

# Hydrogeochemical Characterization and Identification of Water-Rock Interaction Processes in an Area Affected by Karstic Subsidence

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## INTRODUCTION

Spain is the European country where the subsidence risk related to evaporite dissolution has the greatest economic impact (Gutiérrez et al., 2008). Notably, the Ebro valley in the outskirts of Zaragoza is the area where this type of subsidence has the highest detrimental effect. In this sector, the occurrence of sinkholes due to the karstification of the Tertiary Zaragoza Formation underlying the Quaternary alluvium is a relatively frequent phenomenon.

In spite of the importance that subsidence phenomena linked to the development of evaporite karstification have in this region for the assessment of the stability of building foundations and for the development of infrastructures (roads, railways, etc), the relationship between the hydrogeology of the area and the dissolution phenomena remains poorly understood. Moreover, the hydrogeochemical features and controls of this portion of the Ebro valley have not been comprehensively addressed, to our knowledge, by any earlier study.

Thus, the main goal of this study is to obtain a better knowledge of the hydrogeology and hydrogeochemistry of this area in relation to the features and processes involved in the generation of subsidence forms triggered by evaporite karstification. With these aims, the hydrogeochemical variations at several types of water points (springs, wells, sinkhole ponds and ditches) were determined throughout a hydrological year and the observed features were related to the possible water-rock interaction processes, to the composition of the evaporitic materials, alluvial sediments and rocks and to the hydrogeological variations.

## GEOLOGICAL AND HYDROGEOLOGICAL CONTEXT

The studied area is located in the central sector of the Ebro Tertiary Basin, NE Spain. The hydrogeology of the area is characterized by three interconnected unconfined aquifers: (1) the perched alluvial aquifer formed by terrace and pediment deposits, (2) the floodplain fluvial deposits, (3) the highly karstified evaporitic bedrock of the Oligo-Miocene Zaragoza Formation, which locally discharges to the previous one. This formation is mainly composed of Ca sulphates (gypsum;  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and anhydrite;  $\text{CaSO}_4$ ), halite ( $\text{NaCl}$ ), glauberite ( $\text{Na}_2\text{Ca}[\text{SO}_4]_2$ ), with some marls and clays.

## METHODOLOGY

For the purposes of this study, 10 water points were selected, corresponding 6 of them to points in the area upstream from Zaragoza (Zone 1, from now on) and 4 of them to points downstream from the city (Zone 2, from now on). The selection of those points was based on a screening process from the hydrochemical information compiled in the public database maintained by the Ebro Basin Water Authority (Confederación Hidrográfica del Ebro; CHE) and it was intended to obtain a variety of hydrogeochemical features supposedly corresponding to different degrees of interaction between the groundwaters circulating through the perched alluvial aquifer and the groundwaters corresponding to the underlying evaporitic aquifer. Apart from these points, the hydrochemical information from two points which can be considered as representative from the water quality in the channels used for irrigation in each of the studied

areas (the Imperial Channel and the Urdan Channel, used for Zones 1 and 2, respectively) was also obtained.

For each selected point (including the two sampling points for irrigation waters), between 3 and 7 sampling campaigns were carried out distributed throughout the period between January of 2011 and January of 2012. At each sampling point, some parameters were determined *in situ* (pH, temperature, conductivity, alkalinity) and water samples were taken for their subsequent chemical analyses in the laboratory. The analysed elements and ions are Na, Ca, Mg, K, Al, Si, Cl and sulphate.

In order to identify the main geochemical processes influencing the observed hydrochemistry in the sampling points, speciation-solubility calculations were also carried out with the assistance of the PHREEQC code (Parkhurst and Appelo, 1999) and using the WATEQ4f database (Ball and Nordstrom, 1991) distributed with the program.

## RESULTS AND DISCUSSION

The observed hydrochemistry for all the studied points corresponds to Na-Ca-Cl- $\text{SO}_4$  waters with pH values varying generally between 6.7 and 8.5. As a general trend, the highest measured pH values are those from the irrigation waters, which are also the points displaying the lowest alkalinity values and conductivities from their respective zones. More in detail, the conductivity values in the sampled waters from Zone 1 are generally remarkably lower than the values obtained for the selected points in Zone 2. As a general observation, the main hydrogeochemical

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feature of the studied area is the existence of large hydrogeochemical variations, even within each of the studied zones and for the same type of sampled water points. This would suggest the presence of also highly variable hydrogeological and hydrogeochemical processes in the system.

Apart from that, one of the most remarkable hydrogeochemical features that can be deduced for the studied systems is an almost perfect 1:1 correlation between the molar dissolved contents of Na and Cl ( $R^2$  around 0.98) for all the sampling points. This observation stands for both the Zone 1 and 2 and would be consistent with the existence of halite dissolution as the main source for Na and Cl in the studied system. A similar situation can be described for the good correlation ( $R^2$  close to 0.97) between the Ca and  $SO_4$  dissolved molar contents (Fig. 1) in both studied areas. The stoichiometry Ca- $SO_4$  deduced from their correlation can be mostly attributed to gypsum or anhydrite dissolution. However, the observed Ca values are, as a general trend, slightly higher than sulphate values in the same waters and, therefore, other processes must account for the excess of dissolved calcium.

In spite of the existence of the already described good Na:Cl and Ca: $SO_4$  correlations, the correlation between Cl and  $SO_4$  dissolved molar contents is much poorer, especially for the samples from Zone 1 (Fig. 1). This would imply that halite and gypsum/anhydrite dissolution processes are not taking place with the same extent at different water points of the system. Apart from the already-described Na:Cl and Ca: $SO_4$  correlations, there are also significant correlations between the dissolved molar Mg and Sr contents with both Ca and  $SO_4$  contents.

The comparison of the hydrogeochemistry observed at the different sampling points which could be considered as representative from the underlying evaporitic aquifer shows that there are large differences from one point to another. This suggests the existence of also important lateral variations in the mineralogical composition of these materials even for points spatially very close to each other.

The results from speciation-solubility calculations show that most of the

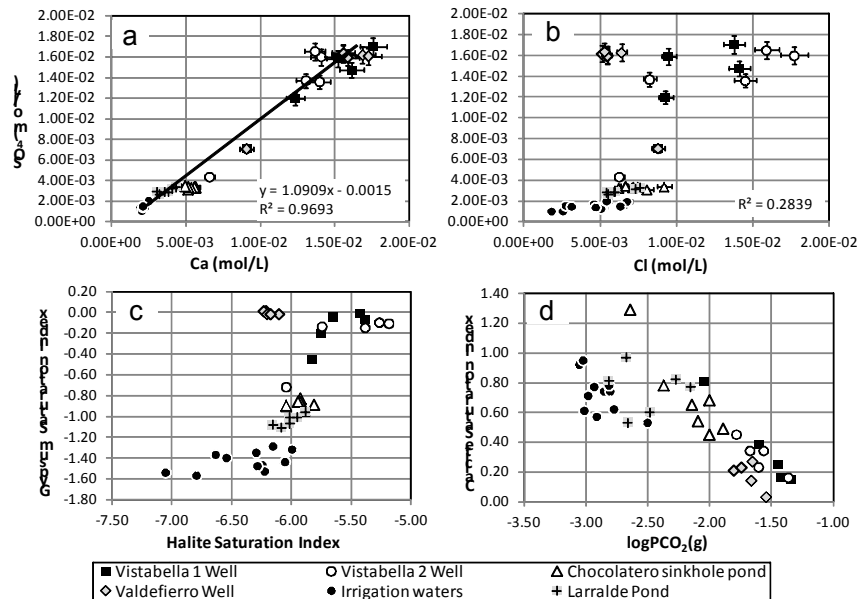


Fig. 1. Hydrogeochemical correlations (a, b) and saturation indexes with respect to some of the possible phases in contact with the groundwaters (c, d) in one of the studied zones (Zone 1, shown as an example).

sampled groundwaters are clearly undersaturated with respect to gypsum and halite (Fig. 1). However, whereas the groundwaters sampled through pumping wells from a depth corresponding to the evaporitic aquifer are generally close to equilibrium with respect to gypsum, this situation is never observed to take place with respect to halite. This would imply that the availability of halite in this portion of the evaporitic aquifer is very restricted.

Moreover, the stronger undersaturation degrees with respect to both mineral phases in the two studied zones are associated not only to the waters used for irrigation and to the surficial wells, clearly influenced by irrigation effects, but also to three of the sinkhole ponds included in the study. This suggests that the hydrochemical and, therefore, the hydrogeological behavior of those ponds is more linked to the hydrogeological features of the perched alluvial aquifer than to the ones of the evaporitic aquifer.

In addition to the dissolution of gypsum and halite, the hydrogeochemistry of the studied areas seems to be very influenced by carbonate dissolution and precipitation processes triggered by the input of  $CO_2(g)$  probably derived, at least partially, from the interaction with the soils developed in the alluvial aquifer. This can be deduced from the facts that all the sampled waters are in equilibrium with partial pressures of  $CO_2(g)$  clearly higher than atmospheric

and that most of them are also in equilibrium or oversaturated with respect to calcite (Fig. 1). Calcite dissolution could also account for the interpreted excess of dissolved calcium compared to sulphate, which has been described above.

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