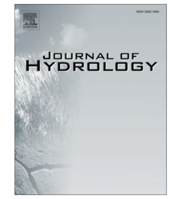
Journal of Hydrology 529 (2015) 1874–1889

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol



Evaluation of geochemical and hydrogeological processes by geochemical modeling in an area affected by evaporite karstification

P. Acero [a,*], L.F. Auqué [a], J.P. Galve [b], F. Gutiérrez [a], D. Carbonel [a], M.J. Gimeno [a], Y. Yechieli [c,d], M.P. Asta [a,e], J.B. Gómez [a]

[a] Earth Sciences Department, University of Zaragoza, c/Pedro Cerbuna 12, 50009 Zaragoza, Spain
[b] Department of Geodynamics, University of Granada, Campus de Fuentenueva s/n, 18071 Granada, Spain
[c] Geological Survey of Israel, 30 Malkhei Israel Street, Israel
[d] Department of Environmental Hydrology & Microbiology, Zuckerberg Institute for Water Research, Blaustein Institutes for Desert Studies, Ben Gurion University of the Negev, Sede Boqer, Israel
[e] Environmental Microbiology Laboratory, École Polytechnique Fédérale de Lausanne, EPFL ENAC IIE EML, CE 1 543 (Centre Est), Station 6, CH-1015 Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 22 September 2014
Received in revised form 23 June 2015
Accepted 18 July 2015
Available online 29 July 2015
This manuscript was handled by Laurent Charlet, Editor-in-Chief, with the assistance of Nico Goldscheider, Associate Editor

Keywords:
Hydrochemistry
Water mixing
Sinkholes
Mass-balance calculations

SUMMARY

The Ebro Valley in the outskirts of Zaragoza (NE Spain) is severely affected by evaporite karstification, leading to multiple problems related to subsidence and sinkhole formation. In this work, a combination of inverse (mixing + mass-balance) and forward (reaction-path) geochemical calculations is applied for the quantification of the main karstification processes and seasonal variations in this area. The obtained results prove the suitability of the applied methodology for the characterization of similar problems in other areas with scarce geological and hydrogeological information.

The hydrogeology and hydrochemistry of the system can be mainly attributed to the mixing of variable proportions of concentrated groundwater from the evaporitic aquifer and more dilute water from the overlying alluvial aquifer. The existence of a good connection between these aquifers is supported by: (1) the fast changes in the hydrochemistry of the karst aquifer related to recharge by irrigation, and (2) the deduced input of evaporitic groundwater in the alluvial materials. The evolution in some parts of the alluvial/evaporitic aquifer system is clearly dominated by the seasonal variations in the recharge by dilute irrigation waters (up to 95% of water volume in some sinkhole ponds), whereas other points seem to be clearly determined by the hydrochemistry of the concentrated evaporitic aquifer groundwater (up to 50% of the water volume in some springs).

The following reactions, previous or superimposed to mixing processes, explain the observed hydrochemistry in the studied area: dissolution of halite (NaCl), gypsum ($CaSO_4{\cdot}2H_2O$)/anhydrite ($CaSO_4$) and dolomite ($CaMg(CO_3)_2$), CO_2(g) input and degassing and calcite ($CaCO_3$) dissolution/precipitation. The modeling results suggest the existence of a large spatial variability in the composition of the evaporitic groundwater, mainly caused by large differences in the availability of halite in contact with the groundwater.

Active subsidence associated with halite dissolution is expected to continue in the study area, together with the episodic increase of gypsum dissolution associated with the input of dilute irrigation waters.

1. Introduction

In karst terrains, subsurface dissolution of carbonate and/or evaporitic materials by groundwater may lead to the gravitational instability and internal erosion of the overlying sediments, eventually resulting in the settlement of the ground surface (e.g. Waltham et al., 2005; Gutiérrez, 2010). This subsidence hazard may constitute a significant limitation for development and may lead to high risk scenarios in areas with human structures and activities, causing significant direct and indirect economic losses (Gutiérrez et al., 2008a).

Mitigating the sinkhole risk in a cost-effective way requires a detailed knowledge on the processes and factors involved in karstification. Among other features, the mineralogy, hydrochemistry and hydrogeology of the target areas need to be well-known in order to understand the processes leading to sinkhole development (Lamont-Black et al., 2002). However, a drawback commonly

* Corresponding author. Tel.: +34 976 761067; fax: +34 976 761106.
E-mail address: patri.acero@gmail.com (P. Acero).

http://dx.doi.org/10.1016/j.jhydrol.2015.07.028
0022-1694/

encountered for the detailed characterization of these types of processes in many evaporite karst systems is the scarcity of appropriate boreholes providing direct information from the target geologic materials and the associated groundwater.

In order to overcome this limitation, a cost-effective approach that can be applied to infer a general hydrogeological model and the associated geochemical processes, including karstification, is the analysis of hydrochemical information and geochemical calculations. This methodology has been extensively applied in many karst aquifers aimed at identifying flow patterns, calculating mixing ratios, identifying geochemical reactions along groundwater flow-paths and pinpointing hydraulic connections between aquifers. Nevertheless, the vast majority of earlier works dealing with karst hydrogeology and geochemistry have been carried out in carbonate aquifers (Plummer et al., 1990; Lee and Krothe, 2001; López-Chicano et al., 2001; Uliana and Sharp, 2001; Wang and Luo, 2001; Aquilina et al., 2003, 2005, 2006 and references therein; Barbieri et al., 2005; Tuccimei et al., 2005; Moral et al., 2008; Auqué et al., 2009; Moore et al., 2009; Belkhiri et al., 2010; Dassi, 2011; Barberá and Andreo, 2012 and references therein; Bicalho et al., 2012; Carucci et al., 2012; Huang and Chen, 2012 and references therein; Wong et al., 2012; Markovic et al., 2013; Xie et al., 2013), whereas the works focused on evaporite karst systems are much more scarce (Kaçaroglu et al., 2001; Günay, 2002; Land, 2003; Lamont-Black et al., 2005; Yechieli et al., 2006; Omelon et al., 2006; Chiesi et al., 2010; Fidelibus et al., 2011; Apaydin and Aktas, 2012). Moreover, in spite of the large potential of mass-balance and reaction-path geochemical calculations to shed light on the hydrogeological and geochemical processes in karst systems, this methodology has not been applied, to our knowledge, to any evaporite karst system.

Thus, the main goal of this study is to explore the practicality of hydrochemical data and the application of geochemical modeling to quantify the relative importance of the different processes involved in evaporite karstification and to assess the role of their seasonal variations. This approach has been applied to a stretch of the Ebro Valley alluvial evaporite karst, including Zaragoza city (NE Spain). Even though this is one of the areas in the world where subsidence risk related to evaporite dissolution has the greatest economic impact (Gutiérrez et al., 2008a; Galve et al., 2009) and where more studies on evaporite karst subsidence have been published (Gutiérrez et al., 2007, 2008a; Castañeda et al., 2009; Galve et al., 2009; Guerrero et al., 2013), a detailed assessment of the hydrogeochemical and hydrogeological processes behind these highly hazardous phenomena has not been carried out yet. The interpretation of modeling results will allow identifying differences in the hydrogeology and mineralogy of different portions of the studied system and some of the main current uncertainties about the Ebro Valley alluvial evaporite karst.

2. Study area

2.1. Geological setting and climate

The studied area is a 60 km-long reach of the Ebro River valley located in the central sector of the Ebro Tertiary Basin (NE Spain), which constitutes the southern foreland basin of the Pyrenees (Fig. 1a). In this section of the Ebro Valley, the river has carved into subhorizontally lying evaporites of the Oligo-Miocene Zaragoza Formation (Quirantes, 1978; Ortí and Salvany, 1997). In the subsurface, the formation is primarily composed of anhydrite ($CaSO_4$)/gypsum ($CaSO_4{\cdot}2H_2O$), halite (NaCl) and glauberite ($Na_2Ca(SO_4)_2$), with interlayered marls and lutites including calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and quartz (SiO_2) (Salvany et al., 2007 and references therein; Guerrero et al., 2008a,b, 2013). In outcrop, the evaporitic succession exhibits around 300 m of laminated and nodular secondary gypsum derived from the hydration of anhydrite or from the replacement of glauberite. The evaporitic formation changes laterally into impervious and insoluble clay facies, which probably act as a hydrogeological barrier for the evaporite karst aquifer in the eastern (downstream) sector of the studied area (Fig. 1b). In the studied reach of the valley, the terrace and pediment deposits overlying the evaporitic materials may reach 80 m in thickness and fill basins several kilometers long generated by dissolution-induced synsedimentary subsidence (Guerrero et al., 2013 and references therein). These alluvial deposits mainly consist of gravels dominated by siliciclastic and carbonate pebbles with a sand–silt matrix, commonly cemented by carbonates.

Sinkholes resulting from karstification of the evaporitic materials are a common geomorphological feature in the area. Some sinkholes in the valley bottom are permanently filled with water (Fig. 2) and, therefore, may provide information on the hydrochemical and hydrogeological features of the alluvial-karst aquifer system.

The climate in this region is Mediterranean with strong continental influence, characterized by hot summers and cold winters. The mean monthly temperature ranges from 9 °C to 21 °C (Ninyerola et al., 2005). The average annual precipitation in the Zaragoza area is around 340 mm and it shows a considerable inter-annual variability. A significant proportion of the precipitation corresponds to intense, short-duration convective storms that commonly occur in spring and autumn. The year 2011, corresponding to the sampling campaign specifically carried out for this study, showed a total precipitation of 315 mm, indicating a slightly dryer year in relation to the average. The mean annual reference evapotranspiration in Ebro Valley exceeds 1150 mm, indicating a negative water balance of more than 800 mm and, therefore, a climate characterized by semiarid conditions (Diputación General de Aragón, 2007).

2.2. Hydrogeology

Two main interconnected aquifers can be identified in the study area: (1) the alluvial aquifer, composed by the alluvium underlying the valley bottom and the associated terrace deposits at the valley margins; (2) the karst aquifer developed in the evaporitic bedrock. The effluent Ebro River and the associated valley bottom alluvium acts as the base level for the alluvial-karst aquifer system and the general flow direction in the alluvial aquifer is toward the river (Fig. 1). The largest proportion of water input to the system in the studied stretch of the valley is anthropogenic-induced recharge in the urban area of Zaragoza and irrigation, which represents more than 90% of the groundwater input (Durán et al., 2005). The main irrigation sources are the Ebro River, the Imperial Canal and the Urdana ditch (Fig. 1a and b). Irrigation processes are the main cause of the seasonal variations in the water table, which may rise several meters by the end of the irrigation season (around September), when the river flow is usually low. On top of that, irrigation has a clear impact on sinkhole hazard in the area, as proven by the higher probability of sinkhole occurrence in irrigated lands and by their frequency decrease when changes in land use involve the interruption of irrigation (Gutiérrez et al., 2007).

The Ebro River is essentially an allocthonous drainage in the study area and its flow is mainly related to runoff derived from its northern headwaters (i.e. the Pyrenees). Irrigation started to have a significant impact on the alluvial aquifer of the river by the end of the 18th Century, with the construction of the Imperial Canal, which takes water from the Ebro River 70 km upstream of Zaragoza city. Although there are no hydrogeological data available previous to the development of that major irrigation