Hydrological and geochemical processes constraining groundwater salinity in wetland areas related to evaporitic (karst) systems. A case study from Southern Spain

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Abstract

Chemical and isotopic evolution of groundwater in an evaporite karst plateau (including wetland areas and saline to hyper-saline springs) located at S Spain was studied. Physicochemical parameters, major ions and stable isotopes were analyzed in rain, brine spring, wetland and leakage water samples, from which the most common mineral saturation indexes were computed and geochemical and isotopic modeling were performed. Results show an apparent relationship between the elevation of brine springs and their water mineralization, indicating that drainage at higher altitude may be associated to gravity-driven flows, since brackish groundwater is isotopically fractionated

23 due to evaporation. On the other hand, the lower altitude springs could drain deeper flows
24 with longer residence time, resulting in highly mineralized and warmer (briny)
25 groundwater. The dissolution of halite and gypsum has proved to be the main geochemical
26 processes, which are favored due by the great ionic strength of groundwater. Calcite
27 precipitation occurs in brackish waters draining wetlands, being boosted by common ion
28 effect (when $CaSO_4$ waters are present) and solute concentration caused by evaporation.
29 Modelling results strongly support the hypothesis that most of the selected springs
30 geochemically evolve in a common (S-N) flowpath. The methods used in this research
31 contribute to a better understanding of the hydrogeological processes occurring in the
32 studied evaporitic system, but also in equivalent hydrological environments worldwide.

33

34 **Key words:** Evaporite (karst) aquifer – Hydrochemistry – Geochemical
35 modelling/evolution – Stable isotopes - Brine springs

36

37 **1. Introduction**

38 Groundwater mineralization is strongly conditioned by the nature of the bedrock,
39 but also by the length, depth, and residence time within the system (Kreitler 1989; Tóth,
40 1999; Edmunds & Smedley, 2000; Goldscheider *et al.,* 2010; Andreo *et al.*, 2016).
41 Additionally, other geology-related factors are geochemically relevant in the chemical
42 composition of groundwater, as the geological structure and the geomorphological
43 framework, whose suitable knowledge becomes essential for a proper understanding of
44 the aquifer behavior (Goldscheider & Andreo, 2007). However, information on the system
45 characteristics is not always available or is scarce, especially in hydrogeological contexts
46 where water resources are limited. This is the case of many evaporitic formations, whose

47 groundwater resources are generally scarce and of poor quality due to its high salinity
48 (Memon *et al*., 1999; Chiesi *et al*., 2010; Apaydin & Aktaş, 2012; Gil-Márquez, *et al*.,
49 2017). In such environments, the presence of highly soluble minerals that constitute
50 subsurface materials, as halite (NaCl) or gypsum ($CaSO_4 \cdot 2H_2O$) and, to a lesser extent,
51 calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), permits a faster water-rock interaction
52 (Appelo & Postma, 2005), with the consequent influence of bedrock nature on
53 groundwater hydrochemistry (Kreitler, 1989; Hanor, 1994; Klimchouk & Aksem, 2005).
54 Likewise in fractured (Nkotagu, 1996; Ryan *et al*., 2013; Roques *et al*., 2014;
55 Gastmans *et al.*, 2016), detrital (Tellam, 1995; Hidalgo & Cruz-Sanjulián, 2001; André *et*
56 *al*., 2005; Mondal *et al*., 2014) or carbonate karst aquifers (Hess & White, 1993; Aquilina
57 et al., 2003; Moral *et al*., 2008; Barberá et al., 2014), the combined application of field
58 explorations and hydrochemical analysis together with geochemical calculations have
59 proved to be helpful for inferring the functioning of the aquifers connected with evaporitic
60 settings, even if their geological knowledge is scarce (Acero *et al*., 2015). Additionally,
61 isotopic analysis have also been applied to deduce the predominant geochemical
62 processes taking place within a specific groundwater flowpath (Wilson & Long, 1993;
63 Burg & Heaton, 1998; Portugal *et al*., 2005; Cartwright, 2010; Carol & Alvarez, 2016).
64 Physical-chemical processes such as evaporation/condensation, some chemical reactions
65 and microbial metabolism that promotes stable isotope fractioning (leaving a fingerprint
66 on the isotopic composition of groundwater), can be used as natural tracer for determining
67 recharge areas, groundwater origin (meteoric, marine, fossil, magmatic, etc.) and, in
68 general, to identify specific water-rock interaction mechanisms (Geyh *et al*., 2001; Mook,
69 2001). In scientific literature, speleological exploration and surveys have been done on
70 evaporite karst media but investigations focused on hydrogeochemical topics are less
71 frequent (Calaforra & Pulido-Bosch, 1993; Fontes & Matray, 1993; Klimchouk & Aksem

2005; Acero *et al*., 2015), even less those describing isotopic processes (Eastoe *et al*., 1999; Kohfahl *et al*., 2008).

At the southern sector of the so-called Subbetic Domain of the Betic Cordillera (S Spain), a large outcrop made up by Upper Triassic (Keuper) clays and evaporite rocks (gypsum, anhydrite and halite) is found, including blocks from other lithologies (limestones, dolostones, sandstones, etc.) of Triassic to Miocene ages (Pérez-López & Sanz de Galdeano, 1994). All these materials, named as Chaotic Subbetic Complexes – CSC- Unit (Vera & Martín-Algarra, 2004), emerge as a chaotic mega-breccia apparently with a disorganized structure. Low permeability and aquitard behavior have been traditionally attributed to the CSC Unit (López-Chicano *et al.*, 2001; Martos-Rosillo *et al*., 2013, among others). Nevertheless, dissolution processes (karstification) affecting evaporitic rocks contribute to the development of secondary porosity and permeability and favor a rapid geomorphological evolution of exokarst features: sinkholes and surface depressions (Calaforra & Pulido-Bosch, 1999; Gutiérrez *et al.*, 2008).

In general, most of the exokarst landforms are placed in smooth-relief areas where a poorly defined drainage network exists. Some of these endorheic depressions can be flooded temporary or even permanently, originating wetland and ephemeral lakes of variable size but of great environmental value (Rodríguez-Rodríguez *et al.*, 2006, Menz & Fenk, 2007; Kohfahl *et al*., 2008). Consequently, most of the surface depressions can contribute to the recharge of underlying aquifers, even more considering the existence of sinkholes, actives during rainstorm events, and artificial ditches, built to force wetland drainage. Thus, groundwater would flow from those wetlands located at relatively high topographic position towards other wetlands or springs situated at lower altitude, coinciding with the base levels for CSC outcrops. All these characteristics confer these materials a certain complexity, being its hydrogeological behavior comparable to the

97 Regional Gravity-Driven Groundwater Flow Model proposed by Tóth (1963, 1970) for
98 large sedimentary basins, with groundwater flows of different length and scales. In this
99 context, wetlands and springs placed at lower altitudes would be associated with large
100 (regional) groundwater flows, of longer residence time within the system, and they
101 normally drain high salinity (Na-Cl facies) and temperature water, mostly connected with
102 ascending flows (Andreo *et al*., 2016). However, if local groundwater flow paths occur
103 relatively close to the surface, from recharge areas to close discharge zones, waters
104 generally present lower salinity and temperature, as well as calcium-sulphate facies, due
105 to the shortest residence time within the CSC.

106 In this study, an attempt for gaining deeper knowledge on groundwater flows and
107 geochemical processes that take place in evaporite-karst systems has been carried out,
108 considering as pilot site a clayey-evaporitic plateau belonging to the CSC. The analysis
109 of the major hydrochemical components and environmental isotopes, from the selected
110 transit and discharge points, has been performed in combination to isotopic calculations
111 and the application of general low temperature geochemical modelling approaches
112 (inverse model). This provides more reliable quantitative information on the water-rock
113 interactions, geochemical processes and, ultimately, on the hydrogeological behavior of
114 the system that would not be available whether experimental or modelling approaches
115 were applied individually. From these results, a hydrogeochemical conceptual model of
116 the investigated system has been established, including a reliable representation of the
117 hydrogeological functioning of the investigated area, but potentially applicable to other
118 evaporitic karst environments. Thus, one interesting issue of this research is the
119 combination of different techniques, including chemical and isotopic analysis and, more
120 specifically, geochemical computations, could be useful for assessing the water-rock
121 interaction and the hydrogeological processes taking place in other poorly-studied

aquifers. It also will provide the basis for a proper management of groundwater dependent ecosystems, such as the aforementioned wetlands, but also for other hydrological contexts where brine waters might cause quality deterioration of freshwater in river and reservoirs.

2. Location, climate, geological and hydrogeological settings

Brujuelo area is a clayey-evaporitic plateau included in a larger olistostromic outcropping belonging to CSC Unit. This zone is located S of Jaén province (S Spain; Fig. 1), approximately 15 km NE from the homonymous city. It is situated in a relatively high plain, corresponding to the watersheds of two tributaries of Guadalquivir River: Salado stream, to the E, and Cañada de las Charcas stream, to the W (Fig. 1). Prevailing climate in the area is of temperate Mediterranean type, with a marked seasonal pattern in the annual distribution of precipitation. Rainfall mainly occurs in winter and spring, whereas summer season is generally dry (rainfall is absent). The mean annual precipitation in the region is 506 mm (Andreo *et al*., 2005). During the study period, the annual rainfall recorded in the 2013/2014 and 2014/2015 water years were 425 mm and 550 mm, respectively. The mean annual temperature for the region is 15.3ºC.

➔ **FIGURE 1**

Bedrock is mainly made up of Triassic clays and evaporites, including blocks with different lithologies and ages: Jurassic dolostones and limestones, Cretaceous marly-limestones and marls and Tertiary blocks (calcareous sandstones and marls). Triassic materials largely outcrop in the area, particularly multi-coloured clays, sandstones, subvolcanic rocks (ophites) and evaporites (gypsum and halite). Small blocks of limestones and brecciated dolomites (Muschelkalk) are often found surrounded by the above mentioned materials. Although halite formations are not present on surface (Fig. 1), its existence in depth has been inferred from groundwater hydrochemistry and

147 sampling cores obtained from boreholes drilled in other evaporitic areas of the CSC
148 (Carrasco, 1986). The geological structure is chaotic and apparently disorganized. The
149 outcropping materials present a distinctive degree of folding and brecciation as result of
150 a major tectonic deformation stage in the Alpine orogeny during the Lower and Middle
151 Miocene, when the olistoliths that currently constituted the geological unit suffered
152 gravitational transport processes and massive movements towards the Guadalquivir basin
153 (Vera and Martín-Algarra, 2004). In general terms, the structure can be described as a
154 megabreccia, in which blocks of diverse geologic nature are embedded in a Triassic
155 clayey-gypsiferous matrix. In Brujuelo area, dolomitic olistoliths are fairly abundant. To
156 the S and E of the site, Upper Miocene calcareous sandstones, conglomerates and marls
157 appear discordant over the CSC materials.

158 The test site is characterized by a smooth topography, which has been sculpted by
159 the evolution of the drainage network linked to Guadalquivir River (Fig. 1). Unlike other
160 areas related to CSC materials (Andreo *et al*. 2016; Gil-Márquez et al., 2016, 2017),
161 Brujuelo outcrops does not show abundant exokarst features; only some karst depressions
162 partially flooded during wet periods and some surface collapses. The two most significant
163 karst depressions are occupied by Brujuelo (458 m a.s.l.) and Cirueña (463 m a.s.l.)
164 wetlands. While the first one has a seasonal hydroperiod, the second one is ephemeral.
165 No drainage network exists in the endorheic catchment area of both wetlands.
166 Nevertheless, they are connected by a drainage ditch starting from Cirueña wetland (Fig.
167 1). Brujuelo wetland is artificially drained by means of a similar facility, which begins in
168 its NW border, where a low diameter tunnel connects the wetland to an ephemeral stream
169 (Fig. 1). Consequently, Brujuelo wetland becomes dry during the summer months and
170 Cirueña is flooded only during extraordinary wet periods. A shallow groundwater level is

observed in a well located on western border of the latter wetland, although water table remains below its bottom during low water conditions.

Groundwater drainage of the studied system naturally occurs through several permanent springs, being Don Benito (440 m a.s.l.) and San Carlos (375 m a.s.l.) springs, both located in the left margin of Salado stream (Fig. 1), the most significant. Due to the high salinity of their drained waters, groundwater resources have been traditionally exploited for salt (NaCl) extraction. Between both discharge points, a significant increase in Salado stream flow is observed (Andreo *et al*., 2016). In the central part of the area (Fig. 1), two additional springs are found: Brujuelo (425 m a.s.l.), also used for salt exploitation, and other outlet here called L2 (450 m a.s.l.), placed close to the lower end of the artificial tunnel that drains Brujuelo wetland. Finally, to the S, there is a small leakage (L1, 490 m a.s.l.) that partly drains Miocene materials.

3. Methods

3.1 Sampling routine and analytical methods

From September 2013 to June 2016, hydrodynamic and physicochemical monitoring field campaigns were carried out in Brujuelo area. Spring discharge (OTT® C2 flow meter), water elevation readings, electrical conductivity -EC- and water temperature (WTW® conductivimeter-thermometer 3310) and pH (HACH® HQ40d) *in situ* measurements were taken. Data accuracy were ± 10% for discharge, ± 1 µS/cm for EC, ± 0.1ºC for temperature and ± 0.1 units for pH. The Sampling periodicity was generally fortnightly for L2 and also for Brujuelo, San Carlos and Don Benito springs, and monthly for Brujuelo wetland, although shorter according to the rain episodes. Sampling in L1 and in the well of Brujuelo wetland was occasional.

In addition to field measurements, a total of 207 water samples (from the wetland, wells and springs) were collected and, later, analyzed in the Centre of Hydrogeology of the University of Malaga. Alkalinity (as HCO_3^- + CO_3^{2-}) was determined by volumetric titration using 0.02 N H_2SO_4 to pH 8.3 for CO_3^{2-} (if pH were higher), and then to 4.45 for HCO_3^-. Major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}) and Br^- determinations were performed using high performance liquid chromatography (HPLC, METROHM® Compact 930 IC flex for cations and Compact 881 IC Pro for anions, both supported by automatic samplers) with an accuracy of ± 2%. Due to the high salinity of most samples, they were diluted to 1 mS/cm and then filtered before being introduced in the system. The accuracy of chemical data were checked by the Charge Balance Error (CBE), calculated as the difference among equivalent of cations and anions summations (Σcations – Σanions) divided by the summation of equivalent of all ions (Σcations + Σanions). The mean CBE calculated for the whole set of sample was 2.7%. Errors out of ± 5% were discarded for geochemical computations.

For water isotopes ($\delta^{18}O$ and δ^2H) determinations, two different analytic instruments were used depending on the mineralization of the water samples. Those with mineralization values lower than 20 mS/cm were analysed using a cavity ring-down laser spectrometer (Picarro® CRDS L2120-I, supported by automatic sampler). On the other hand, isotope data of hypersaline waters (EC > 20 mS/cm) were determined by means of isotope-ratio mass spectrometry (IRMS). In both cases, corrected data were referred to the Vienna-Standard Mean Ocean Water (VSMOW).

3.2 Isotope data treatment and modelling

In briny aqueous solutions, the isotope activity ratio differs from the isotope concentration ratio, due to the fractionation occurring between free water molecules and

those associated with the hydration sphere of the cations in water solution (Taube, 1954; Horita, 1989). Thus, to convert $\delta^{18}O$ and $\delta^{2}H$ data from activity scale to concentration scale, the "activity correction" defined by Sofer & Gat (1972, 1975) was applied:

$$\Delta\delta^{2}H = mNaCl\cdot(-0.4) + mMgCl_2\cdot(-5.1) + mMgCl_2\cdot(-6.1) + mKCl\cdot(-0.16) \quad \text{[Eq.1]}$$

$$\Delta\delta^{18}O = mMgCl_2\cdot(1.11) + mCaCl_2\cdot(0.47) + mKCl\cdot(-0.16) \quad \text{[Eq.2]}$$

where m is the molality of the respective ions and $\Delta\delta^{2}H$ and $\Delta\delta^{18}O$ are the differences between the δ-values on the concentration scale and those on the activity scale, defined as "activity corrections".

Isotope evaporation lines were modeled by computing the analytical method described by Gonfiantini (1986), which assumes that the isotopic composition of an evaporating water body varies with the decrease of the remaining water volume fraction.

3.3 Geochemical computations

The required molalities for the isotopic activity corrections, the chemical evolution of evaporated waters, as well as partial pressure of CO_2 and the mineral saturation indexes of calcite, dolomite, gypsum, anhydrite, and halite were calculated using the software PHREEQC (Parkhurst & Appelo, 2013). Due to the high water mineralization, PITZER database (Plummer *et al.*, 1988) was selected for the computations, which include the Pitzer's thermodynamic equations (Pitzer & Mayorga, 1973, 1974; Pitzer & Kim, 1974) for solutions of high ionic strength, for which the Debye–Hückel theory is no longer adequate.

A solute mass transfer along the main flowpath of the hydrogeological system (Brujuelo wetland-San Carlos spring; Fig. 1) has been calculated using NETPATH software (Plummer *et al.*, 1994; El-kadi *et al.*, 2011) to develop a hydrogeochemical

242 conceptual model and test the chemical (dissolution/precipitation) reactions occurring in
243 subsurface. The selected water types (brackish and brine waters) are assumed to represent
244 different residence times within the system and variable mineralogical compositions of
245 the lithologies for which groundwater flows. Gas and mineral phases, cation exchange
246 and thermodynamics constrains used in the calculations were selected depending on the
247 expected mineralogy of the lithologies comprising the evaporitic system. Therefore, CO_2
248 was chosen as the principal gas phase; calcite, dolomite, gypsum and halite as
249 predominant mineral phases and Na^+/Ca^{+2} as the most probable exchange process. The
250 latter was included due to the clayey and evaporitic nature of the host rocks. Six paired
251 simulations were performed following the main S-N groundwater flowpath (Fig. 1), from
252 rainwater (e.g. initial solution) to L1 (e.g. final solutions) and continue progressively (by
253 decreasing altitude) with the rest of water points defining the flow line. The mean solute
254 contents of each water point were used for inverse modelling computations. In the
255 obtained results, negative and positive values (-/+) of the quantities of mass transferred
256 reflect precipitation and dissolution processes, respectively.

257 **4. Results**

258 4.1 Chemical composition of waters

259 Sampled waters in Brujuelo area show a variable degree of mineralization, with a
260 general increase of EC from the southern to the northeastern sectors and from the highest
261 to the lowest altitudes (Tab. 1; Fig. 1). Average EC values range from 1.7 mS/cm, in L1,
262 to 195.5 mS/cm, in San Carlos spring (Tab. 1). Coefficients of variation (*cv*) of EC for the
263 brine springs, but also for L1, are generally low, varying from 0.01 to 0.03 (Tab. 1 and
264 Fig. 2). Those water samples collected in wetlands and in L2 present higher *cv* for EC,
265 with a maximum value of 0.34 in Brujuelo wetland (Tab. 1).

➔ **TABLE 1**

The mean water temperature in the monitored points varies from 15.8 ºC, in L2, to 22.2 ºC, in Don Benito spring (Tab. 1). A slight thermal deviation is observed in brine spring waters, whose temperature values are, on average, 3.9 ºC (Brujuelo spring), 5.2 ºC (San Carlos spring) and 6.9 ºC (Don Benito spring) higher than the mean annual air temperature (15.3 ºC, Andreo *et al*., 2005). Although water temperature in Brujuelo wetland also presents a high mean annual temperature value (20.0 ºC), temperature measurements show a wide range of (annual) variations (Tab. 1).

Na-Cl is the prevailing hydrochemical facies in most of the water samples (Fig. 2A), although Ca-Mg-SO_4 waters are also present in the study site (e.g. Cirueña wetland). Additionally, two samples from Brujuelo wetland show Cl-SO_4 facies with no dominant cation (Fig. 2A). In general terms, Na^+ and Cl^- are the most abundant ions, followed by SO_4^{2-}, Ca^{2+} and, to a lesser extent, Mg^{2+} (Fig. 2B). The highest mean concentrations of Na^+ and Cl^- are found in San Carlos spring (Tab.1 and Fig.2B), followed by Don Benito and Brujuelo springs. SO_4^{2-} and Mg^{2+} are also higher in San Carlos spring (Tab.1 and Fig.2B), whereas Ca^{2+} concentrations are maximum in Brujuelo spring waters (Tab. 1 and Fig. 2B). Mean alkalinity values are in the range 2 - 6.2 meq/l (Tab. 1 and Fig. 2B). K^+ concentrations are below 1 meq/l in most of the samples (Tab. 1 and Fig. 2B), except for the brine spring waters, whose K^+ contents even exceeds alkalinity values. Finally, Br^- concentrations range from 0.02 meq/l to 0.57 meq/l (Tab. 1 and Fig. 2B). On the whole, the more mineralized water, the greater content in most of the major chemical constituents, except for alkalinity.

4.2 Time series of hydrochemical parameters

In the hydrological years 2014/2015 and 2015/2016, Brujuelo wetland hydroperiod lasted from November to June, while Cirueña wetland was never flooded

291 during studied period (Fig. 3A). L2 presents the highest variability in discharge rate (*cv* =
292 1.1; Tab. 1), which increased in winter periods, coinciding with the highest water levels
293 at Brujuelo wetland (Fig. 3A). The highest discharge rate (23.4 l/s) was measured in
294 February 2015 at Don Benito spring (Fig. 3C), with an average value of 7.5 l/s (Tab.1).
295 The outflow of Brujuelo spring and L1 was too low to be measured.

296 ➔ **FIGURE 3**

297 The greatest EC variability was registered in L2 and Brujuelo wetland, with
298 coefficients of variation of 0.23 and 0.34, respectively (Tab. 1). In both cases,
299 mineralization followed an opposite evolution respect to discharge/water level, with lower
300 EC values during high flow and reaching the maximum mineralization towards the
301 beginning of summer (Fig. 3A). Such variations are related to changes in all analyzed
302 ions, but in a lesser extent in the case of alkalinity. Regarding to the brine springs (Fig.
303 3B-D), gradual changes in water mineralization have been observed. A positive trend for
304 EC temporal series is recorded in Brujuelo spring, for the whole monitoring period, and
305 for the last 18 months in Don Benito spring (Fig. 3B-C). Halite-derived solutes (Na^+ and
306 Cl^-) follow a similar trend than that of EC in both springs (Fig. 3B-C), while ions derived
307 from gypsum source (SO_4^- and Ca^{2+}) behave in different pattern. On the other hand, San
308 Carlos spring waters show a descending global trend for EC and Na^+ and Cl^- contents.
309 Measured variations in hydrodynamic and hydrochemical responses of San Carlos spring
310 are likely due to natural discharge, but also influenced by groundwater pumping for salt
311 extraction (Fig. 3D).

312 4.3 Characteristic molar relationships

313 Figure 4 displays the molar relationships between Cl^- and predominant major and
314 trace chemical components. Na^+ covariates with Cl^- (Fig. 4A) following typical 1:1
315 stoichiometric line, which defines NaCl (halite) dissolution reaction. Molar relationships

316 among SO_4^{2-}, Ca^{2+} and Mg^{2+} and Cl^- (Fig. 4B-D) also describe a covariation trend (ratio
317 1:1), which tends to asyntothize (i.e. it deviates from 1:1 line) as Cl^- increases. In general
318 terms, brine spring waters (Brujuelo, San Carlos and Don Benito) are characterized by
319 higher Cl/SO_4, Cl/Ca and Cl/Mg ratios than those from brackish waters (Brujuelo and
320 Cirueña wetlands, L1 and L2).

321 ➔ **FIGURE 4**

322 The comparison of $Na^+ + K^+ - Cl^-$ against $Ca^{2+} + Mg^{2+} - Alk - SO_4^{2-}$ (Fig. 4E) is
323 useful to determine the existence of ion-exchange processes. Most of the brine spring and
324 wetland water samples are scattered in the left-upper plot space, indicating an excess on
325 divalent ions and a lack on monovalent ones. However, brine spring samples are not
326 aligned in the 1:-1 line that defines the ideal ion-exchange. On the contrary, when wetland
327 samples are observed in detail (Fig. 4E) the linear adjustment is better.

328 In the evolution of Cl/Br ratio (Fig. 4F), which is also constrained by the saturation
329 in Cl^-, the molar relationship describes a logarithmic curve that tends to keep stable in the
330 range of high Cl^- (i.e. hypersaline springs). Some samples collected in Brujuelo wetland
331 and in L2 (spring 2015 and 2016; Fig. 4F) are found below the general trend, having lower
332 Cl/Br ratios than is theoretically expected.

333 SO_4^{-2} has been also compared to evaporite and carbonate-derived solutes (Fig. 5).
334 In the Ca^{2+} *vs* SO_4^{2-} scatterplot (Fig. 5A), sample dataset seem to follow a proportional
335 trend, being all water samples scattered below the 1:1 line that control gypsum dissolution
336 reaction. When SO_4^{2-} is plotted against the sum of divalent cations coming from non-
337 carbonate minerals ($Ca^{2+} + Mg^{2+}$ - Alkalinity, Fig. 5B), solute relationship fits better to
338 the covariant line, especially for L2 water samples. In addition, a Ca^{2+} and/or Mg^{2+} excess
339 is observed in the range of high SO_4^{2-} contents for many of Brujuelo wetland waters and
340 for brine springs samples (Fig. 5B). In the molar Ca^{2+} *vs* Mg^{2+} scatterplot (Fig. 5C) two

main groups of samples can be distinguish according to the 1:1 and 3:1 stoichiometric lines, defining dolomite dissolution and dedolomitization processes. Thus, brine spring waters (Brujuelo, San Carlos and Don Benito) show a considerable enrichment in Ca^{2+} compared to Mg^{2+}, close to 3:1 ratio, whereas water samples from L2 and the wetlands (Brujuelo and Cirueña) scatter around 1:1 line (Fig. 5C). In the case of Brujuelo wetland, Mg^{2+} excess in water samples is observed.

➔ **FIGURE 5**

4.4 Mineral saturation of waters

All analyzed water samples were undersaturated respect to halite (Tab. 1), except for the more mineralized waters (brine springs) which were close to equilibrium ($SI_{HAL} \sim 0$), in particular San Carlos spring waters. Concerning to gypsum saturation (SI_{GYP}), only L1 waters were clearly undersaturated respect to this mineral phase, whereas the rest of the considered points presented values close to 0 (Tab. 1). Brine spring water samples had positive values of SI_{GYP}, in the range of 0 - 0.5 (Brujuelo spring and San Carlos spring, respectively), while samples corresponding to both wetlands and L2 waters displayed a slight undersaturation respect to gypsum, with minimum SI_{GYP} in Brujuelo wetland waters (Tab. 1). Most of the sample have positive mean dolomite and calcite saturation indices (SI_{DOL} and SI_{CAL}, respectively), reflecting the oversaturation in both mineral phases. The greater mean values are reached in the wetland waters (Tab. 1), although the single maximum calculated values for both parameters belong to L2, which has a great variability for both parameters. L1 waters are, on average, in equilibrium respect to calcite and dolomite. Partial pressure of CO_2 for Brujuelo wetland is the lowest from the whole set of sample and its mean value ($logPCO_2 = -3.5$) is near the atmospheric equilibrium value. The highest mean values were calculated for the brine springs (Tab. 1), which indicates a greater CO_2 enrichment respect to the atmospheric air.

366 Figure 6 shows the evolution of the saturation indices of halite, gypsum, calcite
367 and dolomite as function of Cl^- contents. It is observed that SI_{HAL} and SI_{GYP} in sampled
368 waters from Brujuelo area follow a saturation trend as Cl^- increases. Such trend is of
369 logarithmic type for halite (Fig. 6A) and it does not show a clear continuity for gypsum
370 (Fig. 6B), but rather seems to draw two independent evolutions: one with a steeper slope
371 in the range of low Cl^- contents, for brackish waters, and other low-angle slope, for brine
372 spring waters. SI_{CAL} and SI_{DOL} evolve in a similar way to that of SI_{GYP} (Fig. 6C and D,
373 respectively), although in the first cases, the evolution trends followed by brackish waters
374 show wider variability in mineral saturation, reaching maximum values that exceed those
375 for brine waters.

376 ➔ **FIGURE 6**

377 4.5 Stable isotope characterization

378 The isotopic composition of rainwater samples have mean values for $\delta^{18}O$ of -6.3
379 ‰ and for $\delta^{2}H$ of -38.2 ‰ (Tab. 1). Average $\delta^{18}O$ and $\delta^{2}H$ of brine waters are close to the
380 latter values (Tab. 1). Brackish water samples are generally more enriched in heavy
381 isotopes, in particular those collected in Brujuelo wetland, with maximum $\delta^{18}O$ and $\delta^{2}H$
382 values, respectively, of 4.0 and 2.1 ‰ (Tab. 1). Mean *d* (deuterium excess) values are
383 negative for L1, L2 and Brujuelo wetland, being in the range of -0.5 and -6.0.

384 The isotopic data ($\delta^{18}O$ *vs* $\delta^{2}H$) of the samples collected from rainwater, leakage
385 points, wetlands and brine springs are represented in figure 7A. From the isotopic
386 determination of rain water samples, a Local Meteoric Water Line (LMWL) with a slope
387 of 8.9 has been calculated for the study area, which is plotted together with the Global
388 Meteoric Water Line (GMWL, Craig & Gordon, 1965) (Fig. 7A). Brine spring waters are
389 grouped in the graph near the meteoric water lines, while most of brackish waters samples
390 present a clear $\delta^{18}O$ enrichment respect to LMWL and GMWL (Fig. 7A). Brujuelo

391 wetland waters are widely dispersed in the plot and they define an evaporation line with
392 a slope of 4.8. The water lines described by L1 and L2 samples have lower slopes than
393 that for Brujuelo wetland (2.6 and 3.9, respectively; Fig. 7A). L1 samples plot notably
394 below the rest of the samples, whereas L2 ones, more widely scattered, are distributed
395 closer to Brujuelo wetland samples. Many of L2 samples fit in the water line calculated
396 for Brujuelo wetland, coinciding with high water periods.

397 ➔ **FIGURE 7**

398 Figure 7B shows the $\delta^{18}O$ values *versus* the Cl^- content. The mean $\delta^{18}O$ (-6.3‰)
399 value of rainwater (Tab. 1) is displayed in the graph as reference. Brine springs samples
400 are distributed around the mean $\delta^{18}O$. Samples plotted above that value in figure 7B show
401 isotopic fractioning. L1 waters present a slight $\delta^{18}O$ enrichment, although they do not
402 show any substantial variation in mineralization (Fig. 7B). On the contrary, those samples
403 belonging to L2 and Brujuelo wetland that are markedly affected by evaporation have a
404 clear increasing of Cl^- content. Gonfiantini's equations (1986) have been used to simulate
405 the variation of the isotopic composition of an evaporating water body as the residual
406 liquid fraction decreases. Cirueña well water and the less fractionated water sample of
407 Brujuelo wetland have been selected as initial solutions. Simultaneously, the theoretical
408 Cl^- enrichment has been computed using PHREEQC software. The simulated evolutions
409 are shown in figure 7B as lines with crosses. Most Brujuelo wetland and L2 water samples
410 plot near the second of the computed lines.

411 4.6 Geochemical modelling

412 Modelling results show higher dissolution rates of halite (up to 3,030.74 mmol/kg
413 of water) in the simulation steps, specifically in the groundwater drained by brine springs
414 (steps E and F, Tab. 2, Fig. 8). Among the brackish waters, in Cirueña wetland (step B)
415 the maximum halite dissolution rate is computed (95.71 mmol/kg water). Gypsum

dissolution occurs in every simulation step considered, reaching higher rate in Brujuelo spring (step E) and decreasing towards San Carlos spring (step F), where solute (Na^+ and Cl^-) mass transferred is greater (Tab 2, Fig. 8). Dissolved CO_2 and calcite precipitation rate are maximum in San Carlos spring, as well as the excess of Ca^{2+} respect to Na^+ (Tab. 2). Calcite precipitation also takes place in simulations steps B and C, whose final solutions belong to both wetland waters, while calcite dissolution is only significant in L2 (step D, Tab. 2). Dolomite dissolution, as occurs with gypsum and halite dissolution, has been determined in every simulation step (Tab. 2).

➔ **TABLE 2**

➔ **FIGURE 8**

5 Interpretation and discussion

5.1 Factors controlling the chemical composition of waters

The origin of natural occurring brines have been traditionally attributed to three main natural processes: (i) Subaerial evaporation of continental or sea waters (Wilson & Long, 1993; Long *et al*., 2009; Kohfahl *et al*., 2015), (ii) subsurface dissolution of evaporite rocks (Johnson, 1981; Hanor, 1994; Memon *et al*., 1999; Calaforra *et al*., 2002; Naderi *et al*., 2016), and (iii) reverse osmosis produced when groundwater is forced to flow through low permeability materials (Berry, 1968; Demir, 1988). In the study site, the occurrence of the first mechanism is unlikely derived from the large distance from sea (approximately 130 km) and the small flooding wetland area, which could not have such influence on groundwater. Reverse osmosis could be also rejected, since it occurrence would require very specific conditions (Graf, 1982) and its actual implications in natural environments are not believe to be of great importance according to many authors (Fontes & Matray, 1993; Tóth, 1999). On the contrary, the abundant presence of evaporitic rocks in Brujuelo area, having high solubility, is the main source of mineralization. The fact Na^+

441 and Cl^- contents, increases towards lower altitudes (Tab. 1), where salt rock formations
442 are located (Calaforra, 1998; Andreo *et al*., 2016), and the rise of gypsum-derived solutes
443 (SO_4^{2-}, Ca^{2+}) parallel to mineralization (Figs. 2B and 4B-C), point out that way.

444 Moreover, the intrinsic geological complexity characteristic of the CSC Unit, with
445 a chaotic structure can play an important role in hydrochemistry. For instance, the uneven
446 location of halite, of greater abundance at depth (Carrasco, 1986), favors the existence of
447 more mineralized waters towards lower altitudes (Tab.1 and Fig.8), parallel to a change
448 of major ions proportions (Fig. 2, Tab. 1). Additionally, the high solubility of the
449 evaporites permits faster dissolution/karstification processes, giving place to karst
450 conduits and cavities that contribute to increase the hydrogeological complexity of the
451 system, with the subsequent implications over the water-rock interaction (Calaforra &
452 Pulido-Bosch, 1999; Gil-Márquez *et al*., 2017). Karst depressions, including the basins of
453 Cirueña and Brujuelo wetlands, and some sinkholes and small collapses found in the area,
454 especially near L2, highlight the karst development of the study site.

455 Additionally, climate conditions of Brujuelo area, with high evapotranspiration
456 rates, especially during the summer, have also a significant influence on water chemistry.
457 The concentration of solutes due to evaporation not only affects wetland waters that are
458 exposed to the atmosphere, but also groundwater related to the formers. Such influence
459 has been observed at different CSC areas (Rodríguez-Rodríguez *et al.*, 2006; Kohfahl *et*
460 *al*., 2008; Gil-Márquez *et al*., 2016), providing the wetland-soil-aquifer system high
461 sensitivity to variations in hydrological regimes due to climate change or human activities.

462 5.2 Hydrological processes affecting surface water and shallow groundwater

463 Groundwater recharge in Brujuelo area is produced by direct rainfall infiltration
464 through the Triassic evaporites and carbonates exposures and, to a lesser extent, across

465 the outcropping Miocene deposits. Additionally, localized infiltration may be favored
466 through the wetland-soil continuum or in artificial trenches. Therefore, apart from the
467 mineral dissolution of the evaporitic bedrock, the mentioned infiltration mechanisms have
468 also a significant influence on the chemical and isotopic composition of water, which
469 provide valuable information related to hydrological processes.

470 The values of $\delta^{18}O$ and $\delta^{2}H$ in rainwater (Tab. 1) were measured in samples taken
471 in autumn and spring times, when infiltration is largest in the Mediterranean region. Thus,
472 the isotope composition of groundwater of Brujuelo area must be in agreement with those
473 for the average yearly rainfall (Mook *et al.*, 2001). Brine waters have values close to that
474 mean annual value, while only some brackish samples may be considered near it (Tab. 1,
475 Fig 7B). In general, they present an enrichment in heavy isotopes, especially $\delta^{18}O$, which
476 is interpreted as isotopic fractioning due to evaporation (Mook *et al.*, 2001). Nevertheless,
477 each sampling point define evaporation lines with different slopes, denoting site-specific
478 isotope fractionation processes.

479 L1 samples, for instance, are aligned defining a slope of 2.6 (Fig. 7A),
480 considerably lower than the rest of the calculated lines. Evaporation processes taking
481 place in small grain size soils under dry conditions can generate the observed trend
482 (Sonntag *et al*., 1985). The slope of the regression line for Brujuelo wetland samples (4.8,
483 Fig 7A) is characteristic of free surface waters directly exposed to the atmosphere (Mook,
484 2001). The only sample from Cirueña wetland plots over Brujuelo wetland evaporation
485 line in figure 7A, although its deviation from the mean annual rain value is smaller (Fig.
486 7B), probably caused by the renewal of water in the well and by a greater water column
487 on it than in Brujuelo wetland. Finally, L2 $\delta^{18}O$ and $\delta^{2}H$ contents define a 3.8 slope line
488 (Fig 7A), close to the values expected in waters in contact with the atmosphere.

Evaporation substantially influences surface and shallow groundwater chemistry. When comparing Cl^- content *versus* $\delta^{18}O$ (Fig. 7B), it is observed how mineralization increases as L2 and Brujuelo wetland samples move away from the mean isotopic rainwater values, although this observation is not applicable to L1. All Brujuelo wetland waters fall between the isotopic and chemical evolution lines calculated starting from its most evaporated sample and from Cirueña wetland well, except for the one taken at the beginning of 2014-2015 flooding period; right after a rainfall event that dissolved a thin salt crust deposited over the wetland bed and produced a increment of solutes in its waters (Fig. 3A). The deviation of Brujuelo wetland samples from its own calculated evolution could be explained by a possible groundwater input from the S, where Cirueña wetland is placed (Fig. 1). Finally, L2 samples show greater mineralization than that explained by evaporation produced in the wetlands, especially those less fractionated (Fig. 7B).

The rapid discharge response observed in L2 after the increase of Brujuelo wetland water level (Fig. 3A) reveals a certain karst behavior. This, together with the short distance between both points (590 m), suggests the existence of a local hydrogeological connection between them, which would explain their chemical and isotopic similarities (Figs. 2 and 7, respectively) under high water conditions. Towards the end of spring time, when the increase of evaporation rate produces a greater isotopic fractionation of Brujuelo wetland waters, a similar effect is observed in L2 waters and, therefore, they fit reasonably well with the wetland equation line (Fig. 7A). Under these circumstances, water mineralization in both points would be highly influenced on solute concentration taking place at the wetland waters affected by evaporation (Gonfiantini, 1986). On the other hand, those L2 samples that show less similarity in mineralization values to Brujuelo wetland ones were collected in summer, when the wetland is normally dry. Thus, the influence of groundwater originated by diffuse recharge would be greater, leading to an enrichment of

514 $\delta^{18}O$, similar to that observed for L1 (Fig. 7A), which would produce a decline of L2
515 evaporation line respect to Brujuelo wetland one. Then, mineralization in L2 would not
516 only depend on solute concentration due to evaporation, but rather on dissolution
517 processes within the system (Carol & Álvarez, 2016).

518 The Cl/Br ratios observed in water samples from the area (Fig. 4F) are consistent
519 with the proposed discussion. Low mineralized L1 waters (Fig. 2, Tab. 1) have Cl/Br
520 values near 300, which is the expected ratio for inland recharge waters (Edmunds &
521 Smedley, 2000; Davis *et al*., 2004). On the opposite side of the plot (Fig. 4F), brine springs
522 present high rCl/Br, close to 10,000, pointing that the great mineralization of its water is
523 due to the dissolution of NaCl (Herrmann, 1972). Finally, L2 and wetlands samples scatter
524 between both ends, in a theoretical evolution line that indicate transition from meteoric
525 waters towards more enriched in halite-derived solutes waters (Alcalá & Custodio, 2008).
526 However, some L2 and, especially, Brujuelo wetland samples plot below the line caused
527 by an enrichment in Br^- respect Cl^-, typically produced by evaporation of saline waters.

528 5.3 Hydrochemical processes and geochemical evolution of high salinity groundwater

529 The 1:1 Na-Cl molar relationship defined by the whole set of samples (Fig. 4A)
530 clearly indicates that the origin of both ions in the groundwater of the study site is related
531 to halite dissolution (Appelo & Postma, 2005). Not only massive salt rock exists, present
532 at depth (Carrasco, 1986), which provides Na^+ and Cl^- to the brine springs (Fig. 2), but
533 also halite minerals included within other shallower evaporitic rocks, as it can be inferred
534 from the chemical composition of the studied brackish waters. Such observation has also
535 been made in other areas where the CSC outcrops (Calaforra, 1998; Kohfahl *et al*., 2008).
536 The massive presence of halite at depth would explain the progressive increment of
537 mineralization (Tab. 1 and Fig. 8), mainly due to Na^+ and Cl^- (Fig. 2B). However, the
538 asymptotic evolution of SI_{HAL} as mineralization increases (Fig. 6A) allows the continuous

539 incorporation of Na^+ and Cl^- even when their concentration is in the range of the observed
540 for brine springs (Tab. 1, Fig. 2B), as modelling results prove (Tab. 2, Fig. 8). This
541 suggests that waters with higher mineralization could have undergone a longer
542 geochemical evolution. Some variations observed from brine springs evolutions series
543 support that assumption. On the one hand, the increase of mineralization values observed
544 in Brujuelo spring during 2014 (Fig. 3B), a year considered as dry (see section 2), would
545 be caused by a reduction of the recently infiltrated water and, therefore a greater influence
546 of long residence groundwater flows. As for the dilutions produced in Don Benito spring,
547 they respond to recharge periods when an increase of discharge occurs, in which the
548 proportion of meteoric water would be greater.

549 The abundance of gypsum (and other evaporites bearing SO_4^{2-}) in study area
550 bedrock also has great hydrochemical implications, as it can be inferred for the good
551 correlation in SO_4^{2-} *vs* Ca^{2+} and Mg^{2+} relationships (Fig. 5A-B). It is observed how the
552 relative abundance of SO_4^{2-} diminishes from Cirueña wetland waters, which is the highest
553 water point located over the CSC outcrop in the area, towards lower places (Figs. 2B and
554 5B). This is influenced by the fact that, contrary to SI_{HAL}, SI_{GYP} rapidly reaches its
555 equilibrium stage as Cl^- increases (Fig. 6B). On the other hand, the addition of NaCl to
556 aqueous solutions produce an increment of its ionic strength that allows a greater
557 dissolution of gypsum (Zen, 1965; Calaforra, 1998). However, such increase is not steady
558 and it reaches a maximum at NaCl molarities near the values observed at the brine springs.
559 This reveals that the diminution of SO_4^{2-} compared to Cl^- (Figs. 4B and 6B), is related to
560 thermodynamic equilibrium. Thereby, the diminution and latter stabilization of the
561 rSO_4/Cl is not due to the lack of gypsum (or other evaporites containing sulfate) at depth,
562 but to the gradual evolution of its saturation state. In this context, the rSO_4/Cl could be
563 used as a rough indicator residence time in the evaporitic system for groundwater, as

564 gypsum dissolution in geochemically evolved water is much lower than halite dissolution
565 rate (Tab. 2, Fig. 8).

566 As it is expected from an area in which gypsum is abundant, geochemical
567 evolution of Ca^{2+} content in groundwater is similar to that for SO_4^{2+} (Fig. 4B-C).
568 However, the comparison among Ca^{2+} and SO_4^{2-} molar contents (Fig. 5C), do not follow
569 the ideal 1:1 stoichiometric line that define gypsum dissolution. This may partially be due
570 to calcite precipitation, as the high SI_{CAL} (Tab. 1 and Fig. 6) and modelling result suggest
571 (Tab. 2 and Fig. 8), probably due to common ion effect. The evolution of Mg^{2+} as
572 mineralization rises (Fig. 4D) resembles to those for SO_4^{2-} and Ca^{2+}, which may be an
573 indication of the existence of a source of Mg^{2+} related to evaporite dissolution. If both
574 main divalent ions are considered when comparing to SO_4^{2-} molarities (Fig. 5B), then the
575 distribution of samples keep better a 1:1 relationship, defining the theoretical dissolution
576 of sulfated evaporite rocks containing Ca^{2+} and Mg^{2+}. Despite minerals bearing Mg^{2+} in
577 their crystalline structure, such as epsomite ($MgSO_4 \cdot 7H_2O$) or hexahydrite
578 ($MgSO_4 \cdot 6H_2O$) among others, are not the main minerals that constitute the evaporite
579 rocks of the CSC, their existence at depth, even in small quantities, could explain the
580 pointed observation. Those minerals are characterized by higher solubility products than
581 gypsum one and they remain unsaturated along the geochemical evolution flowpath here
582 studied. A prolonged water-rock interaction could have allowed their enough dissolution
583 to cause the deviation here observed.

584 The presence of dolostone rocks interbedded in subsurface may also have some
585 influence on the Mg^{2+} abundance observed in groundwater from Brujuelo area. The Mg^{2+}
586 *vs* Ca^{2+} relationship (Fig. 5C) of the brackish water samples, close to the 1:1 line, indicates
587 that dolomite dissolution occurs, which is supported by the modelling results (Tab. 2). On
588 the other hand, water samples from brine springs, are close to the 3:1 stoichiometric line

589 defining dedolomitization (Fig. 5C), a composed geochemical process involving multi-
590 mineral phases such as gypsum, calcite and dolomite (Appelo & Postma, 2005). This is,
591 the presence of rich-SO_4^{2-} fluids in dissolution, as the main product in the gypsum
592 dissolution reaction, could induce calcite precipitation (common ion effect) due to Ca^{2+}
593 oversaturation, and a subsequent subsaturation in this mineral. This combined effect
594 accelerates the dolomite dissolution reaction kinetics as consequence of the high
595 capability of the water to dissolve more and more carbonate minerals (if calcite and
596 dolomite availability is enough), resulting in a greater Mg^{2+} mass transference (Wigley,
597 1973; Appelo & Postma, 2005; Moral *et al.*, 2008). The slight deviation from the 3:1 line
598 of some brine groundwater samples (Fig. 5C), especially those from San Carlos spring,
599 indicates their enrichment in Mg^{2+}. Therefore, as discussed in previous paragraphs, those
600 waters more geochemically evolved would have undergone a longer water-rock
601 interaction, allowing the dissolution of less abundant evaporitic minerals containing Mg^{2+}.

602 5.4 Groundwater flow implications on evaporite waters

603 The hydrogeological functioning of the CSC has been discussed in previous works
604 and some conceptual models have been proposed for the whole unit and/or for specific
605 locations (Calaforra *et al*., 2002; Rodríguez-Rodríguez *et al*., 2006; Kohfahl *et al*., 2008;
606 Andreo *et al*., 2016). The reverse evolution among the mineralization of groundwater and
607 its altitude has been formerly observed, being attributed to the presence of massive halite
608 at depth (Calaforra *et al*., 2002), but also to the longer residence times of groundwater
609 flows within the evaporite materials (Andreo *et al*., 2016). Furthermore, the groundwater
610 dependence of the wetlands has been formerly discussed: while some authors stated that
611 this relationship is restricted to some cases (Rodríguez-Rodríguez *et al*. 2006), others
612 pointed out that it systematically occurs, in a lesser or in a greater extent, in every wetland
613 of the CSC (Andreo *et al*., 2016). If the wetland-groundwater interaction is assumed, the

614 influence of the identified hydrogeochemical processes, the free-surface/shallow water
615 evaporation and the mineral dissolution of the evaporite bedrock, over the wetland water
616 chemistry need to be accepted (Kohfahl *et al*., 2008; Gil-Márquez *et al*., 2016). The results
617 derived from this research have permitted to reinforce the previously developed
618 hydrogeological conceptual model proposed by Andreo *et al*. (2016), by means of a
619 complete hydrogeochemical characterization of the studied system, based on the
620 geochemical and isotopic evidences (Fig. 8).

621 Figure 8 summarizes the main hydrogeological and geochemical processes that
622 occur in the Brujuelo area. The aquifer functioning consists of the hierarchization of
623 groundwater flow system, with diverse flow routes having variable lengths, depths and
624 residence times: all these factors strongly constrains the observed water quality. The
625 geochemical evolution of groundwater is coherent with a preferential S-N flowpath (but
626 also with a theoretical Tóth-like gravity-driven flow model, as is schematized in Fig. 8),
627 from the highest areas (L1) towards the base level of the hydrogeological system (San
628 Carlos spring) at the bottom of Salado stream (Figs. 1 and 8). Once rainwater percolated
629 the soil layer, it quickly acquire mineralization due to water-rock interaction and,
630 consequently, to the dissolution of all available mineral species in the bedrock (step A;
631 Tab. 2, Fig. 8), according to their solubility. Such geochemical process is enhanced along
632 the main groundwater flow direction except for calcite, which precipitates in the wetland
633 waters (steps B and C; Tab. 2, Fig. 8), triggered by common ion effect. This chemical
634 phenomena is produced by the further Ca^{2+} releasing on wetland waters as consequence
635 of gypsum dissolution, and favored by the solute concentration that the free-surface water
636 evaporation promotes (Fig. 7). The observed hydraulic/hydrogeological connection
637 between Brujuelo wetland and L2 (step D) and the high variability of the monitored
638 natural responses in the leakage (Fig. 3A) can explain a rapid groundwater flow that does

not permit a great water-rock interaction. The absence of significant mass transfer in step D results (Tab. 2, Fig. 8), except for calcite dissolution, reinforces the latter hypothesis. The two last simulation steps (E and F) involving brine springs (Brujuelo and San Carlos, respectively) highlight significant hydrochemical changes that denote the most evolved geochemical stage of the high salinity groundwater. Halite and, to a lesser extent, gypsum dissolution were found as the predominant geochemical processes along the simulated groundwater flowpath, reaching the highest reaction rates (note the multipliers at the horizontal axes of their mass transfer diagrams on Fig. 8) in the waters of the more distant outlets in the composited flow routine. The highest mineral dissolution rates together with the slightly higher temperature of the brine groundwater (Tab. 1) suggest that water originates from upward regional flows (Fig. 8).

Contrary to other evaporitic environments surrounding the Mediterranean area (Celico *et al.,* 2008; Chiesi *et al.*, 2010; Acero *et al*., 2015), the occurrence of deep ascending regional groundwater flows is considered to be of great importance on the hydrochemistry of brine springs in the CSC (Andreo *et al*., 2016; Tab. 3), similarly to other settings such as Palo Duro Basin (Texas, USA; Knauth, 1988; Eastoe *et al*., 1999). However, there is no evidence of connate origin of groundwater or relict brine existance within the CSC (Tab. 3). Additionally, the high solubility of evaporitic rocks allows its dissolution/karstification, favoring the appearance of conduit flow of shorter residence time. Such phenomenon is also observed in other evaporitic formations, and it generally permits a good interaction between groundwater and surface water ecosystems (Tab. 3). This relationship is very often restricted to one direction (either recharge or discharge; Memon, *et al*., 1999; Chiesi *et al.*, 2010), although in other cases the interaction is produced in both ways, when the phreatic level intersect the surface of karst depressions (Acero, *et* al., 2010; Andreo, *et al*., 2016), leading to wetland areas.

664 ➔ **TABLE 3**

665 **6. Conclusions**

666 In this study, a realistic understanding of the main geochemical processes that
667 occur in an evaporite-karst plateau in Southern Spain has been presented, integrating
668 information derived from the chemical and isotopic signatures of wetland and spring
669 waters and also from inverse geochemical modelling approaches. This information has
670 enhanced the knowledge on the hydrogeological functioning of the evaporitic materials
671 belonging to CSC Unit, traditionally characterized by low permeability. These advances
672 in the knowledge about the hydrological and geochemical processes constraining
673 groundwater salinity have made possible the development of a comprehensive
674 hydrogeochemical conceptual model for the considered system.

675 The geochemical evolution of groundwater monitored in the study site is
676 dependent on the mineral availability that determines the predominant hydrochemical
677 facies, but also on the residence time of groundwater flows, which constrain the range of
678 mineralization in the waters sampled. Free-surface evaporation of wetland waters and
679 local karstification have also a great influence on the shallow groundwater chemistry.

680 Two main groups of waters have been identified according to their chemical and
681 isotopic composition. Brackish waters (wetlands and leakages) show Cl-SO_4-Na-Ca
682 facies, high annual hydrochemical variability and strong meteoric dependence, but also a
683 distinctive isotopic fingerprint. On the other hand, brine springs have Cl-Na waters,
684 saturated in all the mineral species considered (gypsum, calcite and dolomite), except for
685 halite. The slightly higher temperature of groundwater towards the north of the system
686 respect to the mean annual air temperature suggests the influence of upward deep
687 groundwater flows on the spring waters, while the higher amount of Na^+ and Cl^- (SI_{HAL}

688 close to equilibrium) reflects a longer residence time allowing an intense water-rock
689 interaction.

690 The evolution of groundwater geochemistry along the considered flowpath is
691 mainly affected by halite dissolution, which enhance the ionic strength of the solution and
692 promotes a greater gypsum dissolution reactivity. Calcite precipitation is preferentially
693 occurring in wetland waters, driven by common ion effect, which is produced by the high
694 gypsum-derived Ca^{2+} in its waters and favored by the solute concentration that free-
695 surface water evaporation originates.

696 The study of the chemical and isotopic composition of the groundwater of the
697 evaporite-karst system, combined with geochemical inverse modelling, reinforce and
698 complement the current hydrogeological knowledge about the test site. Therefore, results
699 could be used to define specific actions for the adequate management, protection and, if
700 necessary, restoration of the associated wetlands and for the mitigation of the effects of
701 the briny groundwater over the quality of dependent-water resources downstream.

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952 **Table and figure captions**

953 Figure 1. Location and geological-hydrogeological settings of Brujuelo area (S Spain).

954 Figure 2. (A) Piper diagram showing the proportions of major ions dissolved in water
955 samples. (B) Average solute concentrations for each monitoring point against mean total
956 dissolved solids (TDS). Standard deviation of solute contents (vertical interval) and TDS
957 corresponding to individual ions (horizontal interval) are also shown.

958 Figure 3. Temporal evolution of discharge rate/wetland stage, water temperature and
959 major chemical components of water samples from Brujuelo wetland and L2 (A),
960 Brujuelo (B), Don Benito (C) and San Carlos springs (D).

961 Figure 4. Scatterplots displaying the ionic relationships Cl^- *vs* Na^+ (A), Cl^- *vs* SO_4^{2-} (B),
962 Cl^- *vs* Ca^{2+} (C), Cl^- *vs* Mg^{2+} (D), $Ca^{2+} + Mg^{2+}$–SO_4^{2-}–HCO_3^- *vs* Na^++K^+–Cl^- (E), and rCl/Br
963 *vs* Cl^- (F).

964 Figure 5. (A) Scatter diagrams showing the ionic relationships between SO_4^{2-} *vs* Ca^{2+}, (B)
965 SO_4^{2-} *vs* non-carbonate source Ca^{2+}+Mg^{2+} and (C) Ca^{2+} *vs* Mg^{2+}.

966 Figure 6. Saturation indices of halite (A), gypsum (B), calcite (C) and dolomite (D) against
967 dissolved Cl^-.

968 Figure 7. Relationship between $\delta^{18}O$ *vs* $\delta^{2}H$ from water samples (A). Global (GMWL)
969 and Local (LMWL) Meteoric Water Lines and computed evaporation lines are displayed.
970 $\delta^{18}O$ *vs* Cl^- content (B). Isotopic and chemical evolution computed lines are also shown.

971 Figure 8. Idealized conceptual model of Brujuelo area based on geological interpretation,
972 hydrogeological observations and geochemical data. Asterisks (*) in mass transfer
973 diagrams represent incongruent model outputs. Note that in final solutions of E and F
974 simulation steps, horizontal axes have been rescaled.

975 Table 1. Main statistical descriptors (*n,* number of samples/measurements; *min,*
976 minimum; *max,* maximum; *mean,* average; *σ,* standard deviation and *cv,* coefficient of
977 variation) of physico-chemical data from surface water, groundwater and rainwater.
978 Units: discharge rate/wetland stage (flow/w. stage) in l/s and cm, electrical conductivity
979 (EC) in mS/cm, water temperature (Temp) in ºC, pH in unit of pH, major ions in mg/l,
980 mineral saturation indexes are dimensionless, isotopic values in ‰ VSMOW (Vienna
981 Standard Mean Ocean Water).

982 Table 2. Simulations steps for inverse geochemical modelling and mass transfer results
983 along the main S-N groundwater flowpath. Units in mmol/kg water. Negative values
984 indicate precipitation of the mineral phase, while positive values dissolution. (-)
985 incongruent model output.

986 Table 3. Comparative table of different hydrogeological functioning models previously
987 proposed for evaporitic systems worldwide.