

Preliminary Assessment of Hydrogeochemical Features and Processes in an Area Affected by Evaporite Karstic Subsidence

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INTRODUCTION.

The dissolution of soluble minerals in carbonates or evaporitic sediments due to the action of groundwater flow may cause the gravitational deformation and internal erosion of the overlying sediments, eventually leading to the settlement of the ground surface. Commonly, the geomorphic expression of these hazardous subsidence phenomena corresponds to closed depressions designated as sinkholes.

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 the subsidence has the highest detrimental effect. In this sector, the occurrence of sinkholes due to the alluvial karstification of the Tertiary Zaragoza Formation (gypsum, halite, glauberite) underlying Quaternary alluvium is a relatively frequent phenomenon. The occurrence and reactivation of sinkholes in this mantled karst setting have led to the demolition of many buildings and affect numerous linear infrastructures, including the high-speed Madrid-Barcelona railway (Guerrero et al., 2008; Galve et al., 2009).

In this study, the hydrogeochemical features and processes involved in the development of sinkholes in the surroundings of Zaragoza city were investigated in order to propose a preliminary conceptual model. Further testing of the model would help us to improve our understanding of the poorly explored hydrogeological and geochemical processes underlying the sinkhole phenomenon. This achievement would allow us to increase

our capability to assess subsidence hazard in the area and mitigate the associated risk.

GEOLOGICAL AND HYDROGEOLOGICAL CONTEXT

The study area is located in the central sector of the Ebro Tertiary Basin, NE Spain (Fig. 1). 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 discharges in the previous one. This formation is mainly composed of Ca sulphates (gypsum; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and anhydrite; CaSO_4), halite (NaCl), glauberite ($\text{Na}_2\text{Ca}[\text{SO}_4]_2$), with some marls and clays.

METHODOLOGY

In order to characterize the main hydrochemical features of the Ebro River alluvial aquifer, in the studied areas, a revision of the hydrochemical information compiled in the public database maintained by the Ebro Basin Water Authority (Confederación Hidrográfica del Ebro; CHE) was carried out. The goal of this screening process was to select those water points (wells, springs, boreholes, etc) whose hydrochemical data could be considered as representative of the Ebro alluvial aquifer groundwaters. Moreover, the hydrogeochemistry of ten additional water points (sinkhole ponds, deep wells and springs), whose waters are thought to correspond to mixtures between different types of waters (mainly irrigation waters and groundwaters from the Ebro alluvial aquifer and from the underlying evaporitic aquifer), was

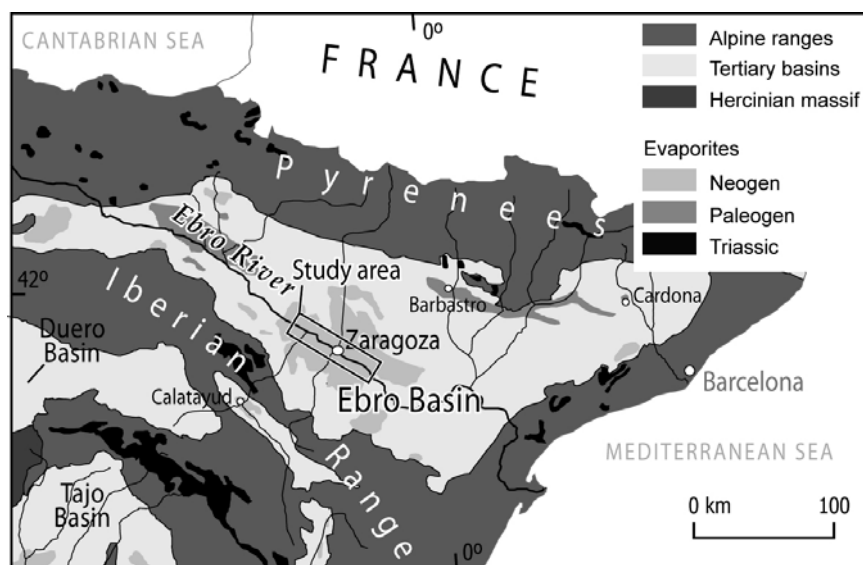


fig 1. Geological sketch of the studied area.

palabras clave: Aluvial del Ebro, Dolina, Karstificación, Modelización geoquímica.

key words: Ebro alluvial, Sinkhole, Karstification, Geochemical modeling.

extensively studied. Two types of studies were carried out in these points: 1) monitoring of the evolution of temperature and electric conductivity in five sinkhole ponds from the three studied areas, aimed at detecting the possible seasonal variations in the hydrogeological and hydrogeochemical behavior of the underlying evaporitic or alluvial aquifer, and 2) general hydrogeochemical characterization by means of monthly water sampling and analyses in the ten representative points selected in the area (including the five sinkhole ponds cited above), followed by data interpretation with the assistance of geochemical calculations

RESULTS AND DISCUSSION

Several ion-ion plots were done to ascertain the possible water-rock interactions responsible for the dissolved contents of different elements in the studied waters. The molar dissolved contents of Na and Cl in the water samples representing the Ebro alluvial aquifer are almost perfectly correlated ($R^2=0.96$) and consistent with their origin as derived from halite dissolution. This correlation implies that other possible processes, such as glauberite dissolution or Na-exchange, play a minor role in this portion of the Ebro alluvial aquifer. On the other hand, a good correlation ($R^2= 0.95$) between the Ca and sulfate molar contents can also be inferred for these waters and it can be mostly attributed to gypsum or anhydrite dissolution.

With regard to the ten water points possibly representing mixtures of different water types and sources, their hydrogeochemistry is characterized by pH values between 6.9 and 8.5 and fairly constant water temperatures around 13-18°C. However, the rest of the hydrochemical features are notably different. The most outstanding feature of the studied sinkhole pond group is probably the highly variable salinity range (with electric conductivities between $1.6 \text{ mS} \cdot \text{cm}^{-1}$ and almost $30 \text{ mS} \cdot \text{cm}^{-1}$).

In spite of the differences between the various sampling points, the evolution observed for the electric conductivity throughout the hydrological year in the five studied sinkhole ponds displays a similar sharp decrease between April and May and a subsequent increase towards October. This behavior seems to be clearly attributable to the beginning

of the irrigation period around April, which would have increased the mixing proportion of this type of waters in the sampling points, causing the observed dilution. From May towards the winter, the decrease in the irrigation and the progressive evaporative increase of dissolved contents in the irrigation waters, together with the enlarged effect of evapotranspiration on the alluvial aquifer during the summer, could explain why the target sampling points show progressively more saline features along this period. Another important hypothesis which can be preliminarily formulated in the light of the observed evolution is that the response of the studied system to the changes in the irrigation is apparently extremely fast.

In order to identify the main geochemical processes influencing the observed hydrochemistry in the sampling points, speciation-solubility calculations were 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. Most of the samples from the studied points are clearly undersaturated with respect to the main mineral phases possible in the system, including those present in the evaporitic bedrock whose dissolution may trigger the sinkhole formation and other forms of karstic subsidence in the area (e.g. gypsum, anhydrite, halite, glauberite). This result indicates that the waters observed in the studied sinkholes and in the saline spring still have a potential for evaporitic bedrock karstification. However, it is not clear whether this feature is representative from the groundwaters circulating through the evaporitic aquifer or it is the consequence of dilution of those waters by mixing with the rest of possible end-members.

All the samples included in the calculations display $\text{CO}_2(\text{g})$ partial pressures clearly higher than the atmosphere, which could be attributed to the interaction with carbonate minerals and/or to edaphic processes. Moreover, most of the samples seem to be oversaturated with respect to several carbonate phases (calcite, dolomite), which might be an artifact due to $\text{CO}_2(\text{g})$ degassing during their outflow towards surface conditions or even during sampling.

As described in previous sections, one of the main lines of future activity will

consist in the hydrochemical characterization of the three main water types (evaporitic, alluvial, irrigation) which, by means of mixing, are thought to determine the observed hydrochemistry and its variations throughout the year. Once this task is accomplished, a comprehensive conceptual model for each studied area will be proposed and its validity and limitations will be tested with the assistance of geochemical modeling, (possibly including isotope modeling). This would allow quantitatively defining a better local hydrogeological and hydrogeochemical model for the studied areas, including seasonal variations,.

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REFERENCES.

- Ball, J., Nordstrom, D.K. (1991): *User's manual for WATEQ4f with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters*. U.S. Geological Survey Water-Resources Investigation Report 91-183.
- Galve, J., Gutiérrez, F., Lucha, P., Bonachea, J., Remondo, J., Cendrero, A., Gutiérrez, M., Gimeno, M., Pardo, G., Sánchez, J. (2009): *Sinkholes in the salt-bearing evaporite karst of the Ebro River valley upstream of Zaragoza city (NE Spain): Geomorphological mapping and analysis as a basis for risk management*. *Geomorphology*, **108**, 145-158.
- Guerrero, J.; Gutiérrez, F.; Bonachea, J. & Lucha, P. (2008): *A sinkhole susceptibility zonation based on paleokarst analysis along a stretch of the Madrid-Barcelona high-speed railway built over gypsum- and salt-bearing evaporites (NE Spain)*. *Eng. Geol.*, **102**, 62-73.
- Gutiérrez, F., Calaforra, J. M., Cardona, F., Orti, F., Duran, J. J., Garay, P. (2008): *Geological and environmental implications of the evaporite karst in Spain*. *Environ. Geol.*, **53**, 951-965.
- Parkhurst, D. L., Appelo, C.A.J. (1999): *User's Guide to PHREEQC (Version 2), a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. *Water Resources Research Investigations Report 99-4259*, 312 pp.