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Geochemical evolution of groundwater in an evaporite karst system: Brujuelo area (Jaén, S Spain)

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Abstract

Chemical evolution of groundwater along two main flowpaths was studied in Brujuelo area, an evaporite plateau characterized by the presence of wetlands and drained by hyper-saline springs. Major ions were analyzed, saturation indexes of the main mineral species were computed, and inverse geochemical modeling was performed. Results show a relationship between elevation and water mineralization, indicating that drainage at higher altitude (brackish water) may be associated to gravity-driven flows while lower altitude springs could drain regional groundwater flows (brine water). Modeling results strongly support the hypothesis that most of the selected springs geochemically evolve in a common (S-N) flowpath.

Keywords: Evaporite rocks; groundwater flowpath; hyper-saline springs, geochemical evolution, inverse modeling

1. Introduction

In small drainage basins, groundwater mineralization and its hydrochemical facies are related to the length, depth and residence time of subsurface water flows. Such idealization stated by Tóth[1] is useful to explain the hydrochemical variability found in this type of hydrological contexts. Additionally, the presence of evaporitic rock formations plays a significant role in the chemistry of groundwater. The high solubility of gypsum, anhydrite and halite, among other evaporite minerals, allows a greater and faster water-rock interaction, giving place to heterogeneous groundwater flows, with different salinity values (from fresh to brackish waters), and from recharge areas to discharge zones.

In Andalusia, in the Guadalquivir foreland basin (southern Spain, Fig. 1), a wide extension of terrain constituted fundamentally by Upper Triassic (Keuper) clays and evaporite rocks (gypsum and salt) exists, including other lithological blocks (olistolites) of Triassic to Miocene ages[2]. All these materials, termed as Chaotic Subbetic Complexes –CSC- Unit[3], appear as a chaotic mega-breccia highly deformed, whose hydrogeological behavior resembles to the Regional Gravity-Driven Groundwater Flow Model proposed by Tóth[1], with groundwater flows at different length and at various scales. In this context, wetlands and springs placed at lower altitudes are associated with large (regional) groundwater flows, of greater residence time within the system, and they normally drain high salinity (Na-Cl facies) and temperature water mostly connected with ascending flow. However, if local groundwater flow paths occur relatively close to the surface, from recharge areas to directly adjacent discharge zones, waters generally present lower salinity and temperature values and also calcium-sulphate facies, due to the lowest residence time of these flows within the CSC.

This work aims to gain deeper knowledge on the groundwater flow and geochemical processes that take place in a clayey-evaporitic CSC outcrop of around 10 km^2 (Brujuelo area, Fig. 1), by means of application of hydrochemical and geochemical modeling tools. This is particularly important when brine waters might cause quality deterioration of freshwater downstream, but also for the management of groundwater dependent ecosystems, such as the aforementioned wetlands.

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2. Geological and hydrogeological settings

Brujuelo area is located in Jaén province (S Spain), 14 km northeast of Jaén capital city, in the water divide between two tributaries of Guadalquivir River (Fig. 1): Salado (saline) and Cañada de las Charcas streams. In the central part, a karst endorheic depression of 146 ha exists, in which two ephemeral wetlands (Cirueña and Brujuelo) are located. The first one (placed at 464 m a.s.l.) is connected through a drainage ditch to the second (at 458 m a.s.l.), which is also artificially drained by a second trench towards a stream. Consequently, Brujuelo wetland gets dry during the summer months and Cirueña only become flooded during extraordinary wet periods. Arroyo Salado constitutes the hydrogeological base level of the system, where the main discharge points are placed (Fig. 1), from 440 m a.s.l. (Don Benito spring) to 375 m a.s.l. (San Carlos spring). Between them, a significant increase of flow rate is produced as consequence of the groundwater contribution[2]. Other discharge points are Brujuelo spring (425 m a.s.l.) and a small outflow near the exit of the drainage tunnel of Brujuelo wetland (Brujuelo outflow), placed at 450 m a.s.l.

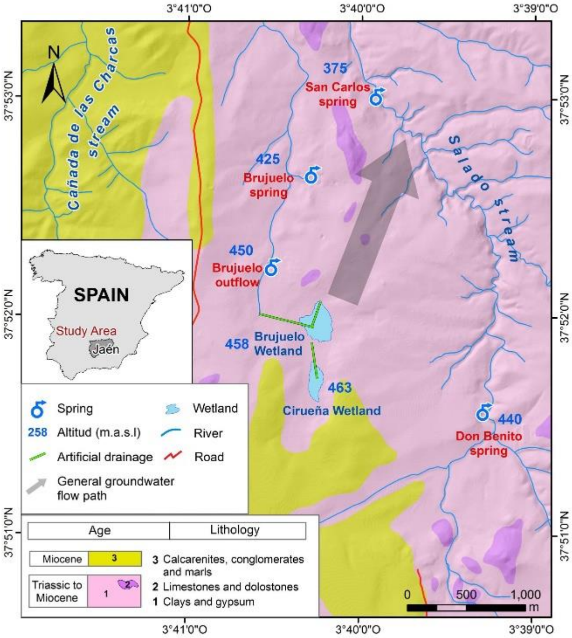

Fig. 1. Geological and hydrological settings

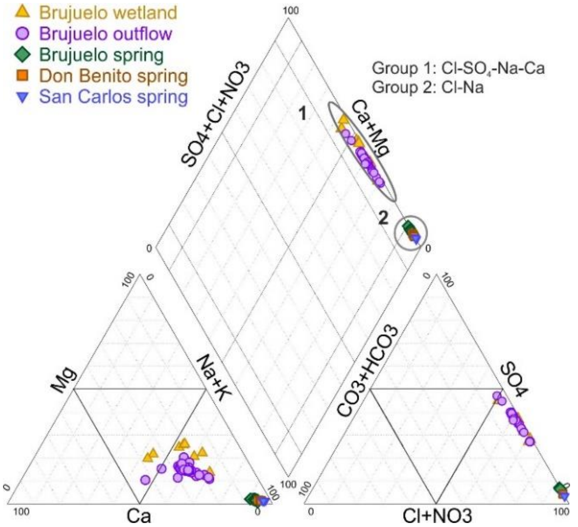

Fig. 2. Piper diagram showing two distinguished water types

3. Methodology

Physico-chemical parameters (electrical conductivity –EC-, water temperature, and pH) have been fortnightly measured and water samples have been collected for laboratory analysis. Cations and anions were analysed by high pressure liquid chromatography (*Metrohm 792 Basic IC* and *Metrohm Compact 881 IC pro*, respectively) and Total Alkalinity (TAC) was determined by titration method with H_2SO_4 0.02 N to a pH of 4.45.

Partial pressure of CO_2 and the saturation indexes of calcite, dolomite, anhydrite, gypsum and halite were calculated using the software PHREEQC[4]. Due to the high mineralization of the samples, Pitzer database[5] was selected for the calculations. Solute mass transfer was performed with the software NETPATH-WIN[6].

4. Results and discussions

Two groups of waters have been identified according to their chemical composition (Fig. 2, Tab. 1). Group 1 (Brujuelo wetland and Brujuelo outflow) show Cl-Na to Cl-SO_4-Na-Ca facies and a high annual hydrochemical variability. They are subsaturated in halite, in equilibrium with gypsum and oversaturated in calcite and dolomite (Tab 1). On the other hand, waters of group 2 coming from Brujuelo, Don Benito and San Carlos springs show high TDS and Cl-Na facies. These samples are saturated in all the considered species except for halite (although close to saturation, particularly in San Carlos). In all cases, Cl-Na relationship is evident (Fig. 3a) and NaCl dissolution is related to altitude: the lower the altitude of the spring, the higher salinity and the closer to equilibrium in halite (Tab.1, Fig. 3d).

Table 1. Summary of mean (m) and standard deviation values (σ) of main physico-chemical parameters, major component and saturation indexes (SI) of the studied wetland and spring waters, sorted by altitude.

Group	Name	Elevation (m a .s.l.)		T (°C)	pH	TDS (g/l)	ALK (meq/l)	Cl^- (meq/l)	SO_4^{2-} (meq/l)	Ca^{2+} (meq/l)	Mg^{2+} (meq/l)	Na^+ (meq/l)	K^+ (meq/l)	SI CAL	SI DOL	SI GYP	SI ANH	SI HAL
1	Brujuelo Wetland	458	m	19.0	8.4	10.23	1.9	111.3	56.5	36.4	36.8	98.0	0.6	1.23	2.55	-0.08	-0.5	-3.94
			σ	7.28	0.64	4.98	1.05	58.41	24.58	14.41	18.31	61.15	0.33	0.3	0.7	0.21	0.26	0.55
	Brujuelo Outflow	450	m	14.2	7.9	9.27	3.1	91.9	56.6	38.1	22.4	88.7	0.6	0.99	1.82	0.03	-0.45	-3.95
			σ	3.12	0.24	2.15	0.37	29.3	8.57	4.33	4.82	28.47	0.16	0.25	0.54	0.05	0.07	0.26
2	Don Benito Spring	440	m	22.2	6.6	175.67	4.7	2879.1	127.4	112.0	42.8	2780.7	7.8	0.83	1.46	0.19	-0.07	-0.76
			σ	0.13	0.17	3.66	0.11	84.8	4.7	9.74	3.79	67.22	0.61	0.18	0.36	0.05	0.05	0.03
	Brujuelo Spring	425	m	18.5	7.0	115.17	3.0	1815.9	124.9	108.2	35.1	1817.1	3.1	0.59	0.82	0.12	-0.24	-1.3
			σ	2.27	0.3	3.39	0.06	53.13	3.3	9.71	6.7	80.58	0.44	0.28	0.57	0.04	0.06	0.03
	San Carlos Spring	375	m	20.2	6.7	231.79	3.5	3905.9	133.7	99.8	51.7	3628.5	9.6	1.06	2.12	0.33	0.11	-0.31
			σ	1.9	0.23	10.05	0.09	209.58	8.51	7.41	4.95	195.27	0.93	0.23	0.45	0.08	0.1	0.08

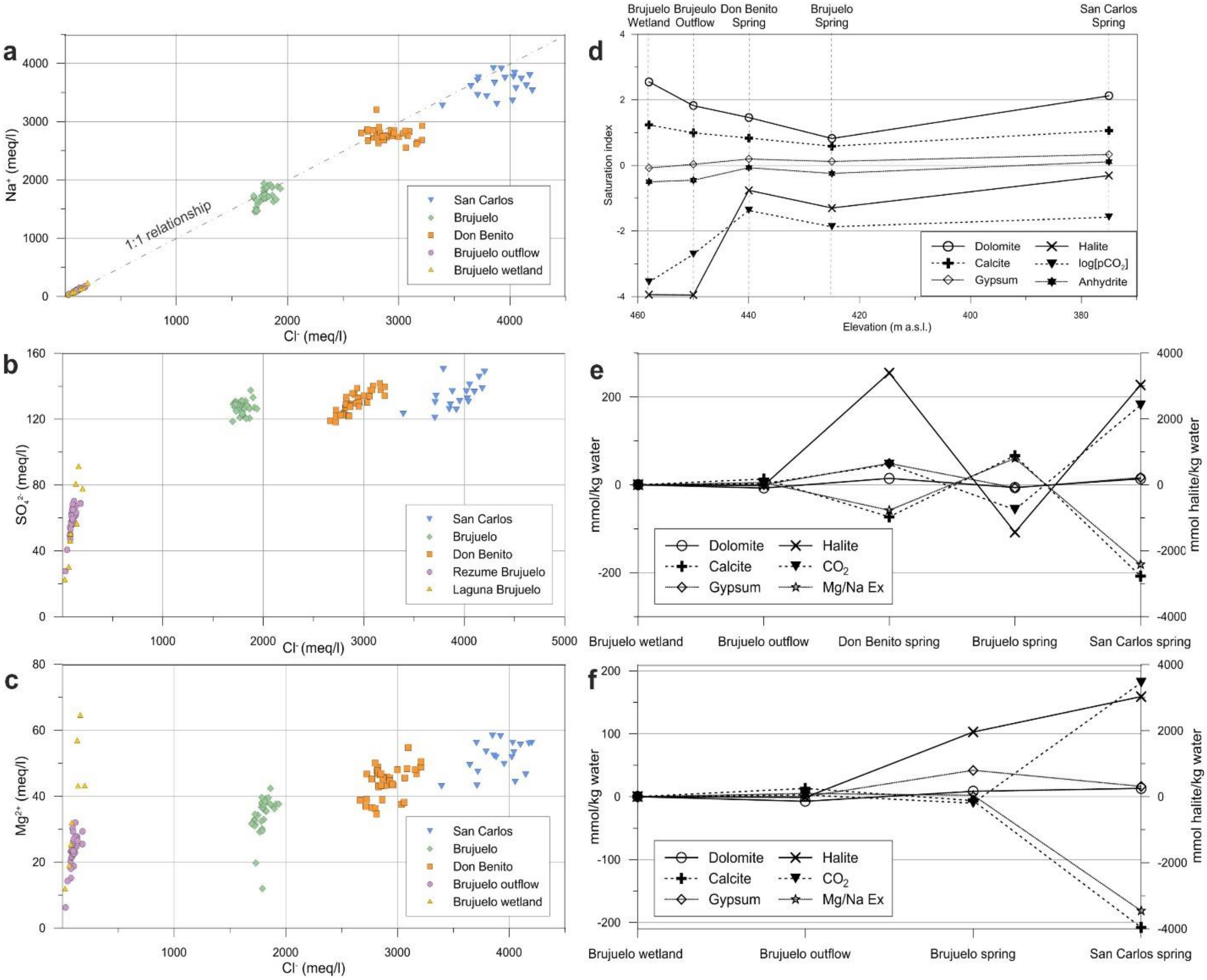

Fig. 3. Ionic relationships between Cl^- and Na^+ (a),Cl^- and SO_4^{2-} (b) and Cl^- and Mg^{2+}(c). Mean saturation indexes compared to altitude (d).Solute mass transfer results for scenario A (e) and B (f).

The two groups can be also distinguished from its solute (Cl^-, SO_4^{2-} and Mg^{2+} concentrations) load (Fig. 3b,c). Group 1, not saturated in gypsum or anhydrite, have a good Cl^--SO_4^{2-} statistical correlation, whereas group 2 has reached a maximum SO_4^{2-} concentration, not showing any significant trend when Cl^- rises (Fig. 3b). The case of Mg^{2+} is similar although with a slight increment for the most mineralized waters (Fig. 3c). It is observed that wetland waters have great variability, which can be favored by evaporation processes. Thus, group 1 could be linked to meteoric water, local and medium length groundwater flows, whereas group 2 would be related to longer and deeper groundwater flows. The latter hypothesis is consistent with the increase of water temperature observed in the springs with higher TDS (Tab. 1).

Regarding saturation indexes (Fig. 3d), calcite and dolomite saturation indexes generally display a descending trend as altitude decreases, whereas halite, gypsum and anhydrite ones, as well as partial pressure of CO_2, evolve in an opposite way. However, Don Benito spring waters present a notable deviation regarding the immediately above (Brujuelo outflow) and below (Brujuelo spring) discharge points. Furthermore, San Carlos Spring water suffers a significant change in dolomite saturation, promoted by higher concentration of Mg^{2+} and alkalinity values. The existence of a dolomitic block between Brujuelo and San Carlos spring could be the source of those increments, although it would be also possible that these rises were related to the presence in the evaporite rocks of minerals with magnesium in their crystalline structure (i.e. epsomite, hexahydrite, etc.), or both circumstances simultaneously.

For inverse modeling, two scenarios have been assumed: A) a flowpath that include all the studied points, sorted by altitude (Fig. 3e) and B) two independent flowpaths starting from the wetland: one towards Don Benito Spring and other northwards, including the rest of springs (Fig. 3f). In case A, ignoring the first step, each mineral species that is dissolved in one simulation step will be precipitated in the next one and *vice versa*. On the contrary, if Don Benito is considered as the final water of a different flowpath (scenario B), the mineral phases will be evolving in the same direction as groundwater flows toward the north. This fact would explain why Don Benito chemistry is not coherent to the observed general trends.

5. Conclusions

The application of hydrochemical methods and geochemical modeling tools has permitted to identify two groups of waters in the evaporite karst system of Brujuelo area (S Spain): one (brackish water) related to gravity-driven flows and another one (brine water) associated with longer and deeper groundwater flows. Inverse geochemical modeling has been performed for two different scenarios, resulting as the most plausible the one that take into consideration two different flowpaths starting from Brujuelo wetland: one northwards and another to eastwards. Due to the geological particularities of the evaporite media, the hydrogeochemical approach contribute to achieve an appropriate hydrogeological characterization, although assumptions hypothesized in this work would be reinforced in the future by applying non-conventional techniques such as age dating ones.

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