



# The role of evapotranspiration in the groundwater hydrochemistry of an arid coastal wetland (Península Valdés, Argentina)



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## HIGHLIGHTS

- Tidal inflow and evapotranspiration processes condition the salinity of the marsh.
- The total evaporation of marine water led the halite and gypsum precipitation.
- The dissolution of soluble salts condition the groundwater quality of Fracasso marsh.

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## ABSTRACT

Coastal wetlands are complex hydrogeological systems, in which saline groundwater usually occurs. Salinity can be attributed to many origins, such as dissolution of minerals in the sediments, marine contribution and evapotranspiration, among others. The aim of this paper is to evaluate the processes that condition the hydrochemistry of an arid marsh, Playa Fracasso, located in Patagonia, Argentina. A study of the dynamics and geochemistry of the groundwater was carried out in each hydrogeomorphological unit, using major ion and isotope (<sup>18</sup>O and <sup>2</sup>H) data, soil profiles descriptions and measurements, and recording of water tables in relation to the tidal flow. Water balances and analytical models based on isotope data were used to quantify the evaporation processes and to define the role of evaporation in the chemical composition of water. The results obtained show that the groundwater salinity of the marsh comes mainly from the tidal inflow, to which the halite and gypsum dissolution is added. These mineral facies are the result of the total evaporation of the marine water flooding that occurs mostly at the spring high tides. The isotope relationships in the fan and bajada samples show the occurrence of evaporation processes. Such processes, however, are not mainly responsible for the saline content of groundwater, which is actually generated by the dissolution of the typical evaporite facies of the arid environment sediments. It is concluded that the evapotranspiration processes condition groundwater quality. This is not only due to the saline enrichment caused by the evapotranspiration of shallow water, but also because such processes are the main drivers of the formation of soluble salts, which are then incorporated into the water by groundwater or tidal flow.

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## 1. Introduction

Coastal wetlands are natural buffers between terrestrial and marine environments and play physical and bio-ecological protection roles. They are important components of the hydrological cycle, both locally and within the regional context, because they act as natural sponges, for instance, reducing the impact of flooding, and of water and sediment pollution, as well as providing refuge to numerous bird, fish and native

plant species (Bullock and Acreman, 2003). The hydrological processes that occur in them determine the environmental characteristics of each type of wetland. Small changes in the hydrological regime can generate modifications, i.e., in the ground water chemistry, in the development of the soil profile, in the vegetation, etc. (Mitsch and Gosselink, 2000; Curreli et al., 2013; Carling et al., 2013).

Coastal wetlands are complex hydrogeological systems, with the usual occurrence of saline groundwater. Salinity can be attributed to many origins, such as the dissolution of minerals of the sediments (Logan and Nicholson, 1998; Malcolm and Soulsby, 2001; Carol et al., 2009), marine contribution (Jorgensen, 2002; Kim et al., 2003; Carol et al., 2012), evaporation (Robinson and Gunatilaka, 1991; Humphries et al., 2011a,b;

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Carol et al., 2013) and transpiration by vegetation (Fass et al., 2007), among others. Estimating the hydrogeochemical processes of wetlands requires understanding in detail the different components of the hydrological cycle (Guardo, 1999; Drexler et al., 2004). In arid regions, evapotranspiration (ET) is the main mechanism of groundwater loss in shallow aquifers (Sanderson and Cooper, 2008), while in hydrologically closed basins all the loss of surface water and groundwater is through ET.

Many coastal wetlands occur along the Argentine Patagonian coast, where arid environments predominate. Such environments have been studied mainly for their ecological and edaphic features (Bortolus et al., 2009; Bala et al., 2008; Bouza et al., 2008; Ríos, 2010; Ríos et al., 2012). The aim of this study is to evaluate the processes that condition the groundwater hydrochemistry of the Playa Fracasso coastal wetland (Península Valdés, Argentina, Fig. 1), with emphasis on the role played by evapotranspiration in the development of these environments.

## 2. Methodology

### 2.1. Study area

The study area is located on the coast of the San José Gulf within the Área Natural Protegida Península Valdés (Península Valdés Protected Natural Area; Fig. 1). According to the precipitation data from the La Adela Farm (1901–2006) and the records of the weather station (1982–2002) of the CENPAT (National Patagonian Centre), the mean annual precipitation is 230 mm, with no definite trend throughout the year. The mean annual temperature is 13.4 °C, fluctuating between mean extremes of 6.4 °C in July to 20.4 °C in January and the potential evapotranspiration, estimated for reference following Thornthwaite and Mather (1957), is 700 mm/year. Under such conditions, the climate is classified as arid, mesothermal according to Thornthwaite (Burgos and Vidal, 1951).

At a regional scale, the outcropping geology of the Península Valdés is mainly characterised by the Tertiary marine sediments of the Puerto Madryn Formation, the Plio-Pleistocene Rodados Patagónicos (Patagonian Shingle Formation) and the presence of two saline playa lakes, Salina Grande and Salina Chica, located in the middle southern sector. The two salt pans are the result of the dominant arid climate, constituting a typical Patagonian evaporitic environment with deposits of halite and

gypsum (Alonzo, 2006). The Puerto Madryn and Rodados Patagónicos formations outcrop mainly at the cliffs that surround almost all of the Península Valdés coasts, including the coast of Playa Fracasso. The Tertiary sediments are mainly represented by sand, silt and clay with an important tuffaceous component and intercalations of shell and gypsum levels. Overlying them are the Plio-Pleistocene gravels of the Rodados Patagónicos and Quaternary alluvial and colluvial deposits, which are a remobilization of the abovementioned deposits (Haller et al., 2001). On the coast, there are thin eolian layers (no more than 0.5 m), which mainly overlie the alluvial deposits.

### 2.2. Materials and methods

The identification of the main hydrogeomorphological units was based on the analysis of previous edaphic information (Ríos, 2010), the differentiation of geomorphological units from satellite images (Google Earth) and the corresponding field control. In each geomorphological unit, pits were performed in which the soil profiles and the sedimentological and hydrogeological characteristics of the materials were described; soil samples were also taken for laboratory analysis. In order to complete the hydrogeomorphological characterisation, a piezometer was installed associated with each pit, so as to identify the hydrological behaviour of the different landforms in the recharge–conduction–discharge circuit. The piezometers constitute a monitoring network of 13 shallow manually drilled boreholes (depths of up to 2.3 m). The boreholes were levelled with an optical level (Kern GK1-AC).

In the laboratory, soil texture was analyzed following the Bouyoucos method and the electrical conductivity of the saturation extract was determined in an aqueous 1:2.5 suspension after being air-dried and passed through a 2-mm sieve.

The evapotranspiration was calculated at a daily time step with the Balshort v.3.0 software (Carrica, 1993). The inputs of this soil water balance model are the monthly potential evapotranspiration (ET), daily precipitation and the texture and field capacity of the soils. The ET was estimated according to Thornthwaite and Mather (1957) and the daily precipitation was provided by the neighbouring station of the CENPAT, located in the city of Puerto Madryn (Fig. 1). The texture and field capacity of the soil were selected from the software options

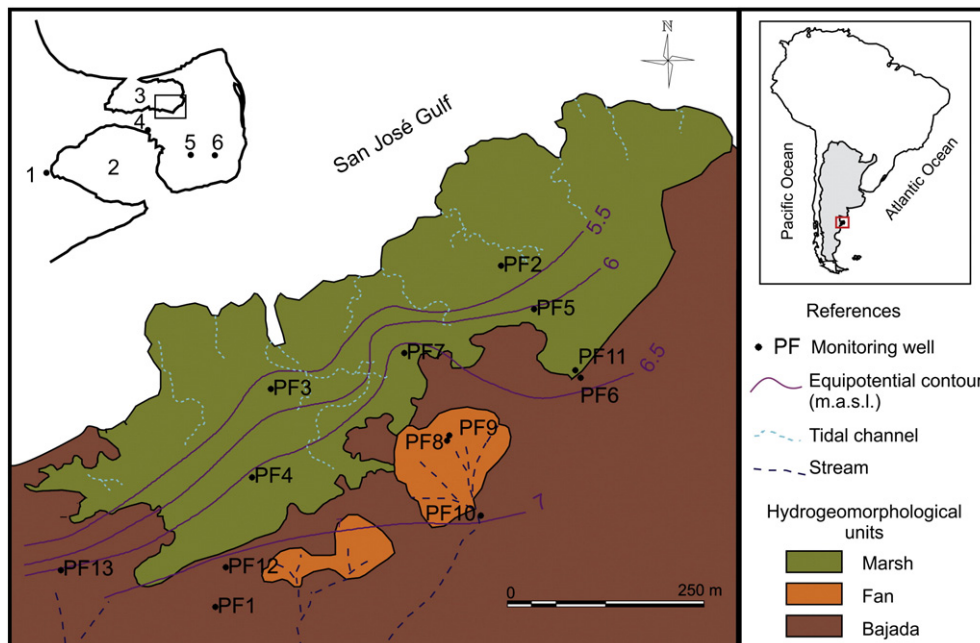


Fig. 1. Study area location, hydrogeomorphological units, monitoring network and equipotential map. The numbers in the upper left scheme mean: (1) Puerto Madryn; (2) Nuevo Gulf; (3) San José Gulf; (4) La Adela Farm; (5) Salina Grande; (6) Salina Chica.

according to the laboratory determinations and to Rostagno (1981). Finally, with the evapotranspiration (EVTR) and excess (EXC) daily values obtained with the Balshort software, the accumulated monthly values for each month of the 1982–2012 period were calculated; then, the monthly averages for the entire period were used in the analysis. The water balances were performed for each geomorphological unit, with texture and field capacity being the differential variables.

About 40 samples of groundwater (PF) and seawater were collected for isotopic and chemical laboratory determinations. Besides, the piezometric levels were measured, always during the low tide period, throughout three sampling campaigns over a two-year period (November 2010–February 2012). At the same time, the pH, Eh, temperature and electrical conductivity (EC) were measured in the field with a multiparameter portable meter (Hanna HI 9828).

In order to analyze the influence of the tides, by monitoring the water table fluctuations and salinity variations, three automatic water level data loggers (two Cera Diver Schlumberger and one CTD-Diver Schlumberger) and a barometric pressure data logger (Baro-Diver Schlumberger) were installed in piezometers PF5, PF6 and PF11 (Fig. 1). All divers measure absolute pressure and temperature, and the CTD-Diver (located at point PF11) also measures water conductivity. They were all set up to record data at intervals of 15 min.

Water sample collection, preservation, and chemical analysis of the major ion ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ ) were carried out in accordance with the standard methods proposed by the American Public Health Association (APHA, AWWA and WPCF, 1997). The charge balance error was below 5% for all samples. Ionic speciation and saturation indices (SI) were estimated using PHREEQC 2.13 (Parkhurst and Appelo, 1999). Isotopic ratios  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  were measured by laser spectroscopy with Los Gatos Research equipment (Lis et al., 2008). Results are reported following the usual convention  $\delta$  (‰) vs. V-SMOW (Gonfiantini, 1978). Analytical uncertainties were  $\pm 0.3\%$  for  $^{18}\text{O}$  and  $\pm 1\%$  for  $^2\text{H}$ . The hydrogeochemical evolution of the water was studied on the basis of evaporation processes by means of chemical relations, which were quantified by the analytical model. In the model, it was considered that evaporation increases the concentration of dissolved species in water. Solute concentration can be expressed as a function of the evaporated water fraction. Therefore, the enriched concentration  $C'$  can be estimated as follows:

$$C' = \frac{C_0}{(1-x)} \quad (1)$$

where  $C_0$  is the initial concentration,  $x$  is the evaporated water fraction; i.e.,  $x = V/V_0$  ( $0 < x < 1$ ), with  $V$  being the present volume and  $V_0$  the initial volume.

Gonfiantini (1986) gives a detailed description of isotopic enrichment for a drying-up water body, without inflow and outflow, and from which the water is removed only by evaporation, based on the approach by Craig and Gordon (1965). Gonfiantini states that the isotopic composition of water,  $\delta$ , varies with the decrease in the residual or remaining water volume fraction,  $f = V/V_0$ . The relationship between these two variables can be expressed as:

$$\frac{d\delta}{d \ln f} = \frac{h(\delta - \delta_\alpha) - (\delta + 1) \left( \Delta\epsilon + \frac{\epsilon}{\alpha} \right)}{1 - h + \Delta\epsilon} \quad (2)$$

where  $h$  is the relative humidity of the air;  $\delta_\alpha$  the isotopic composition of atmospheric water vapour;  $\alpha$  the equilibrium fractionation factor, being  $\epsilon = \alpha - 1$ . After adequate integration, with  $\delta_0$  defined as the initial isotopic composition of water at  $f = 1$ , Gonfiantini's expression for  $\delta$  ( $f$ ) becomes:

$$\delta = \left( \delta_0 - \frac{A}{B} \right) f^B + \frac{A}{B} \quad (3)$$

with A and B given by:

$$A = \frac{h\delta_a + \Delta\epsilon + \frac{\epsilon}{\alpha}}{1 - h + \Delta\epsilon} \quad (4)$$

$$B = \frac{h - \Delta\epsilon - \frac{\epsilon}{\alpha}}{1 - h + \Delta\epsilon} \quad (5)$$

For the evaporation line calculation,  $C_0$  was considered as the average isotopic content of precipitation, determined by local rainfall sampling, and the average relative humidity of 0.70 was obtained at the CENPAT station, located in the city of Puerto Madryn. Besides, in order to evaluate possible interactions between the studied hydrogeomorphological environments, theoretical calculations of water mixtures were also made.

### 3. Results

#### 3.1. Hydrogeomorphology

Geomorphological units constitute hydrogeomorphological units where the lithological characteristics, as well as the topographical location and their distance to the coast, condition the hydrology of each of these environments. In the study area, the main hydrogeomorphological units are a marsh, fans and bajadas (Fig. 1).

Topographically, the marsh is located in the lower sector, with heights between 5.5 and 7.5 m.a.s.l. and very gentle slopes ranging from 0% to 2%. The lithology consists of sediments of marine origin, mainly represented by fine beach sands over which mainly silt loam and silty soils develop. The daily soil water balance indicates a monthly average evapotranspiration for the 1982–2012 period of 151 mm/year, varying between 6 and 20 mm (June–July and October, respectively). The excesses, obtained by the same methodology, are 9 mm/year, occurring between April and July and are null for the rest of the year. These results, as well as the ones that correspond to the fan and bajada hydrogeomorphological units, are summarized in Tables 1 and 2.

The fans, easily identifiable on the images due to their fan-shaped planform and their null vegetation, are smaller units that develop over the bajadas and the marsh. They are mainly formed by fine sand and silt of the alluvial deposits from which soils, whose dominant texture is sandy loam, are developed. In this case, the soil water balance indicates a monthly average evapotranspiration (1982–2012) of 136 mm/year (Table 1), varying between 7 mm (January) and 16 mm (October; Table 2). The obtained excesses are 24 mm/year (Table 1), distributed over almost the entire year but with peaks between April and July (Table 2).

The bajadas constitute the main geomorphological unit that surrounds and partially overlies the marsh. Topographically, this unit shows a gentle slope area towards the wetland, decreasing in its vicinity and varying between 4% and 2%. Its deposits are constituted by the remobilized sediments of the Puerto Madryn and Rodados Patagónicos

**Table 1**

Average monthly accumulated EVTR and EXC values (mm) for the 1982–2012 period in each hydrogeomorphological unit.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
<i>Bajadas</i>													
EVTR	6	13	15	10	10	8	8	11	13	14	11	10	128
EXC	0	2	2	8	6	3	3	2	1	3	0	2	32
<i>Fans</i>													
EVTR	7	13	15	11	10	8	8	12	14	16	12	11	136
EXC	0	1	1	7	4	2	2	1	1	2	0	2	24
<i>Marsh</i>													
EVTR	13	12	14	10	9	6	6	10	15	20	18	17	151
EXC	0	0	0	5	2	0	1	0	0	0	0	0	9



**Table 2**  
Synthesis of the values used in the Balshort balance and the results obtained.

	Bajadas	Fans	Marsh
Soil texture	Sandy	Sandy loam	Silty loam and silty
Balshort texture	Sandy	Sandy loam	Silty
Field capacity (mm/m)	37	50	125
Annual Precipitation (mm) (1982–2012)	230	230	230
Annual EVTR (mm) (1982–2012)	128	136	151
Annual EVTR % (1982–2012)	56	59	66
Annual EXC (mm) (1982–2012)	32	24	9
Annual EXC % (1982–2012)	58	41	14

formations, both outcropping at the pediments and cliffs that surround the bajadas outside the study area. The deposits are mainly of the sandy type with intercalations of gravel and shell levels, and with a variable percentage of silty matrices. The soil texture is mostly sandy but some fractions are loamy sand, whereas in the SW sector there are a few intercalations of the sandy clay type. In this unit, the monthly average evapotranspiration (1982–2012) is 128 mm/year, varying between 6 and 15 mm. The calculated excesses are 32 mm/year, distributed over almost the entire year but with peaks between April and May (see Tables 1 and 2).

### 3.2. Hydrodynamic and groundwater salinity

The groundwater flow is from the bajadas and fans circulating through the marsh and discharging towards the sea (Fig. 1). The thickness of the unsaturated zone (UZ) in the bajada varies between 0.5 and 1.6 m, depending on the monitoring point. Although the equipotential map (Fig. 1) shows that the area of the bajadas works as a groundwater circulation sector, the high permeability of the surface sediments (sand and gravel) indicates that this landform represents a recharge area. The fans have an UZ thickness of up to 0.7 m. They also work as a circulation area, and since they are constituted by sand, they also act as a preferential recharge area. In the case of the marsh, the UZ thickness is between 0.3 and 0.9 m and, while functioning as a circulation and discharge area of the continental sector, its hydrodynamics are also controlled by the tidal flows. The flooding of the marsh occurs at the spring high tide and, due to the infiltration of marine water, an elevation of the water table levels takes place, a process that does not occur in the bajada or fan units (Fig. 2). At quadrature, there is no oscillation of the water table levels and the groundwater flow is always towards the sea.

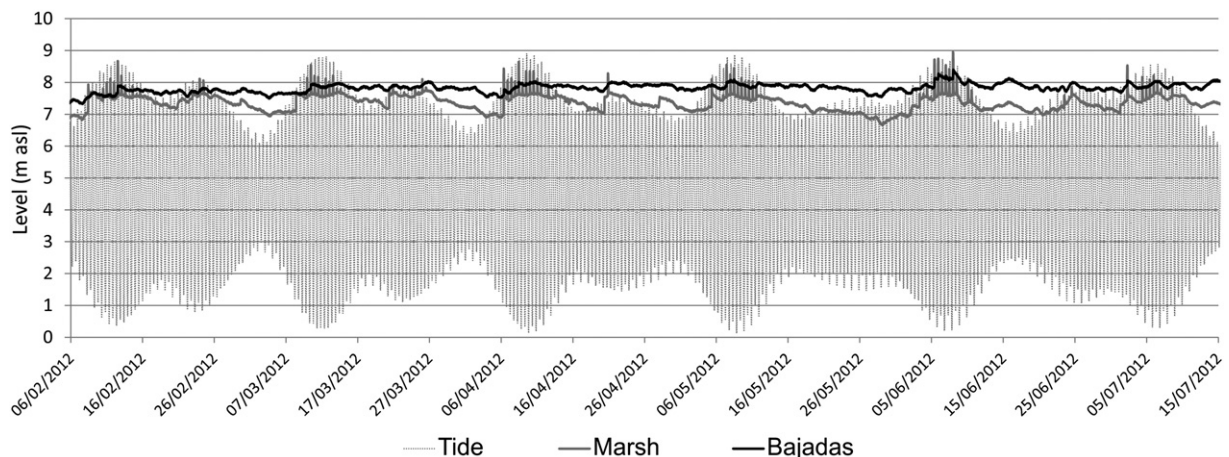
Groundwater is highly saline in all hydrogeological units. The salinity in the marsh varies between 16 g/L and 74 g/L, in the bajadas between 5 g/L and 29 g/L, and in the fans between 43 g/L and 88 g/L. During the spring high tide – where the marsh is flooded by the tidal flow – it is observed that in the marsh well that has continuous records of water levels and EC there is an abrupt EC increase associated with an elevation of the water table levels. In turn, at quadrature, slight increases in the water EC are mainly recorded during sunshine hours without any variations being registered in the water table levels (Fig. 3).

### 3.3. Environmental isotopes

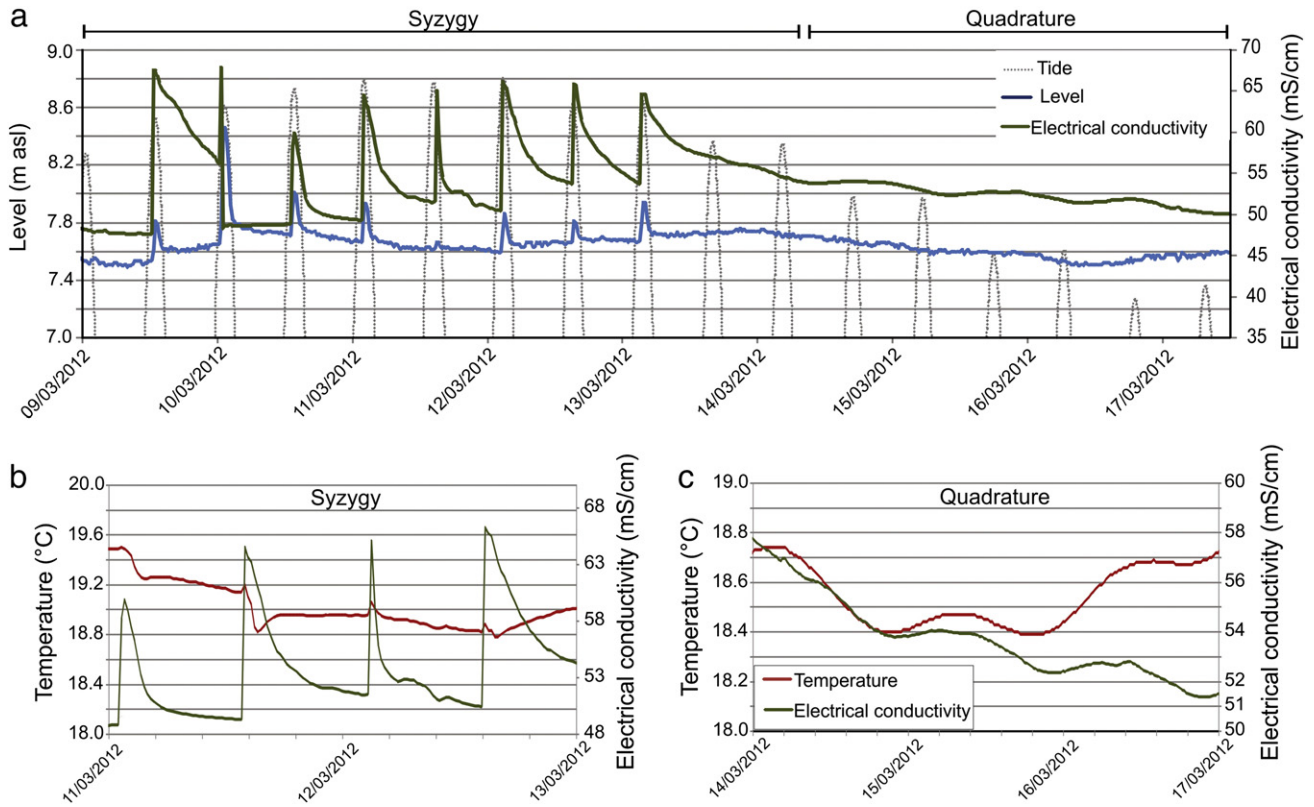
The isotopic values of the groundwater samples vary in the bajadas between  $-7.0\%$  and  $-4.6\%$  for  $\delta^{18}\text{O}$  and between  $-61\%$  and  $-43\%$  for  $\delta^2\text{H}$ . In the case of the fans, the values vary between  $-4.5\%$  and  $-2.5\%$  for  $\delta^{18}\text{O}$  and  $-43\%$  to  $-33\%$  for  $\delta^2\text{H}$ , while in the marsh the contents vary between  $-5.2$  and  $0.4\%$  for  $\delta^{18}\text{O}$  and between  $-42$  and  $1\%$  for  $\delta^2\text{H}$ . It is observed in the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  graph (Fig. 4) that the groundwater samples of the bajadas and fans deviate from the local meteoric line defined by the  $\delta^2\text{H} = 7.48 \delta^{18}\text{O} + 1.2$  equation (Alvarez et al., 2012) and are located around the evaporation line estimated according to Gonfiantini (1986).

Considering the average compositions of the rains as the initial concentration, the isotopic contents of the bajada groundwater are indicative of evaporation percentages between 3 and 13% and for the fans between 12 and 22% (Fig. 4). In turn, most of the marsh groundwater samples have an isotopic content similar to seawater, not showing a real tendency to deviate towards an evaporation line. In a theoretical mixture between the bajada and fan mean isotopic compositions (continental inflow to the marsh) and seawater (tidal flow), it is estimated that the mentioned deviation is attributed to percentages of mixing between 10% and 75% of seawater with respect to the bajadas or between 5% to 72% with respect to the fan mean compositions (Fig. 4).

The deuterium excess (d), an indicator of evaporation, together with the content of  $\text{Cl}^-$  indicates that the bajada and fan samples behave differently with respect to the marsh (Fig. 4). It can be observed that in the bajada and fan groundwater samples the deuterium excess has a tendency to decrease from the precipitation values (between 5 and 2) to values of  $-8$  in the bajadas and  $-13$  in the fans, a tendency that is associated with an increase in the  $\text{Cl}^-$  concentration. In the case of the marsh, the groundwater samples have deuterium excesses similar to seawater, and there is an increase in chloride concentration without registering significant variations in deuterium excess. The graph of the theoretical evaporation line in relation to deuterium and chloride contents shows that in all of the hydrogeomorphological units groundwater has higher chloride values than the ones that could be obtained by evaporation processes alone. According to the deuterium excess, the evaporation values



**Fig. 2.** Graph with the predicted tides and the measured water level fluctuations in the marsh (diver placed in PF5) and in the bajadas (diver placed in PF6).



**Fig. 3.** (a) Electrical conductivity and water level records; (b) detail of the electrical conductivity and temperature records at spring tides; (c) detail of the conductivity and temperature records at quadrature tides.

correspond to the estimate based on the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  relationship, while chloride evidences the NaCl type mineral dissolution of the sediment.

These processes are evident in the  $\delta^{18}\text{O}$  vs. Cl graph, where samples of the marsh show an increase in their chloride concentration from a seawater value without registering isotopic enrichment (Fig. 4c). It is clear that in this environment, where there is abundant vegetation, the evapotranspiration can also generate an increase in groundwater salt concentration without isotopic enrichment. Meanwhile, in the bajada and fan samples, though they show isotopic enrichment by evaporation, the chloride concentration is greater than the one expected by evaporation alone, evidencing the dissolution of evaporate deposits.

### 3.4. Hydrochemistry of major ions

Considering that the studied wetland is an environment where mineral facies that can easily pass into solution occur, such as halite, gypsum and carbonates, an analysis of its components depending on the composition of the major ions was performed. The observed relationships between the major ions show that each hydrogeomorphological unit has distinctive chemical characteristics (Figs. 5 and 6). The  $\text{Na}^+$  increases linearly with the  $\text{Cl}^-$ , showing in most of the samples of the three units a  $\text{Na}^+/\text{Cl}^-$  ratio between 0.8 and 1.0 (Fig. 5 a–b). An increase in  $\text{Ca}^{2+}$  depending on  $\text{SO}_4^{2-}$  is observed mainly in the marsh and fans, with  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  ratios close to 0.4, which indicates a slight  $\text{SO}_4^{2-}$  excess with respect to  $\text{Ca}^{2+}$ . In the bajadas, the  $\text{SO}_4^{2-}$  content tends to be lower and the  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  ratio varies between 0.4 and 1.0 (Fig. 5c–d). The  $\text{HCO}_3^-$  is the least predominant among the major ions, and its values do not show any clear tendency with respect to the  $\text{Ca}^{2+}$ . The  $\text{Ca}^{2+}/\text{HCO}_3^-$  ratio in the bajadas and fans is close to 1.0, while in the marsh the values fluctuate between 2.0 and 10.0 (Fig. 5e–f).

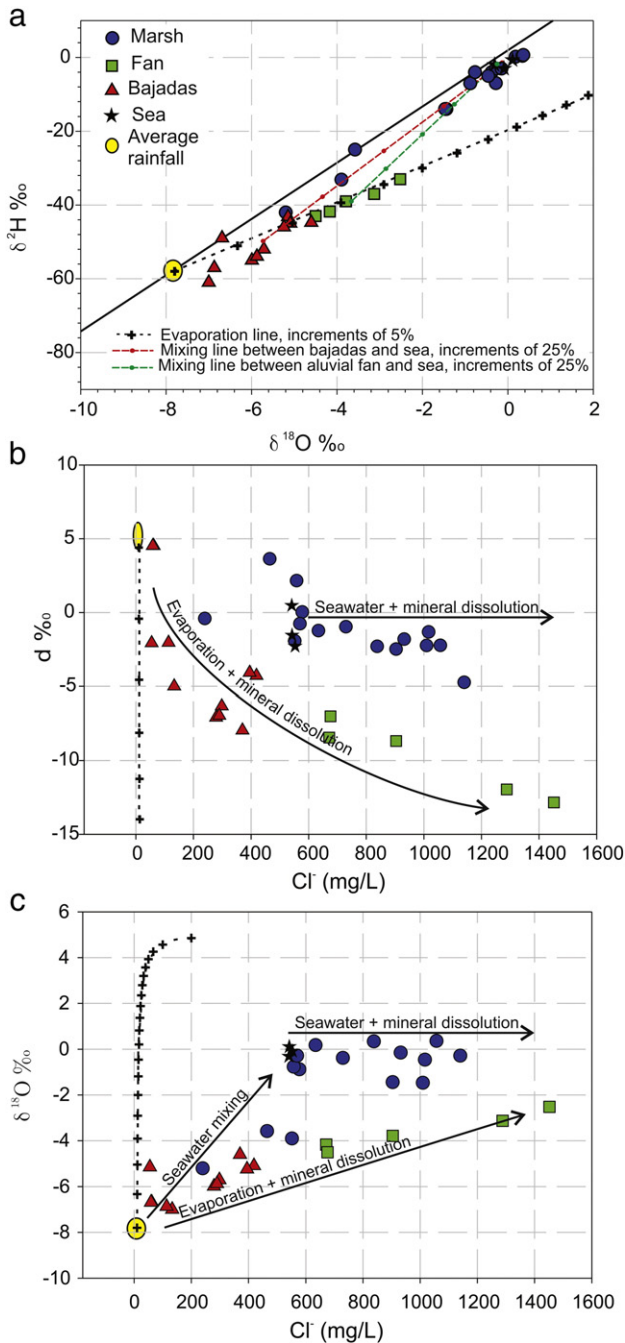
As dominant anions,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  tend to increase linearly, showing in the bajada groundwater a  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio that varies between 0.13 and 0.29, whereas in the marsh it is close to 0.1 and in the fans

between 0.05 and 0.10 (Fig. 6a–b). In turn, the  $\text{Ca}^{2+}$  and  $\text{Na}^+$  concentrations increase in each hydrogeomorphological unit but with different ratios. The  $\text{Na}^+/\text{Ca}^{2+}$  ratio in the bajadas ranges from 4.5 to 11.9, in the marsh it is close to 20 (similar to the seawater value), while in the fans it varies between 23 and 35 (Fig. 6c–d).

The analysis of the calcite saturation indices (SI) shows that the groundwater at the bajadas and fans is supersaturated with respect to calcite, with values between 0.1 and 1.8, and between 0.4 and 0.8, respectively, while the marsh has sub- and supersaturated values (between  $-0.4$  and  $0.5$ ), with ranges similar to those of seawater (Fig. 7a). All hydrogeomorphological units have SI values that are undersaturated with respect to gypsum, with both the SI and the  $\text{SO}_4^{2-}$  concentrations being greater than in seawater in the majority of the bajada and fan samples (Fig. 7b). With respect to halite, the SI are also lower than 0 (undersaturated values) in all of the hydrogeomorphological units. The lower SI values (between  $-4.2$  and  $-2.7$ ) are associated with the lower  $\text{Cl}^-$  concentrations and correspond to the bajada samples. The SI values with respect to halite in the fans vary between  $-2.2$  and  $-1.6$ , and in the marsh between  $-3.1$  and  $-1.8$ , being  $-$  as well as the  $\text{Cl}^-$  concentrations  $-$  greater than those of seawater in most of the samples (Fig. 7c).

## 4. Discussion

The climatic characteristics of the studied wetland determine that the evapotranspiration processes dominate in the hydrological balance. Among all of the hydrogeomorphological units, evapotranspiration is slightly higher in the marsh, with an estimated percentage (from the soil water balances) of 66%; and in the fans and bajadas of 59% and 56%, respectively (Table 2). Under these conditions, chemical precipitation and salt retention in the soil, as a result of an evaporation sequence, are common processes in wetlands such as the one studied, where evapotranspiration exceeds precipitation (Barnes et al., 2002;



**Fig. 4.** (a)  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  graph where evaporation and mixing are shown; (b) deuterium excess vs. Cl graph; (c)  $\delta^{18}\text{O}$  vs. Cl graph.

Humphries et al., 2011a,b). In the Península Valdés area, the predominance of evapotranspiration led to the existence within the detrital surface sediments of evaporite facies such as gypsum, halite (Brodtkorb, 1982, 1999) and carbonates (mainly calcium carbonate) as common minerals in the matrix sediments (Bouza, 2012). In wetlands of arid regions, the dissolution of these mineral facies is an important contribution of ions in solution to the surface water and groundwater (Banat et al., 2006; Humphries et al., 2011b).

The observed differences in the water chemistry of each hydrogeomorphological unit show that different processes are operating in each environment. The ionic relationships in the marsh show that groundwater comes mainly from the tidal inflow, to which the halite and gypsum dissolution is added. These processes are evident in the

ionic and isotopic relations and in the halite and gypsum SI values. Almost all marsh samples show ionic ratios  $\text{Na}^+/\text{Cl}^-$  (0.78–0.96),  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  (0.27–0.50),  $\text{SO}_4^{2-}/\text{Cl}^-$  (0.09–0.12) and  $\text{Na}^+/\text{Ca}^{2+}$  (17–22) with similar values to those of seawater,  $\text{Na}^+/\text{Cl}^-$  (0.80–0.90),  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  (0.38–0.45),  $\text{SO}_4^{2-}/\text{Cl}^-$  (0.09–0.11) and  $\text{Na}^+/\text{Ca}^{2+}$  (20–21), with a proportional increase in the content of these ions from the composition of seawater (Figs. 5 and 6). As the gypsum and halite SI values are undersaturated (−0.70 to −0.10 and −3.11 to −1.82, respectively), these mineral facies are dissolved when seawater enters the aquifer, producing an increase in  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  from an initial solution of marine composition (Figs. 5, 6 and 7). It is also important to note that the marsh is the only hydrogeomorphological unit with some water samples undersaturated in calcite (−0.45 to 0.48), a mineral that could also be dissolved and may increase groundwater salinity.

The  $\delta^2\text{H}$  (−14 to 0.43),  $\delta^{18}\text{O}$  (−1.44 to 0.34) and the deuterium excess (−4.73 to 0.04) values of almost all of the marsh samples show that groundwater has similar isotopic values to those in seawater ( $\delta^2\text{H}$ : −3.0 to 0.2,  $\delta^{18}\text{O}$ : −0.15 to 0.17 and d‰: −2.28 to 0.48). However, there is an increase in  $\text{Cl}^-$  contents from an initial value of 550 mg/L, similar to the seawater concentration, to 1140 mg/L (Fig. 4). This shows that there is an increase in groundwater salinity due to seawater infiltration and the salt dissolution from the soil profile. Besides, the presence of abundant vegetation in the marsh allows salinization to occur due to transpiration, a process that generates an increase in salt concentration but without isotopic fractionation (Humphries et al., 2011a,b; Fass et al., 2007).

However, the presence of halite and gypsum in the soils indicates that any water remaining on the surface that has not entered the aquifer is completely evaporated. The salt-leaching process during seawater inflow is also observed during the spring high tides in the groundwater EC records related to the tides and the water table fluctuations. It is important to highlight that, at spring high tides, sharp increases in the EC of groundwater exceeding the average values of EC of seawater occur, associated with sudden rises in the water table levels (Fig. 3a). Meanwhile, the groundwater levels at quadrature do not oscillate with the tide, but slight increases in the EC of groundwater are recorded associated with water temperature increases, which occur mainly during the sunlight hours (Fig. 3a and c). This EC increase is due to evapotranspiration processes, taking place during daylight hours in the water table.

Mixing processes with water from the groundwater discharge also occur in the marsh, as could be observed in the  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  ionic concentrations with intermediate values between those of the bajadas and those of the sea (Figs. 5a,c, 6a and c), but this is not a dominant process. In their isotopic composition, only three samples move from the marine component to the line of mixed water (Fig. 4), with fans and bajadas showing the contribution of groundwater discharge, which is also observed in the flow maps (Fig. 1).

The isotopic ratios of the fan and bajada groundwater show evaporation processes, where the estimated evaporation percentages reach 12% for the bajadas and 22% for the fans (Fig. 4a). These percentages do not correspond with the ionic content, which can be explained — as shown in the deuterium excess and  $\delta^{18}\text{O}$  vs. chloride graphs (Fig. 4b and c) — by the salt dissolution of the sediment. Unlike what happens in the marsh, in these environments the absence of vegetation or its sparsity dismisses transpiration as a possible groundwater salinization process.

The undersaturated halite SI (−4.16 to −2.69 and −2.26 to −1.62) values in both hydrogeomorphological units (bajadas and fans, respectively) show that the water saline enrichment is caused by the rainwater recharge, which partially evaporates and dissolves the evaporite facies of the sediment (Figs. 4 and 7c). Another facies which is dissolved is gypsum, registering undersaturated SI (−1.32 to −0.41) values together with an increase in sulphate content (8 meq/L to 92 meq/L; Fig. 7b). Finally, groundwater in both the bajadas and fans is oversaturated with respect to calcite, which is the reason why



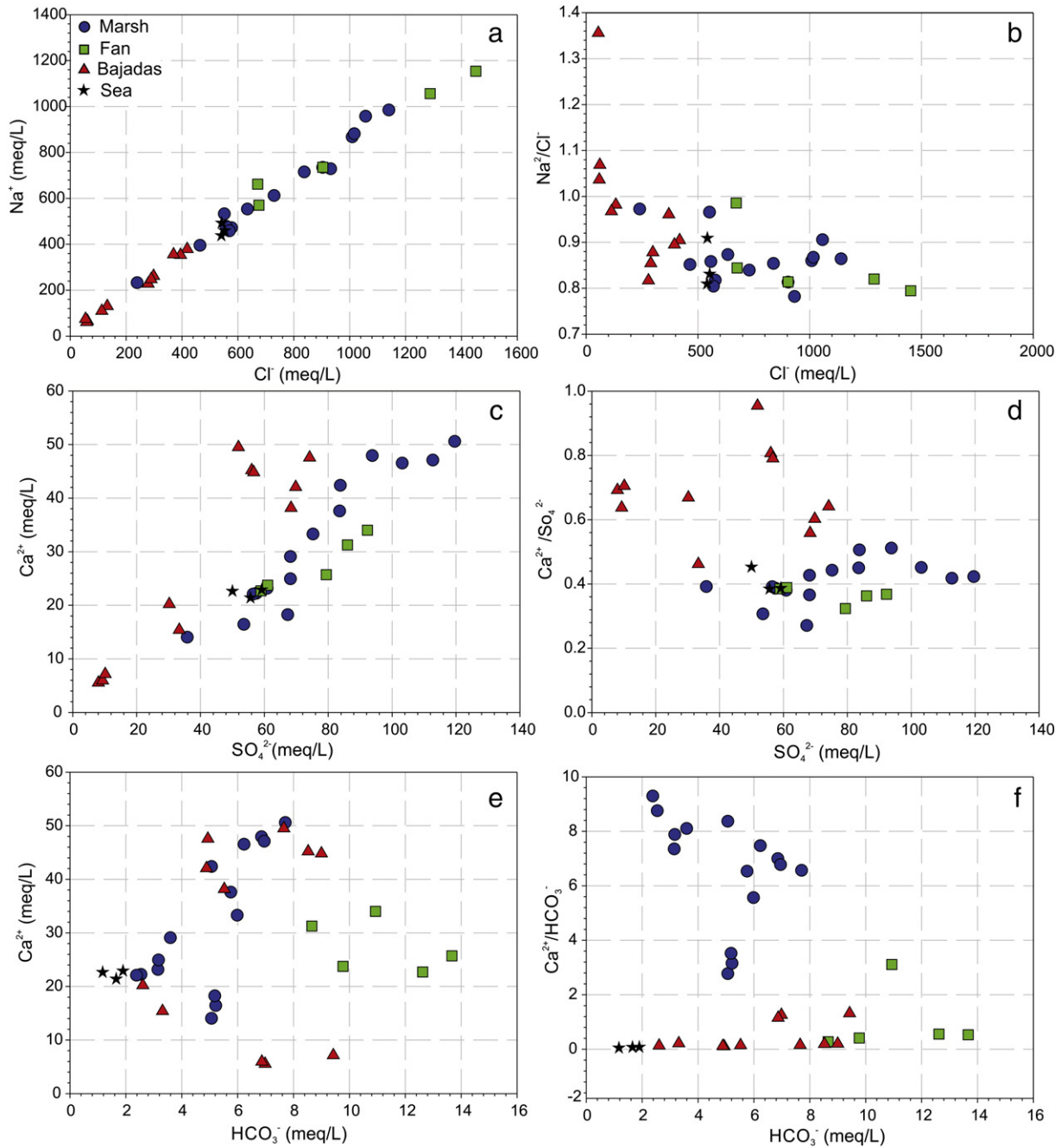


Fig. 5. (a)–(f) Ionic relations.

contributions from the dissolution of calcium carbonate in the sediment are not considered.

### 5. Conclusions

In arid zones, wetland evapotranspiration is the most important component of the hydrological balance, with the contributions related to the tidal flow also standing out in coastal areas. The hydrogeochemical study carried out in the Playa Fracasso wetland, supported by the water balances and hydrodynamic characteristics, demonstrates the role played by evaporation and tidal flows in the processes that condition groundwater quality.

Among the studied hydrogeomorphological units, the marsh is the only one whose hydrodynamics is conditioned by tidal flows. This is reflected in the groundwater chemistry that is mainly of marine origin, enriched by ions in solution originated by the dissolution of evaporite

facies and by evapotranspiration processes. Although environmental isotope relationships indicate that groundwater evaporation is almost null in this environment, the evapotranspiration processes of the seawater that remains on the surface and does not infiltrate into the aquifer are then dissolved by the spring tides and enter into the groundwater by seawater infiltration when the marsh is flooded.

The rainwater that infiltrates in the bajadas and fans is evaporated water; nevertheless, the low percentages of evaporation estimated show that this is not the process responsible for the elevated saline concentrations that occur in the groundwater of these environments. However, as in the marsh, the presence of mineral facies of evaporite origin constitutes the main source of soluble ions in groundwater, which are dissolved by the groundwater flow.

The evaporated values estimated by the balances for the different landforms are always much higher than those calculated by the isotopic

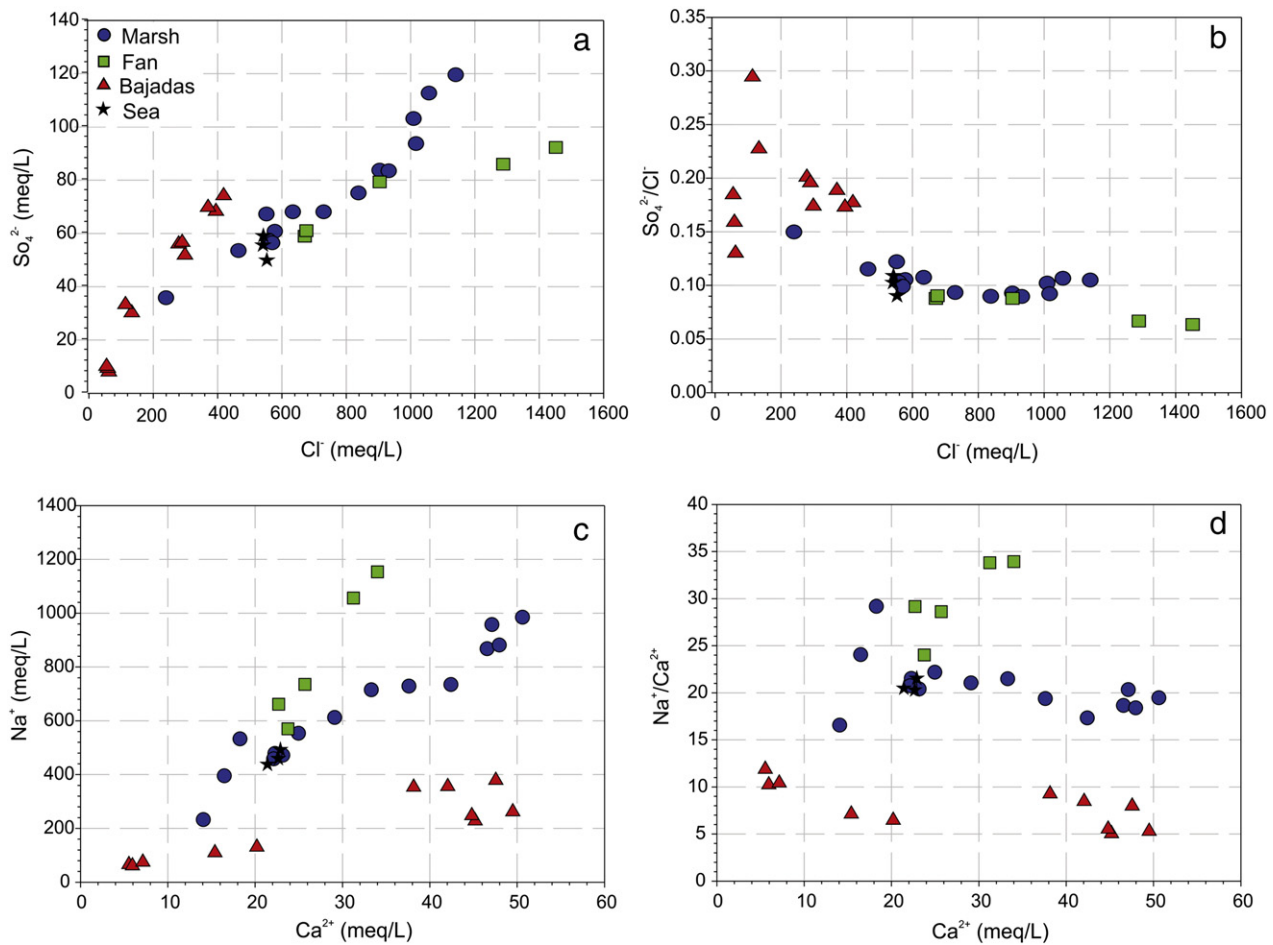


Fig. 6. Ionic relations.

content of the associated groundwater samples. This difference reflects what has been previously interpreted, that is to say, that a portion of the rainwater infiltrates rapidly and, after reaching the aquifer, it experiences little evaporation, as reflected in the isotope, and another portion that remains on the ground until it evaporates completely and from which the salts precipitate, a process in keeping with the arid environment that characterises the site. These salts are then dissolved by the rain or at high tide.

The results obtained show how, directly or indirectly, the evapotranspiration (evaporation and transpiration) processes determine the groundwater hydrochemistry. Evapotranspiration processes have a role mainly related to the development of mineral evapofacies, which are then dissolved by the groundwater flow, and not to the concentration of salts by evaporation.

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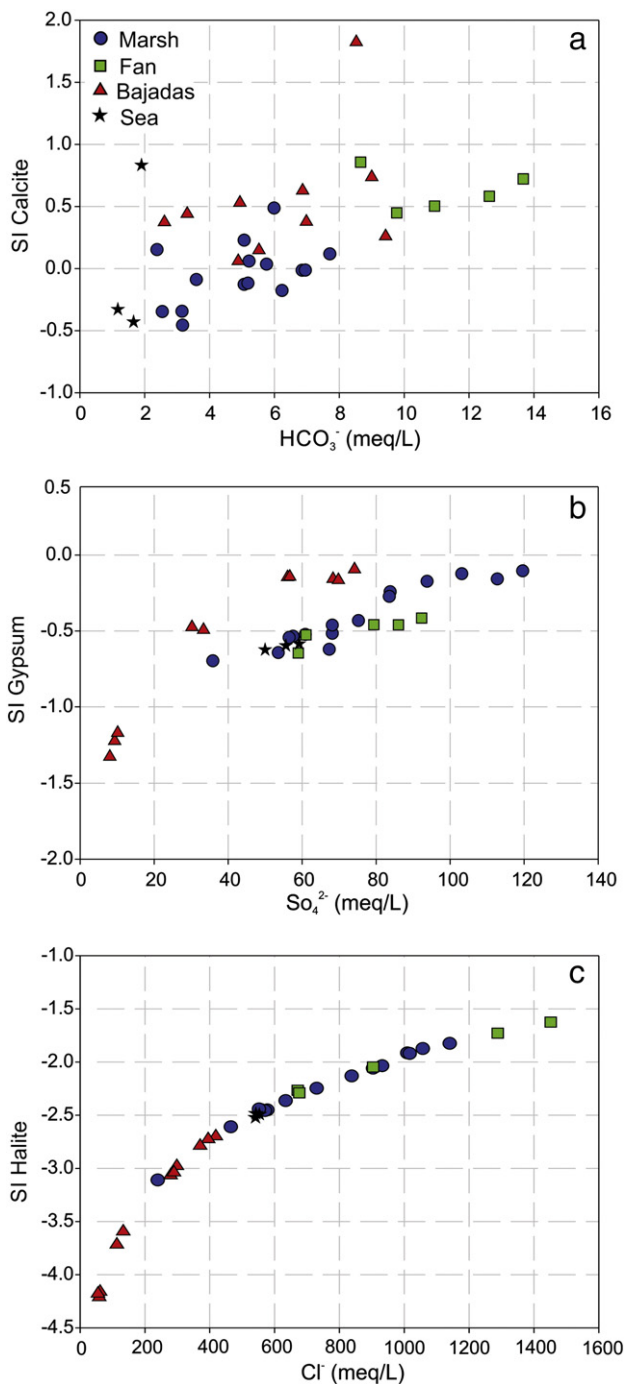


Fig. 7. (a)–(c) Saturation index vs. corresponding anion.

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