ca, Mg, and Sr in water with lower contents. From these values and for each sample, the percentage variations of the strontium content and the sum of the calcium and magnesium can be calculated. The increase in these variations can be explained in terms of greater water maturity, which is the same as longer residence time, and therefore greater possibility of successive water–rock interactions.

Figure 7 shows the evolution with salinity of the Ca, Mg and Sr ions. The latter two, as mentioned above, have similar behavior, whereas calcium shows certain deviations related probably to saturation with calcite and subsequent precipitation. Figure 8 shows the evolution of the strontium ion in correspondence with the maturity index (MI), calculated by the following expression:

Fig. 4 Chloride vs conductivity
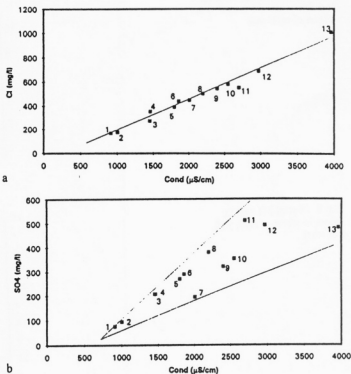(a) and sulfates vs conductivity
(b)



a



b

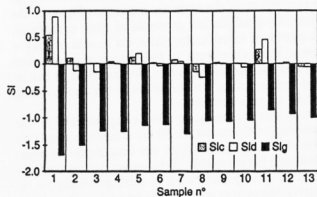Fig. 5 Plot of Cl and SO$_4$
content in waters of each well

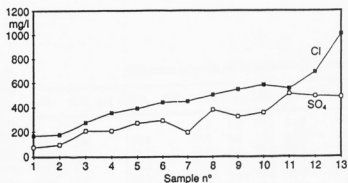



Fig. 6 Bar graph showing changes of saturation indices for calcite (SIc), dolomite (SId), and gypsum (SIg)

$$MI = \frac{\Delta Sr}{\Delta Ca + \Delta Mg}$$

The results appear in Table 3, using sample 1 as the reference water.

Most noteworthy in Figure 8 is that MI does not follow a coherent evolution with the rise in salinity, indicating the influence of other processes that alter the simple model proposed. In fact, three different types of behavior can be distinguished: points 1 and 2, in the northern sector of the aquifer (Sierra del Rollo), show a low degree of maturity, characteristic of water with low salinity and relatively recent infiltration; points 6 and 7, in the central sector and southern strip of the aquifer, present relatively low concentrations of Sr and sulfates; finally, the rest of the waters appear to fit the model proposed.

On the basis of all the foregoing, it can be stated that the hydrogeochemistry of the Crevillente aquifer appears to be determined by the synergistic action of various

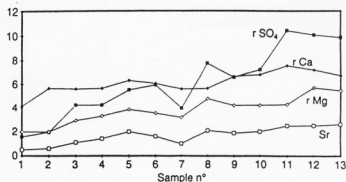Fig. 7  Plot of SO₄, Ca, Mg, and Sr content (in meq l⁻¹) in waters of each well

Fig. 7  Plot of $SO_4$, Ca, Mg, and Sr content (in meq $l^{-1}$) in waters of each well



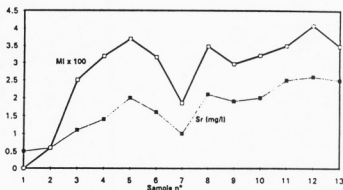Fig. 8  Plot of MI and Sr values in water of each well (see text)



Table 3  Calculation of the maturity index (MI)

| Sample | rCa | rMg | Sr | rCa + rMg | ΔCa + Mg | ΔSr | MI |
|---|---|---|---|---|---|---|---|
| 1 | 4.14 | 1.97 | 0.5 | 6.11 | | | |
| 2 | 5.64 | 1.97 | 0.6 | 7.61 | 1.50 | 0.1 | 0.066 |
| 3 | 5.59 | 2.92 | 1.1 | 8.51 | 2.40 | 0.6 | 0.250 |
| 4 | 5.64 | 3.29 | 1.4 | 8.93 | 2.82 | 0.9 | 0.319 |
| 5 | 6.29 | 3.87 | 2.0 | 10.16 | 4.05 | 1.5 | 0.370 |
| 6 | 6.04 | 3.54 | 1.6 | 9.58 | 3.47 | 1.1 | 0.316 |
| 7 | 5.59 | 3.21 | 1 | 8.80 | 2.69 | 0.5 | 0.185 |
| 8 | 5.94 | 4.77 | 2.1 | 10.71 | 4.60 | 1.6 | 0.348 |
| 9 | 6.64 | 4.20 | 1.9 | 10.84 | 4.73 | 1.4 | 0.296 |
| 10 | 6.79 | 4.20 | 2 | 10.81 | 4.70 | 1.5 | 0.321 |
| 11 | 7.54 | 4.28 | 2.5 | 11.82 | 5.71 | 2 | 0.350 |
| 12 | 7.19 | 5.68 | 2.6 | 10.99 | 4.88 | 2 | 0.409 |
| 13 | 6.69 | 5.43 | 2.6 | 12.12 | 6.01 | 2.1 | 0.349 |

factors: (1) hydrodynamic control, according to the pumping and the declines in piezometric surface; (2) lithological control, according to the presence or absence of dolomite in each sector of the aquifer; (3) structural control, according to the proximity of the evaporitic materials; and (4) climatic control, according to the rate of natural recharge by rainwater infiltration.

The combined effects of these four factors cause alterations in the hydrochemical parameters derived from overexploitation of the aquifer to have different ranges in each sector, although with the common denominator is the progressive deterioration of the chemical quality of the water.

Structural control is a determining factor, which causes, on the one hand, prolonged residence time with the subsequent intensification of water–rock interaction; on the other hand, this control promotes the leaching of the chloride and sulphate ions, fundamentally from the evaporitic substrate, which not only constitutes the impervious bottom of the aquifer, but also constitutes lateral barriers produced by notable tectonic events.

The sulfate ion largely determines the latter interactions, since the calcium involved has great influence over the equilibrium of the carbonates and therefore over the dissolution–precipitation processes of these carbonates. The degree of karstification does not appear to play a relevant role, since from a preliminary approach and according to hydrodynamic data the karstification can be called homogeneous, not only laterally but also in depth, affecting the entire aquifer.

From this reasoning, specific compartments in the aquifer can be differentiated: (1) the northern sector (area of Sierra del Rollo), in which the least degree of overexploitation is appreciable in the waters, having comparably good quality and being in close proximity to recharge; (2) the eastern sector of Tolomo, where there is the influence of sharp piezometric declines and the proximity of the evaporitic materials, with progressively more saline waters; (3) the central sector of Tolomo, with less influence of the evaporitic levels; and (4) the western sector (Suizos Gallery), similar in character to the eastern sector, but with a higher concentration of sulfate.

## Discussion

The above leads us to a series of considerations concerning the conceptual model of this karstic aquifer, which can be extrapolated to many other aquifers with similar geological characteristics (strongly tectonized areas, great thickness of the carbonate series, presence of deep saline materials, etc.).

The first of these considerations concerns the evolution in depth of the karstic aquifer and of the karstification. Among the possible extreme models applicable to the carbonate materials—diffuse flow and free flow (LaMoreaux and others 1975; Atkinson 1977)—it appears that the model most applicable would be the first, comparable to a large degree to an equivalent porous medium. Nevertheless, this is a simplification, given that in this aquifer numerous karstic discontinuities occur at different depths, known from studies carried out using TV cameras inside the various wells of the area (Pulido-Bosch 1991). Although the major part of the wells have high production, some prove negative; both aspects—karstic conduits and sectors with practically no karstification—are characteristics of this karstic aquifer.

Wells had to be deepened as the piezometric levels declined due to overexploitation. It is notable that many of the wells maintained approximately a constant rate of pumping, which would indicate a great constancy in the transmissivity value of the aquifer with depth. At present, the production of many wells has been substantially reduced, as the saturated thickness has been reduced considerably.

Thus, the most accepted conceptual model for vertical zoning of the karstic aquifer [unsaturated zone with eventually suspended karst waters; zone of seasonal piezometric fluctuation, with maximum karstification; and zone with deep circulation "of little-known characteristics" (Sokolov 1967), for example] usually includes a zone of maximum karstification (Mangin 1975; Bakalowicz 1986) with an exponential decrease in the karstification with depth (Milanovich 1981), making this type of aquifer of far less interest for regulation, because of its low storage and being restricted to a narrow strip. Thus it does not appear that the aquifer of the Sierra de Crevillente fits within the classical framework, but rather suits the model of a *completely karstified aquifer* with relative homogeneity.

This raises the question of how it is possible for carbonate material to be homogeneously karstified. The existence of dense fracturing, as in this case, can facilitate the process, together with the presence of a certain porosity in the carbonate matrix. For the normal values of partial pressure of $CO_2$, the water becomes rapidly saturated in $HCO_3$. The mixing processes of the waters (Bogli 1964, 1980) may make the karstification advance in depth, although it would always have to be very localized and never in great quantities, given that the partial pressure of the $CO_2$ in the waters coming form rain infiltration would not differ markedly form each other. In our opinion, the most important process that would encourage the karstifi-

cation to deepen in an roughly homogeneous manner would be a $CO_2$ supply of deep origin, in relation to the great tectonic events evident (Crevillente fault, for example) throughout the geological history of the area. In a sector near the study area, although in a different geological ambit, there is clearly a deep $CO_2$ supply that makes it possible for the waters to contain more than 1800 mg l$^{-1}$ of HCO$_3^-$ [Alto Guadalentin aquifer (Cerón and Pulido-Bosch 1993, 1994]. In the case of the Sierra de Crevillente, the waters of the southern limb of the anticline show a positive thermal anomaly.

The second consideration refers to the importance of the tectonic structure in hydrogeology and hydrogeochemistry. It is, based on hydrogeological criteria, structural and/or general geological aspects can be deduced; the aquifer studied being a good example of this. Due to overexploitation, sectors of the Crevillente aquifer, initially with hydraulic continuity, now are disconnected as the piezometric level has declined below the impervious barriers (probably Keuper materials) situated at a given depth. What has been detected on the southern limb of the Sierra de Crevillente anticline, or what was verified in the Quibas aquifer (situated NW of the study area), reflect that the overexploitation has given rise to five aquifers that follow completely individualized piezometric evolutions (Rodríguez Estrella and others 1983; Rodríguez Estrella and Gómez de las Heras 1986).

The last consideration refers to the lateral and vertical hydrogeochemical variations and their hydrodynamic and geological implications. <u>The waters have deteriorated in quality with the advance of overexploitation, partially alleviated in periods of greater recharge from rainwater infiltration; this deterioration has been far more evident in the areas of greater pumpage (Suizos and Tolomo),</u> although these coincide with areas closer to saline materials (Keuper). This latter aspect allows the use of hydrogeochemical data as possible indicators of the continuity in depth of a given formation that would produce a hydrogeochemical anomaly. Another possibility is a vertical hydrogeochemical zoning, with waters increasing in salinity with depth.

The waters with the least saline content in the aquifer studied are situated on the northern edge, where pumping is not as high (about 1 hm$^3$ yr$^{-1}$), and the piezometric levels, although far below initial values, are not as low and occur where saline materials do not appear to be highly developed.

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