

Environmental isotopes applied to the evaluation and quantification of evaporation processes in wetlands: a case study in the Ajó Coastal Plain wetland, Argentina

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Abstract In the Ajó coastal plain, which occurs in the south of the Samborombón Bay, Argentina, certain sectors of the wetland are influenced by the tidal flow, whereas others are not. In the tidally restricted Ajó wetlands, the evapotranspiration process is one of the most important components of the water balance due to fact that the flat morphology and low soil permeability make the flow of surface and groundwater difficult. Although evaporation is an important component of evapotranspiration, a quantitative estimation of this process is still lacking or poorly known. In this work, we quantify the evaporation term in the tidally restricted wetlands by applying isotopic modelling and assessing the hydrological response of the wetland by means of other methodologies, such as satellite imaging and level measurements. The results show that during deficit periods, the total evaporation ranges between 10 and 33 % of the local precipitation. In groundwater samples, it fluctuates between 2 and 13 %, whereas in surface water it varies between 8 and 20 %. Analyses of the water budget, satellite images and water level time series provide evidence on how evaporation processes regulate the hydrology of the wetland. The water balance suggests

the occurrence of a deficit period, in which the satellite images show a reduction of the waterlogged areas and lakes, and a lowering in surface and groundwater level is recorded.

Keywords Water budget · Environmental isotopes · Wetland · Evaporation

Introduction

Wetlands are natural buffer environments that play physical and bio-ecological protection roles. They act as natural sponges, reducing the impact of flooding and of water and sediment pollution, and as protected areas for birds, fish and native plant species.

Wetlands are hydrologically sensitive environments, which is why it is vital to understand the different components of their water cycle. Many wetlands depend on local rainfall falling on their surface, runoff from an area external to the wetland, groundwater discharge, or tidal flows, among others, or on a combination of these (Custodio 2010). Urban development, agriculture and aquaculture may affect the water cycle negatively, impacting the bio-ecology of coastal wetlands through reductions in suitable habitats, biodiversity and nutrient cycling (Jia et al. 2011; Huang et al. 2012; Cui et al. 2014). The water cycle is also influenced by the hydraulic interventions along stream channels and within catchments. Dams, stream channelization, and levee/canal constructions, for instance, alter the spatial and temporal sediment deposition/erosion process trajectories, as well as the superficial and groundwater exchanges, modifying the natural ecohydrology of the wetlands (Brinson and Malvárez 2002; Teal and Weinstein 2002; Mandal et al. 2013).

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Evapotranspiration is, in certain wetlands, one of the most important components of the water cycle, and it represents the consumptive use of the vegetation, as well as the evaporation of surface water bodies and soils with no vegetation. Its estimation is necessary in order to understand the hydrological processes and suggest alternatives for the sustainable management of water. Due to the hydrological complexity and variability of the different types of wetland, there is no unique approach that is most appropriate to estimate evapotranspiration in these environments (Drexler et al. 2004). The evapotranspiration of wetlands has been estimated as a residual in water balance equations, when inflows, outflows, precipitation, change in storage and groundwater discharge or recharge rates can be estimated (Nuttle and Harvey 1995; Mitsch and Gosslink 2000; Jia et al. 2011; Tadic et al. 2013). More recent advances in measuring wetland evapotranspiration include, for instance, moisture flux towers (Goulden et al. 2007; Zhou et al. 2010), scintillometry (Hemakumara et al. 2003; Lenters et al. 2011), analyses based on the type of vegetation (Koerselman and Beltman 1988; Pauliukonis and Schneider 2001; Acreman et al. 2003), surface renewal methods based on heat fluxes over the canopy (Drexler et al. 2004, 2008), diurnal fluctuations in groundwater levels (Dolan et al. 1984; Mould et al. 2011), remote sensing (Kustas and Norman 1996; Courault et al. 2005; Dabrowska-Zielinska et al. 2010; Sun et al. 2010; Cao and Gao 2013). Hydrogeochemical studies based on the isotope ratio of ^{18}O and ^2H identified the qualitative presence of evaporation in surface and groundwater wetlands (Hunt et al. 1998; Ladouche and Weng 2005; Sikdar and Sahu 2009).

The wetland of the Ajó coastal plain, located on the littoral of the Samborombón Bay (Buenos Aires, Argentina), comprises a strip that has a width of approximately 500 m in the northern sector and 50 km in the southern sector, where it reaches its greatest extension (Fig. 1). The wetland extends over 1200 km², with a height that is rarely higher than 2.5 m.a.s.l., showing the predominance on the surface of clayey–silty sediments and the development of badly-drained soils. Within the wetland there are two sectors: an intertidal sector and another one excluded from the tidal flow. The former develops in a marsh environment with a hydrological behaviour that is directly related to the tidal flows of the Río de la Plata estuary (Carol et al. 2011, 2012). The latter comprises the more continental areas, where former tidal channels form depressed sinuous areas with no integrated drainage. The regional hydraulic gradient of the water table is of the order of 10^{-6} , which is why the natural groundwater drainage towards the bay is almost non-existent. The water table lies close to the surface (less than 1 m deep) and it discharges locally into the depressed areas (Carol 2008). These characteristics

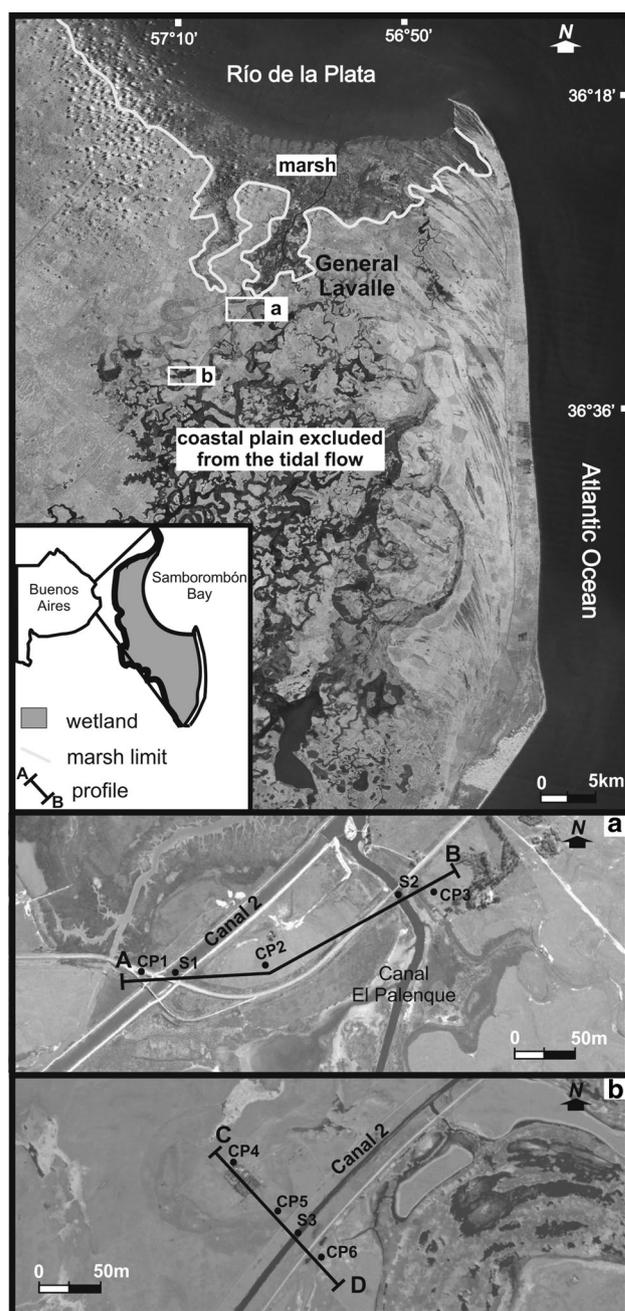


Fig. 1 Location of the study area; **a**, **b** detail of the measurement points and cross-section area

determine that, during rainfall events, rainwater tends to accumulate in the former tidal channels, with water predominantly accumulating on the surface during the months with water excess. Even though the wetland is channelized (Canal 2 and Canal El Palenque), the discharge of the canals is regulated by floodgates that are only opened in case of severe flooding. In turn, the shallow depth of the flooded areas favours evaporation, a process that predominates in periods with water deficit.

The aim of this work is to assess and quantify the evapotranspiration process in the wetland sector excluded from the tidal cycle according to the variations in the hydrodynamics and hydrochemistry of the surface and groundwater, and to quantify such a process on the basis of the hydrogeochemical modeling of environmental isotopes.

Methodology

In this work, environmental isotope data in surface and groundwater are analyzed, together with water balances, satellite images and water level records surveyed between 2005 and 2006.

Water balances were undertaken (Thornthwaite and Mather 1957) for 2005 and 2006 on the basis of monthly temperature and rainfall data from the locality of General Lavalle (Fig. 1). Besides, in order to establish at a global level the periods of water deficit and excess occurring in the region, water balances were carried out considering the climate data of a more extended period (1909–2012).

Landsat visible and near-infrared (VNIR) satellite images were used to assess changes in the water-covered areas, whereas Landsat thermal infrared (TIR) images were used to estimate the variations in surface temperature. On the basis of the water table contour map, surface water (S) and water table (CP) level measurements were carried out in two cross-sections that perpendicularly intersect the groundwater flow and the main canals. The first cross-section is located in the area adjacent to the marsh, whereas the second is located in the central part of the coastal plain (Fig. 1). The groundwater measurement points correspond to 3-m-deep monitoring wells with PVC casing and filter, as well as a pre-filter of carefully selected siliceous gravel.

At the end of a water deficit period (3 March, 2006), surface and groundwater samples were obtained in all the measurement points in order to determine the ¹⁸O and ²H environmental isotope and chloride content. Isotopic ratios, δ¹⁸O and δ²H were measured according to the Coleman et al. (1982) and Panarello and Paricia (1984) methods, respectively, using a Finnigan MAT Delta S mass spectrometer, calibrated against V-SMOW (Gonfiantini 1978). Analytical uncertainties were ±0.2 for δ¹⁸O and ±0.1 for δ²H. The chloride determinations were performed by the conventional methods (Mohr) in accordance with the American Public Health Association (1998).

The hydrogeochemical evolution of the water was studied on the basis of evaporation processes by means of chemical relations, which were quantified by an analytical equation. It was assumed that at the end of the period with water surplus in the wetland there would be a predominance of rainwater accumulated on the surface, whose composition was set as the initial composition. In the

resolution of the equation, it was considered that evaporation increases the concentration of dissolved species in surface water. Solute concentration can be expressed as a function of the evaporated water fraction from a lake. Therefore, the enriched concentration *C'* can be estimated as follows:

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

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 the 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). These conditions apply to the wetland under study due to the fact that no surface watercourses enter or leave it; it accumulates rainwater on the surface and the outflow is regulated by floodgates. Besides, the groundwater flow is not significant, as the slight hydraulic gradient (10⁻⁶) and the low permeability of the sediments (Carol et al. 2008) cause such a flow to be extremely slow, to the point that it could be considered null.

Gonfiantini states that the isotopic composition of surface water, δ, 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:

$$\frac{d\delta}{d \ln f} = \frac{h(\delta - \delta_x) - (\delta + 1)(\Delta \in + \frac{\epsilon}{\alpha})}{1 - h + \Delta \in} \tag{2}$$

where *h* is the relative humidity of the air; δ_{*x*} is the isotopic composition of atmospheric water vapour; α is the equilibrium fractionation factor, being ε = α - 1. After adequate integration, with δ₀ defined as the initial isotopic composition of water at *f* = 1, Gonfiantini's expression for δ(*f*) becomes:

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

with *A* and *B* given by:

$$A = \frac{h\delta_x + \Delta \in + \epsilon / \alpha}{1 - h + \Delta \in} \tag{4}$$

$$B = \frac{h - \Delta \in - \epsilon / \alpha}{1 - h + \Delta \in} \tag{5}$$

Given that the water inflows into the wetland from surface and groundwater flow are not significant, precipitations are the only source of water. On the surface, they are stored in the depressed areas forming lakes, whereas in the subsurface through infiltration they recharge the phreatic water, which occurs at a very shallow depth (generally less than

1 m). For the evaporation line calculation under these conditions, C_0 was considered as the average isotopic ($\delta^{18}\text{O} = -5.8\text{‰}$ and $\delta^2\text{H} = -36.0\text{‰}$) and chloride (10 mg/L) content of precipitation, determined by local rainfall sampling, and the average relative humidity of 0.80 from the General Lavalle station.

Results

Hydrological characterization of the wetlands

The climate is humid temperate with a mean annual precipitation of 1078 mm and alternating dry and wet periods. The monthly water balances estimated by the Thornthwaite and Mather method (Thornthwaite and Mather 1957) on the basis of historical data on precipitation and mean temperatures show that actual evapotranspiration is 759 mm/year, with surpluses being recorded mainly in winter (between March and October) and deficits in summer (between November and February) (Fig. 2). The balances carried out between 2005 and 2006 (Fig. 3) show that in the September 2005—May 2006 period there was a water deficit. Actual evapotranspiration reached values of 686 mm, exceeding the precipitation (646 mm), which is why the evaporation of a portion of the water stored in the soil occurs.

Fig. 2 **a** Precipitation (P), actual evapotranspiration (AET) and mean monthly temperature (T) graph; **b** bar graph showing months with water deficit and surplus

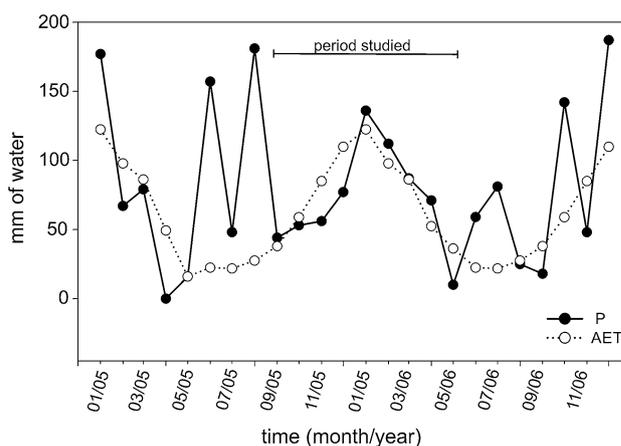
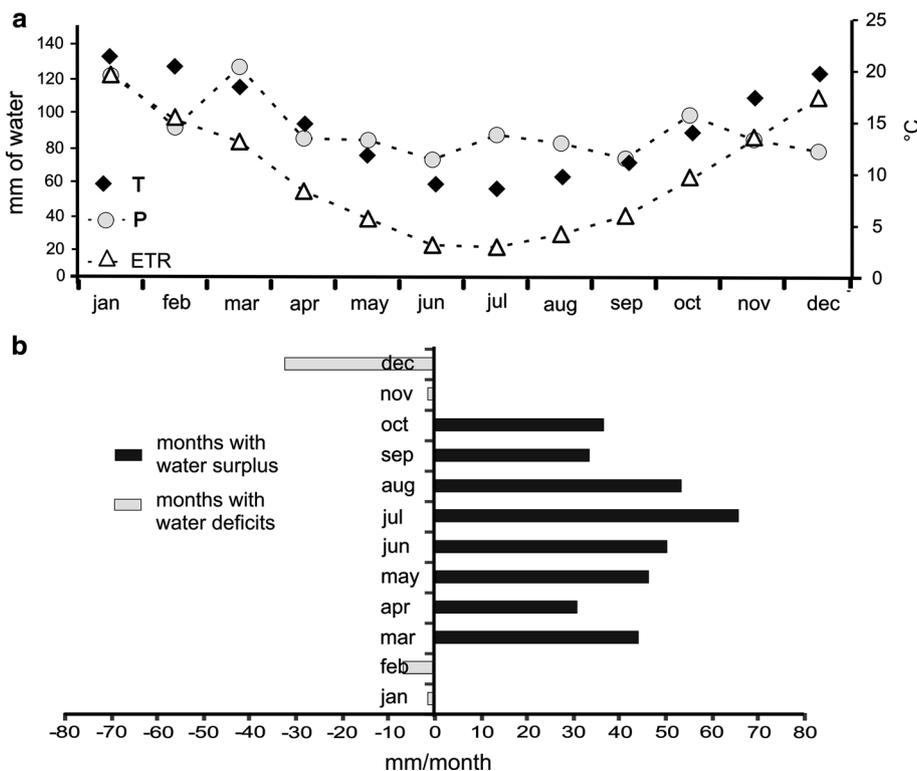


Fig. 3 Monthly precipitation (P) and actual evapotranspiration (AET) for 2005–2006

The analysis of the satellite images between August 2005 and March 2006 shows that towards the end of the months with water surplus (August–October 2005), in the wetland the accumulation of surface water predominates (Fig. 4). The former tidal channels form lakes, which mainly concentrate in the central and southern sectors and which can be observed in the images, in black. Precipitations of 157 and 181 mm recorded in June and August respectively, associated with the low evapotranspiration

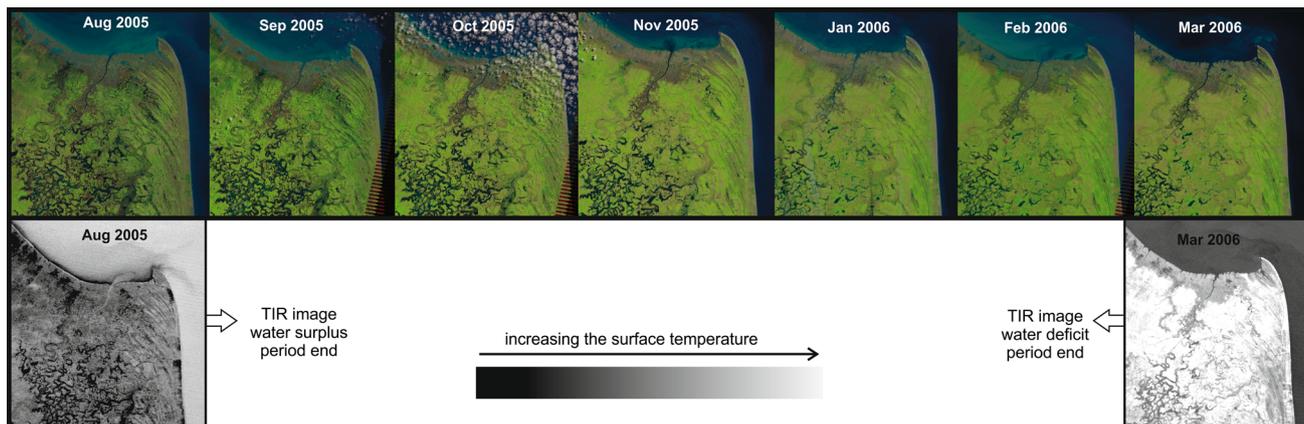


Fig. 4 Landsat images between August 2005 and March 2006. Grayscale images correspond to thermal infrared (TIR) data

occurring in those months (Fig. 3), favor the permanence of water on the surface.

Between August 2005 and March 2006, the increase in surface temperature is evident in the Landsat TIR images (Fig. 4). In August 2005, these show predominating black and dark grey tones (indicating low temperatures), whereas the light grey to white tones (indicating higher temperatures) predominate in March 2006. In this period, precipitations tend to decrease and ambient temperatures are above 15 °C during the months with water deficit. These characteristics lead to a significant decrease in the area covered in water from the beginning to the end of the water deficit period (from November to March). In March 2006, only some former tidal channels with water on the surface can be observed in the southwestern sector (Fig. 4). The higher relevance of evaporation with respect to precipitation as regards the behaviour of the surface water in the wetland during the months with water deficit is evident in January 2006 when, despite the fact that precipitation reached 136 mm (Fig. 3), no increase in the flooded areas was recorded (Fig. 3).

A lowering of the water table and an increase in chloride content in groundwater were recorded between September 2005 and May 2006. In both hydrogeological profiles, it can be observed that in September 2005 the water tables were close to the ground surface (points labelled ‘PC’) and that they deepen during the spring and summer, recording in March 2006 a decrease ranging from 30 to 70 cm (Fig. 5). This deepening of the water tables modifies the surface water—groundwater relation. In September 2005, in the A–B cross-section, groundwater discharges into the canals, whereas in March 2006, this relation is reversed. In the C–D profile, even though both in September 2005 and in March 2006 there is groundwater discharge towards the canal, the hydraulic gradient decreases significantly in March 2006 (Fig. 5). It should be clarified that the decrease

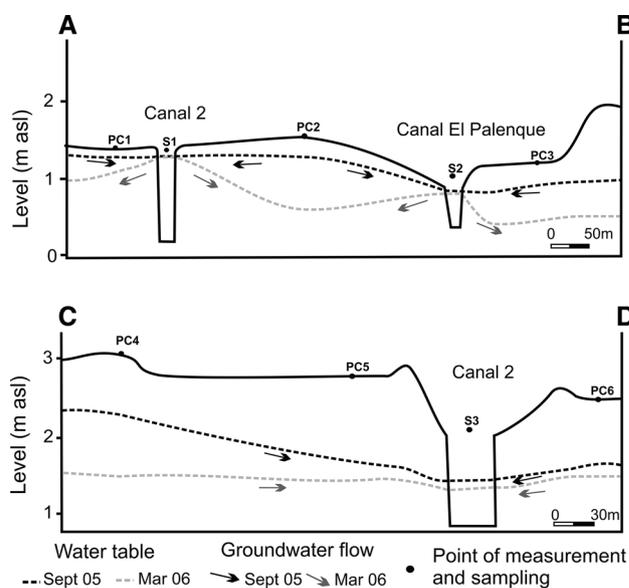


Fig. 5 Topographic profiles indicating the position of the water levels. Location of the cross-section is indicated in Fig. 1

in water levels in the canals is small due to the fact that discharge is regulated by floodgates in order to maximize water accumulation.

Evaporation trend using environmental isotopes

As regards the water chemistry, in the wetland the predominating groundwater is sodium chloride type water. In the relation between $\delta^{18}\text{O}$ as a function of $\delta^2\text{H}$, it can be observed that the surface and groundwater samples deviate from the local meteoric water line $\delta^2\text{H} \text{‰} = 8 \delta^{18}\text{O} \text{‰} + 14$ (Dapeña and Panarello, 2004) and fall along an evaporation line $\delta^2\text{H} \text{‰} = -4.9 \delta^{18}\text{O} \text{‰} - 7.5$ (Fig. 6a). This evaporation line was estimated according to Gonfiantini (1986), by considering a theoretical

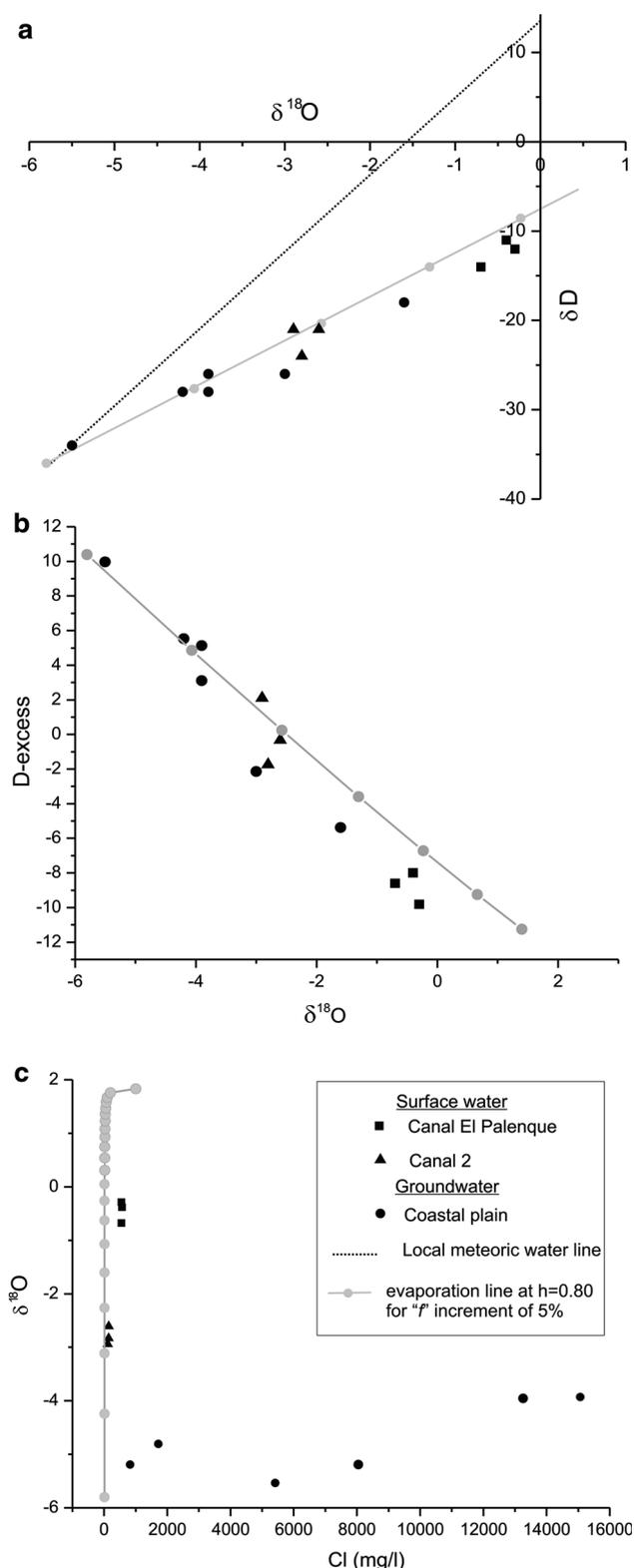


Fig. 6 **a** Relation between environmental isotope content ($\delta^2\text{H}$ as a function of $\delta^{18}\text{O}$); **b** Relation between deuterium excess and $\delta^{18}\text{O}$; **c** Relation between $\delta^{18}\text{O}$ and chloride concentration. In all graphs, both the sampled data and the values estimated by modelling are plotted

evaporation on the basis of the mean values of rainwater isotopes (Panarello and Albero 1983) and the mean atmospheric humidity in the area, which is 0.80. The evaporation line originates from the meteoric water line at $\delta^{18}\text{O} = -5.8\text{‰}$ and $\delta^2\text{H} = -36.0\text{‰}$, with this starting point having 0 % evaporation. As from this point the isotopic enrichment, which occurs due to evaporation, is indicated at 5 % increments in the percentage of evaporation with grey dots on the line (Fig. 6). The location of the samples along the theoretical line makes it possible to quantify the evaporation percentages. Groundwater shows the most variations, with samples in which evaporation percentages between 2 and 13 % can be observed. In turn, the surface water samples related to the Canal 2 show between 8 and 10 % evaporation and those associated with the Canal El Palenque reach evaporation percentages between 17 and 20 %.

The excess of deuterium (d ‰) is a parameter defined by Dansgaard (1964), whose magnitude is controlled by the intensity of evaporation processes (Merlivat and Jouzel 1979). Excess of deuterium values near 14 ‰ are characteristic of meteoric water in the study area (Dapeña and Panarello 2004), while values below this indicate evaporation (the lower the value of excess of deuterium, the greater the evaporation). In the samples, the d ‰ shows values between 10 and -6‰ for groundwater in the coastal plain and between 3 and -10‰ in surface water. These values confirm the relevance of evaporation processes in wetland water, mainly in the surface water where negative values predominate (Fig. 6b).

The relation between the isotopic content ($\delta^{18}\text{O}$) as a function of the chloride concentration shows that only the surface water samples follow a trend directly related to the evaporation of rainwater (Fig. 6c). Both the samples associated with the Canal 2 and those associated with the Canal El Palenque fall along the evaporation line estimated on the basis of evaporation percentages similar to those described above. On the other hand, in the groundwater samples, an increase in chloride concentration associated with a slight isotopic enrichment can be observed.

Discussion

In the different sectors of the Samborombón Bay wetlands, various authors (e.g., Conzonno et al. 2001; Fernandez Cirelli and Miretzky 2004; Carol et al. 2008, 2011; Pousa et al. 2011; Carol and Kruse 2012) quantified the evapotranspiration by means of the Thornthwaite and Mather (1957) method. In every case, the estimated evapotranspiration is similar, with values ranging between 70 and 80 % of the annual precipitation. The mean annual precipitation

is of the order of 1000 mm/year, which means that evapotranspiration varies between 700 and 800 mm/year. It should be noted that the methodology used in those studies does not consider the evaporation and transpiration terms separately. Meanwhile, qualitative analyses, based on the hydrochemistry of major ions (e.g., Fernandez Cirelli and Miretzky 2004) and ^{18}O and ^2H (e.g., Dapeña and Panarello 2004; Carol et al. 2009) of both surface waters and groundwater, identified the evaporation as one of the processes that influences the water chemistry. However, in the literature, a quantitative estimation of the volume of evaporated water is still lacking. The methodology used in this work makes it possible not only to quantify but also to discriminate evaporation and transpiration. Besides, the combined use of images allows the observation of the hydrological response of surface water during the period in which evapotranspiration predominates. As regards groundwater, the response of the water table in this period can also be observed in the hydrogeological profiles obtained through water level measurements.

In the Ajó wetland, the climatic characteristics, the slight hydraulic gradient, the presence of low-permeability sediments and the regulation of the water flow determine that the accumulation of water on the surface of the wetland predominates during rainy periods. These hydrological characteristics that are typical of this wetland allow the application of Gonfiantini's (1986) model to calculate water evaporation, which considers the isotopic enrichment for a drying-up water body, without inflow and outflow, from which the water is removed only by evaporation.

The hydrogeochemical modelling of evaporation—which is based upon the mean values of the environmental isotopes of rainfall and relative humidity—allows for the calculation of the theoretical line along which the wetland surface and groundwater samples fall, and thus quantifies the process of evaporation at the end of a water deficit period. Evaporation in groundwater samples fluctuates between 2 and 13 %, whereas in surface water samples it varies between 8 and 20 %. Deuterium excess values yield similar quantification estimates, in which the low values—above all the negative ones—confirm the relevance of evaporation processes in wetland water. Regarding surface water, the highest evaporation percentages obtained for the Canal El Palenque (between 17 and 20 %) with respect to the Canal 2 (between 8 and 10 %) are due to the fact that in the first case the water body has a larger surface of exposed water and a shallower depth.

If the evaporation percentages obtained by isotopes are compared to the evapotranspiration percentages obtained by water balance, it is possible to discriminate the evaporation and transpiration percentages and thus assess the relevance that water evaporation has in the hydrological cycle of wetlands. Water balances indicate that annually

77 % of rainwater is evapotranspired, whereas a detailed study of the water chemistry suggests that during a water deficit period up to 33 % of the groundwater and water accumulated on the surface may evaporate.

At an annual scale, the water balance shows that between March and October there are water surpluses that favour the formation of lakes. Even though such lakes depend mostly on the accumulation of rainwater, they are also fed by the local discharge of shallow groundwater, which in these periods occurs near the surface. In turn, between November and February there are water deficits, and the increase in evapotranspiration to values greater than those of precipitation causes surface water to be subjected to important evaporation processes, which occur to a lesser extent in the case of shallow groundwater. In this water deficit period (between September 2005 and May 2006), the actual evapotranspiration estimated by water balances is 686 mm (Fig. 3). According to the global estimation carried out on the basis of the environmental isotopes, the direct groundwater evaporation value would be between 13 and 89 mm (corresponding to 2 and 13 %, respectively, of the 686 mm evapotranspired), whereas the evaporation of the surface water in the same period would be between 55 and 137 mm (corresponding to 8 and 20 %, respectively, of the 686 mm evapotranspired).

Isotope content ($\delta^{18}\text{O}$) as a function of chloride indicates that the surface water samples are directly related to rainwater evaporation. There is an increase in chloride in groundwater, which is associated with a slight isotopic enrichment. This tendency may be due to the dissolution of the halite present on the surface of the sediments in some areas of the wetland (Carol et al. 2014). Besides, the presence of vegetation allows the occurrence of salinization due to transpiration, a process which also generates an increase in salt concentration but with no isotopic fractionation (Humphries et al. 2011; Fass et al. 2007). Unlike surface water, which is in direct contact with the atmosphere, groundwater can only evaporate before it infiltrates or through the unsaturated zone, which is why evaporation percentages are expected to be lower.

Conclusions

The study based on environmental isotopes made it possible to estimate the percentage of wetland surface water and groundwater that evaporates, as well as to show how much this represents in the evapotranspiration estimated on the basis of water balances. Besides, the other methodologies used (i.e., satellite image analysis and water level measurements) allowed the visualization of the hydrological response of the wetland in the period in which evapotranspiration dominates the water cycle. The satellite

images provided data on the fluctuations in the waterlogged areas and lakes when there is water deficit, showing that evaporation has regional influence over the entire wetland. Surface and groundwater level measurements show that in the deficit period the levels decrease, as does the hydraulic gradient, and the interrelationship between surface water and groundwater varies.

This work shows how the combination of the different techniques used not only made it possible to quantify evaporation and evapotranspiration, but also gave evidence of the hydrological regulation exercised by this process in the wetland. This methodology, which is supported by a set of techniques, can be applied to wetlands, as well as to other plain environments where evapotranspiration has a significant role in the hydrological behaviour.

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