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Groundwater dependence of coastal lagoons: The case of La Pletera salt marshes (NE Catalonia)

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ABSTRACT

Coastal wetlands are among the most productive ecosystems of the world, playing an important role in coastal defense and wildlife conservation. These ecosystems, however, are usually affected by human activities, which may cause a loss and degradation of their ecological status, a decline of their biodiversity, an alteration of their ecological functioning, and a limitation of their ecosystem services. La Pletera salt marshes (NE Spain) are located in a region mainly dominated by agriculture and tourism activities. Part of these wetlands and lagoons has been affected by an incomplete construction of an urban development and in this moment is the focus of a Life^{+} project, whose aim is to restore this protected area. Several studies have analyzed the role of hydrological regime in nutrients, phytoplankton and zooplankton in this area, however, the role of groundwater was never considered as a relevant factor in the lagoon dynamics, and its influence is still unknown. In this study, the hydrogeological dynamics in La Pletera salt marshes has been analyzed, as a basis to set sustainable management guidelines for this area. In order to determine their dependence on groundwater resources, monthly hydrochemical (with major ions and nutrients) and isotopic ($\delta^{18}O_{H2O}$ and δD) campaigns have been conducted, from November 2014 to October 2015. In particular, groundwater from six wells, surface water from two nearby streams and three permanent lagoons, and sea water was considered in these surveys. Taking into account the meteorological data and the water levels in the lagoons, the General Lake Model has been conducted to determine, not only evaporation and rainfall occurring in the lagoons, but also the total inflows and outflows. In addition, the Gonfiantini isotopic model, together with equilibrium chemical-speciation/mass transfer models, has been used to analyze the evaporation and the physicochemical processes affecting the lagoons. Results show that during the dry season groundwater inputs may account for 15–80% of the water in La Pletera lagoons. Besides, water salinity depends on two main processes: 1) mixing of fresh and sea water occurring within the lagoons or in the aquifer; and 2) evaporation. According to the obtained results, the goal of preserving La Pletera lagoons and their salinity conditions implies maintaining groundwater fluxes towards the ocean, and also the hydraulic connectivity of these lagoons with the aquifer.

1. Introduction

Coastal wetlands have been usually described as the confluence of inland and marine water, being among the most fluctuating and productive ecosystems of the world, and performing a wide range of ecosystem services of socio-economic value to coastal communities. These values include shoreline stabilization, sediment and nutrient retention, high primary and secondary production, fisheries resources, habitat and food resources for terrestrial, aquatic and marine fauna, coastal water quality buffering, biomass and biodiversity reservation, and recreation and tourism amenities (Mitsch and Gosselink, 1993, 2000; Kjerfve, 1994; Costanza et al., 1997; Gopal et al., 2000; Basset et al., 2006; Gedan et al., 2011; Beer and Joyce, 2013). These ecosystems play an important role in coastal defense and wildlife conservation. They can also act as

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sinks or sources of a wide range of substances, such as nutrients, organic matter, pollutants, etc. (Boorman, 1999; Costa et al., 2001, López-Flores et al., 2003; Salvadó et al. 2006).

Coastal lagoons have been classified in different groups depending on their connection to the sea. For instance, Bamber et al. (2001) and Beer and Joyce (2013) have distinguished different sub-types of lagoons according to their physiographic characteristics (isolated lagoons, percolation lagoons, silled lagoons, sluiced lagoons, and lagoonal inlets). Besides, Félix et al. (2015) have simplified their characterization, classifying them in open and closed lagoons, and considering the second group as those that have no connection or a short period of connection to the sea. Closed lagoons have been also termed as landlocked or enclosed lagoons, and have been described as a group of shallow and confined brackish-water systems, highly dependent on freshwater discharges, either from surface run-off or groundwater. Similarly, Kjerfve & Magill (1989) classify lagoons in leaky, restricted and chocked depending on their connection to the sea and to the freshwater circulation. Moreover, in the Mediterranean region there are some coastal aquatic ecosystems, which remain isolated most of the year from any type of surface connection to the sea and to the freshwater sources. These ecosystems, defined as confined coastal lagoons (Trobajo et al 2002), only connect during flooding events, such as sea storms or freshwater floods, but remain without surface inputs the rest of the year (Quintana et al., 1998a; Badosa et al., 2006).

The settlement and structure of biological communities in enclosed lagoons are driven by freshwater inputs, which vary naturally or due to human pressures in their flow rates and biogeochemical characteristics. Changes in the water regime due to human activities have caused water quality degradation, lagoons and wetlands disappearance, or the establishment and expansion of invasive species (Crivelli, 1995; Oltra and Todolí, 2000; Pérez-Ruzafa et al., 2002; O'Connell, 2003; La Jeunesse and Elliott, 2004; Badosa et al., 2007). Furthermore, the level of impact in closed lagoons is also highly dependent on the morphological characteristics of each lagoon, and the result of the combination of both, freshwater inputs and morphological characteristics, determines the particular traits and biological role of these lagoons (Cancela da Fonseca et al., 2001; Basset et al., 2006; Cañedo-Argüelles and Rieradevall, 2010; Félix et al., 2015). Regarding confined wetlands, several studies have analyzed the role of hydrological regime in nutrients dynamics and in the aquatic biota. Sudden inputs during flooding events, and the lack of surface exchanges with the adjacent coastal waters during most of the year strongly determines nutrient dynamics and phytoplankton and zooplankton species composition in these habitats (Quintana et al., 1998a, 1998b; Brucet et al., 2005; Badosa et al., 2006; López-Flores et al., 2006, 2009; López-Flores et al., 2014). However, the role of groundwater has not always been considered as a relevant factor in the lagoon dynamics in ecological studies.

Nevertheless, the aquatic ecosystems dependence on groundwater is well known (Sear et al., 1999), and it has been studied using a wide range of methodologies, characterizing the spatial and temporal variability of surface water-groundwater interactions (Sophocleous, 2002; Kalbus et al., 2006; Martínez-Santos et al., 2010; Menció et al., 2014). For instance, in streams and rivers this relationship has been assessed using: direct measurements of water flux with seepage meters or similar devices (e.g., Kelly and Murdock, 2003); heat tracers or thermal studies based on temperature time series in both surface water and groundwater systems (e.g., Conant et al., 2004; Schmidt et al., 2006); methods based on Darcy's law, such as point measurements that investigate the hydraulic gradient established between groundwater level and stream stage, or potentiometric maps (e.g., Woessener, 2000; Brodie et al., 2007); mass balance methodologies or water budgets, based not only on streamflow measurements (e.g. Harvey and Wagner, 2000; Davie, 2002, Hannula et al., 2003), but also on hydrochemical and environmental tracers (e.g., Négrel et al., 2003; Pretty et al., 2006, Mas-Pla et al., 2013a; Mas-Pla et al., 2013b); and finally, analytical and numerical modeling techniques based on governing mathematical equations (e.g., Nyholm et al., 2002; Rodríguez et al., 2006; Mas-Pla et al., 2012). In the particular case of lagoons, the two main approaches that have been used to assess surface water-groundwater interactions are: heat, geochemical and isotopic tracers (e.g. Mudge et al., 2008; Santos et al., 2008; Shubert et al., 2011; Duque et al., 2016; Sadat-Noori et al., 2016), and modeling (e.g. De Pascalis et al., 2009; Martínez-Alvarez et al., 2011; Hipsey et al., 2014; Read et al., 2014; Yao et al., 2014). Several lake models have been developed for specific purposes, such as lake level, water thermal processes, ice dynamics, or nutrient and quality management. Among these models, the General Lake Model (GLM) has been developed to combine fluxes of mass and energy with a Lagrangian layer structure that adapts to changes in vertical gradients, including energy budget algorithms with mixing schemes (Hipsey et al., 2014). However, most of the studies conducted using this GLM have been specifically used to conduct temperature simulations in lake profiles (e.g. Read et al., 2014; Yao et al., 2014).

La Pletera salt marshes are located in the north of the mouth of the Ter River (NE Spain; Fig. 1), in a region mainly dominated by agriculture and tourism activities. They are composed of several coastal lagoons and wetlands that were affected by the incomplete construction of an urban development in 1987. This area has been the focus of a Life^{+} project (http://lifepletera.com/es/life-pletera/), whose aim is to restore this protected area and to recover its ecological functionality. It has been described as a confined Mediterranean coastal ecosystem due to its isolation from the sea and from continental fresh waters (Trobajo et al 2002; Badosa et al., 2006; López-Flores et al., 2006). Although surface water inputs in this area are well characterized, it is still not well known if groundwater circulation plays a significant role in the hydrological balance of the lagoon.

In this paper, we analyzed the hydrogeological behavior of La Pletera salt marshes, as a representative example of confined coastal lagoons. Our aim was to determine their dependence on groundwater resources to find out if water circulation in such confined lagoons is mainly determined by sudden surface inputs or, on the other hand, it is mainly driven by groundwater circulation. To know the hydrological dynamics is essential in order to set sustainable management guidelines for these specific types of ecosystems. In order to assess the main objective of this project the GLM has been used to analyze, not only the energy fluxes in the lagoon, but also the water mass fluxes, together with geochemical and isotopic modelling. Therefore, this study presents a comprehensive approach of the distinct characterization methods to determine surface water-groundwater interactions in lagoons.

2. Study area

La Pletera salt marshes are located in the Baix Empordà tectonic basin (NE Spain; Fig. 1). This basin was formed during the distensive period of the Alpine orogenesis and is delimited by the Montgrí Range at the north, characterized by Mesozoic limestone formations, and by the Gavarres Range at the south, composed of igneous and metamorphic rocks of Paleozoic age. The basement of this tectonic graben presents Paleozoic and Paleogene sedimentary materials, which were severely affected by the distensive period of the Alpine orogenesis (Mas-Pla and Vilanova, 2001; Montaner, 2010).

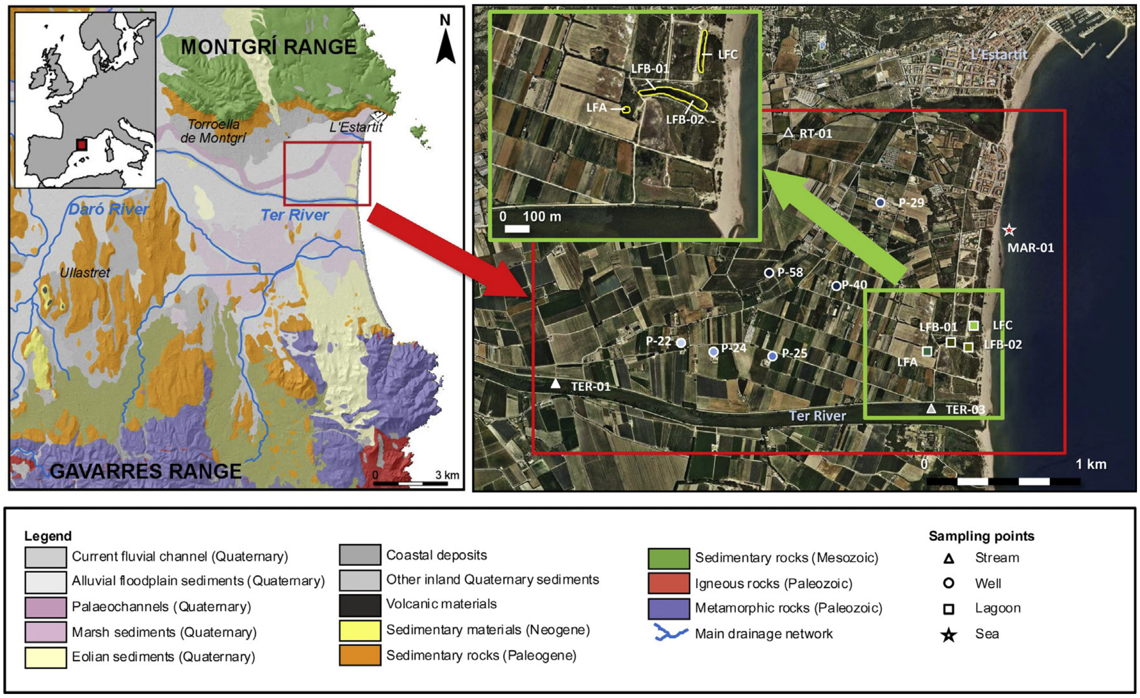

Fig. 1. Geographical and geological setting.

The basin infilling is mainly composed of Quaternary sediments. These sediments consist of fluvial deposits originated by the Ter River, as well as by some other minor streams, with a maximum depth of 50–60 m in the central part of the basin. According to the sedimentary sequence, three principal units can be distinguished (Montaner, 2010):

1) a deep level of fluvial coarse sediments (gravels and sands) about 20 m thick in the littoral area, covered by a 35 m layer of fine sediments (silt and clay);
2) an intermediate level formed by an heterogeneous sediment layer about 5 m thick close to the littoral, where is composed of sands deposited in beach environments; and about 15 m thick in distal parts of the basin, where alluvial sandy-lenticular bodies in a silty-sandy level are distinguished. In both cases, these sediments are covered by a level of fine sediments of 35 m thick;
3) a shallow level with a thickness of 10–20 m, formed by the present prograding alluvial deposits, which near the coast line are substituted by marsh and coastal deposits.

Hydrogeologically, the fluvial sediments can be considered as a multilayer aquifer, with the deep and coarse levels of units 1 and 2 acting as leaky aquifers, and the shallow coarse levels of unit 3 acting as an unconfined aquifer. Geoservei (2008) and Montaner (2010) studied the hydrogeological dynamics of the unconfined aquifer and concluded that: a) there is a gaining stream situation in this shallow aquifer along the study area; and b) old paleochannels act as preferential paths for groundwater due to the presence of coarse sediments. In addition, high salinities have been detected in this aquifer linked to sea water intrusion mainly associated to the estuary character of the Ter River in its lowest reach and to the marsh deposits; while in the areas where the old paleochannels are located, the values of salinity are significantly lower due to a larger groundwater discharge.

The study area presents a subhumid Mediterranean climate with a mean annual temperature of 16 °C, and mean temperatures of 25 °C in summer and 10 °C in winter. Average rainfall is about 590 mm/year, with the highest rainfall periods in spring (140 mm) and autumn (200 mm; Estartit meteorological station, 1966–2016 period; Pascual, 2017; www.meteolesrtartit.cat and Montaner, 2010). The dry and strong wind from the NNW (with common speeds of 100 km/h) is the most prominent feature of the regional meteorology and is a very important factor in the sand transport of this area, exerting a strong influence over the morphology of the beach, the sand dunes, and the overall coastal morphology.

The main river in the study area, the Ter River, presents a mean discharge of 8.74 ± 0.29 m^3/s in Torroella de Montgrí (2006–2016 period; ACA, 2016, www.gencat.net/aca). Although flooding caused by this river usually affected the alluvial plain, the hydrology of this area has been significantly modified since the 1960s, with the regulation of its discharge, based on the construction of several dams upstream and the river channeling in the studied reach in the 1970s (Badosa et al., 2006). In addition, several levees were also constructed in different points of the marsh area, isolating some of the studied lagoons from surficial freshwater runoff.

The herein studied lagoon system of La Pletera salt marshes is composed of three permanent lagoons (LFA, LFB and LFC in Fig. 1 and Table 1). The main characteristics of these lagoons are summarized in Table 1. While the origin of LFA and LFB lagoons was the abandonment of a river channel, LFC was built in a first phase of

Table 1
The main characteristics of the studied lagoons during the studied period (from November 2014 to October 2015).

Lagoon	LFA	LFB	LFC
Max depth (m)	1.5	3.0	1.9
Min depth (m)	0.2	1.6	1.0
Max Volume (m^3)	1295	22956	2391
Min Volume (m^3)	20.5	2432	751
Max Surface (m^2)	5387	17290	2467
Min Surface (m^2)	113	4214	1493
S/V (m^2/m^3)	4.16–5.51	0.75–1.73	1.07–1.98

the Life Restoration Project in 2002. Previous studies conducted in these lagoons have considered them as meso-euhaline water bodies (Badosa et al., 2006; López-Flores et al., 2006; López-Flores et al., 2014).

This zone is subject to a micro-tidal regime, with a spring tidal range about 0.15 m, which is characteristic of the Mediterranean region. These variations are not observed in the lagoons, showing no influence in their water level (Quintana et al., 1998a). The most important water inputs occur suddenly during intense precipitations and cyclonic storm events (mainly in spring and autumn), when freshwater, as well as sea water, may enter these lagoons. In particular, during cyclonic storm events associated to stronger easterly winds (known as "Llevantades"), sea level may rise more than 1 m (Marquès et al., 2001). In these periods, sea waves may enter in some of the lagoons (LFB and LFC) as surface water inputs. This input, together with freshwater surface (overland flow), subsurface (which percolate laterally through the topsoil) and ground water inputs, may cause an increase of 0.3–0.9 m. Therefore, different studies have considered these lagoons as being dependent on sudden and irregular intrusions of seawater (during cyclonic storms) and fresh water (during periods of intense rainfall), and being later affected by the lack of a continuous water supply for long periods of time, thus tending towards their desiccation (Brucet et al., 2005; Badosa et al., 2006; López-Flores et al., 2006, 2009; López-Flores et al., 2014). Such explanations neglected the role of groundwater in the lagoons hydrodynamics.

3. Methods

In order to study the hydrogeological dynamics and the dependence on groundwater of La Pletera lagoons a total of 12 sampling campaigns were conducted, on a monthly basis (from November 2014 to October 2015). In particular, groundwater from six wells, one seawater sample, and eight surface water samples from nearby streams and permanent lagoons was taken in these surveys (Fig. 1). After their collection, samples were stored in a fridge (at 4 °C in a dark environment) for subsequent analyses. Samples for ion analyses were previously filtered (0.22 μm).

Physicochemical parameters, such as pH, electrical conductivity (EC), redox potential (Eh), dissolved O_2 (DO) and temperature were measured *in situ*. Groundwater samples were taken under pumping conditions and a flow cell was used to avoid contact with the atmosphere for the measurement of physicochemical parameters. EC and temperature were determined in the field with a Crison CM35 portable conductivity meter with a temperature measurement capability (accuracy EC $\leq$ 0.5%; temperature $\leq$0.2 °C); pH and Eh were also measured *in situ* with a WTW-330i pH/mV meter (accuracy pH $\leq$ 0.003 pH; Eh $\leq$ 0.2 mV); Dissolved Oxygen was measured with a Crison OXI45 P portable meter (accuracy DO $\leq$ 0.5%).

CO_3^{2-} and HCO_3^- were determined using Gran titration (their inter-day average precision with percent relative standard deviation, RSD%, was <1%); nitrogen as total Kjeldahl nitrogen (TKN) and total organic carbon (TOC) were analyzed using catalytic oxidation (RSD% <1%); Cl^-, SO_4^{2-}, F^-, Br^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, and NH_4^+ were determined using ion chromatography (RSD% of 2.88%, 2.23%, 1.61%, 1.86%, 7.00%, 1.09%, 3.56%, 8.08%, and 2.82%); and NO_2^-, NO_3^-, PO_4^{3-} and Total Phosphorus (TP) were determined by spectrophotometry (RSD% of 2.82%, 2.44%, and 3.42%). The quality of the chemical analysis was checked performing the ionic mass balance, with all samples showing an error lower than 5%.

Isotopic characterization ($\delta^{18}O$ and δD) of water samples was obtained by pyrolysis at 1400 °C, using the Thermo Scientific Flash EA 1112HT with a ConFlo III open split interface, and an Isotope Ratio Mass Spectrometer Thermo Scientific Delta V-Advantage. Values are reported in per mil, using the δ-notation relative to V-SMOW (Vienna Standard Mean Ocean Water) reference material. The average uncertainties for $\delta^{18}O$ and δD on individual analyses for high salinity samples were in the order of ±0.14‰ for $\delta^{18}O$, and ±0.92‰ for δD.

The GLM (General Lake Model), developed by Hipsey et al. (2014), computes vertical profiles of temperature, salinity and density by accounting for the effect of inflows/outflows, mixing and surface heating and cooling. GLM incorporates a flexible lagrangian layer structure similar to the approach of several 1-D lake model designs (Imberger and Patterson 1981; Hamilton and Schladow 1997). The lagrangian design allows for layers to change thickness by contracting and expanding in response to inflows, outflows, mixing and surface mass fluxes. The bathymetry of the lagoons has to be introduced in the model, and as the model progresses through time, density changes due to surface heating, vertical mixing, and inflows and outflows lead to dynamic changes in the layer structure, and therefore to a new lagoon surface and volume which are obtained as an output from the model.

The model accounts for the surface fluxes of momentum, sensible heat and latent heat using the commonly adopted bulk aerodynamic formulae. The flux of evaporation (F_e) in kg m^{-2} s^{-1} is estimated from the formula:

$$F_e = \rho_a C_E U_x (Q_o - Q) \tag{1}$$

where ρ_a is the air density, C_E is the bulk aerodynamic coefficient for latent heat transfer, U_x is the wind velocity, Q_o is the saturation specific humidity at the surface water temperature and Q the specific humidity at the meteorological station. The accuracy of F_e would decrease as the average time for the calculation of F_e increases. For example, different studies (Zhang, 1997) show that monthly mean data can be used to estimate monthly mean surface evaporation to within a relative error of about 10%.

Water levels in the lagoons were considered on a daily basis, determining the mean value of the water level measured every hour, using Schlumberger water level data loggers (accuracy ±2 mm). By means of the bathymetry and the daily water depth, the water volume and surface of the lagoons were determined. With this information, GLM has been used to evaluate the different water fluxes: inflows, outflows, rain and evaporation by adjusting them to the daily known water volume. This process has been developed through the following steps: first total inflows and outflows have been estimated from the known water volumes. Secondly, the evaporation fluxes have been calculated from the model and taken into account together with the rain fluxes in order to get the inflows and outflows due to total water intrusions in the lagoons. Finally, the model was run with these inflows and outflows to corroborate that the total volume and the experimental temperature adjust to experimental values.

IBM SPSS Statistics 23 was used to conduct normality tests (Kolmogorov-Smirnov test) of data, and to evaluate the differences among groups of samples (Mann-Whitney *U* test and Kruskal-Wallis test were used, since most of the variables were not normally distributed). While the Mann-Whitney *U* test is the non-parametric alternative test to the independent sample *t*-test; the Kruskal-Wallis test is a non-parametric test alternative to the One Way ANOVA (Ferrán, 2001). Additionally, bivariate Pearson Correlations have been calculated to analyze whether a statistical significant linear relationship existed between variables and the strength of this relationship.

Hydrochemical data were interpreted with the assistance of the equilibrium chemical-speciation/mass transfer model PHREEQC 3.3.0 (Parkhust and Appello, 1999). A mixing model using the most characteristic samples of sea water and groundwater (M-01 in campaign 2 and P25 in campaign 11), and an evaporation model considering the previous results, were conducted to analyze the origin of lagoon samples. In addition, an inverse model was also conducted to deduce the geochemical reactions that account for the change in chemical composition of water through time, and to calculate the changes in moles of each element by dissolution, precipitation and/or redox changes. This model was conducted using the data of campaigns 3 and 9, being respectively the campaigns characteristic of the lowest and the highest evaporation detected in the lagoons. The uncertainty value taken was 2.5%.

Complementary to the previous analysis, an evaporation model considering the isotopic enrichment of an evaporating surface water body, based on Craig and Gordon (1965) approach, and described also in detail by Gonfiantini (1986), was taken into account. According to Gonfiantini (1986), the isotopic composition of surface water, δ, varies as the residual or remaining fraction of the water volume, $f = V/V_0$, diminishes following a Rayleigh distillation process. The relation between these two variables for high salinity evaporating waters is expressed as:

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

where h is the air relative humidity; a_w is the water activity coefficient; δ_α is the isotopic composition of atmospheric water vapor; α is the equilibrium fractionation factor between liquid and vapor; $\Delta\in$ is the kinetic enrichment factor; and Γ, related to the effect of isotopic fractionation in ion hydration can be described as:

$$\Gamma = \frac{55.56}{Mn(\alpha_H - 1) + 55.56} \tag{3}$$

where M is the salt molality; n is the hydration number, and α_H is the hydration fractionation factor. In the studied samples, the value of M was lower than 4 mols/kg and the value of Γ was close to 1.

In the case of the kinetic enrichment factor, $\Delta\in$, it has been described as:

$$\Delta\in = K\left(1 - \frac{h}{a_w}\right) \tag{4}$$

where K is 14.2‰ for ^{18}O and 12.5‰ for ^{2}H.

And finally, the water activity coefficient (a_w) can be defined, for a sodium chloride solution having an initial activity of 0.98 (similar to seawater), as:

$$a_w = -0.000543f^{-2} - 0.018521f^{-1} + 0.99931 \tag{5}$$

For those cases where the lake volume varies along the evaporation processes, if the inflow becomes negligible, the evolving lake-water isotopic composition may be estimated integrating Eq. (1) by steps.

All the meteorological data required for Gonfiantini and General Lake models, such as temperature, precipitations and air relative humidity, were obtained from the Estartit weather station in a daily or hourly basis (Fig. 1).

4. Results

4.1. General Lake model

The General Lake Model (GLM) has been used in this study to determine inflows, outflows, rain and evaporation affecting La Pletera lagoons, taking into account the meteorological data in this area, and also the bathymetry and the daily water level variations of the three lagoons (Fig. 2). In this model, inflow and outflow are interpreted as the total surface, subsurface and groundwater flows entering or outgoing the lagoons, apart from rainfall and evaporation. Monthly results of these models are summarized in Tables 2 a, 2b and 2c, considering the monthly period between sampling campaigns.

The most important cyclonic storm events, with direct sea water inputs into some of the lagoons, occurred in November of 2014, and March and October of 2015 (Fig. 2). These events also coincided with the most important rainfall episodes, with accumulated precipitations of 113.4, 59.8 and 59.0 mm, respectively. Additionally, freshwater subsurface inputs and groundwater inputs occurred, implying an increase of the total volume of water. In Tables 2a, 2b and 2c, positive differences in the relation between inflow and outflow (In-Out) are detected in these periods in all the lagoons (except for LFC in March), being also the periods with the highest modeled inflows. Moreover, the highest outflows were also detected during and after these storm events (Tables 2a, 2b and 2c).

In some other periods a positive difference between inflow and outflow has been detected (Tables 2a, 2b and 2c), indicating the occurrence of higher groundwater inputs in the lagoons. This is the case of the summer season, when positive values are obtained in all the lagoons. In this season, some of the highest values of monthly % of evaporation are detected, especially in LFA. While in LFB and LFC the highest % are detected from March to August, with mean values of 17.1 ± 1.7% and 10.6 ± 2.8%; in LFA, due to the significant reduction of the water volume remained in the lagoon, the highest values of monthly % of evaporation are detected between March and October, with 24.0 ± 8.5%.

4.2. Hydrochemical and isotopic data

The Piper diagram has been used to classify and describe the different water samples in the study area. According to this diagram (Fig. 3), and the hydrochemical data summarized in Table 3 (and Supplementary Material SM1 and SM2), two main groups of samples can be distinguished:

- A first group is composed of freshwater samples, from both the alluvial aquifer and streams. This group presents a Ca-HCO_3 facies and a low EC, with mean ± standard deviation values of 1,200 ± 265 and 999 ± 890 μS/cm, respectively; tending to higher concentrations of Na^+ and Cl^- close to the sea (showing in these cases Na-Ca-HCO_3 facies). However, significant differences between aquifer and stream samples have been also observed (Table 3 and Fig. 4). This is the case of DO, N_{org}, TOC, PO_4^{3-}-P, NO_2^--N, which usually present higher concentrations in surface waters than in groundwaters, or the concentrations of HCO_3^-, SO_4^{2-}, Mg^{2+} and Ca^{2+}, which are significantly higher in the aquifer samples.
- The second group is constituted by high salinity samples (with a Na-Cl facies) from the sea and lagoons, but also by some of the stream samples collected close to the mouth of the Ter River during storm events. Although sea and lagoon samples show similar EC values, the variability in the lagoons EC values is higher, showing a mean ± standard deviation of 44,700 ± 22,800 μS/cm (Table 3). Regarding the main ions concentrations, these two groups of samples do not present significant differences in Na^+, Cl^-, Br^-, K^+ and Mg^{2+}; but significant differences are observed in Ca^{2+} and SO_4^{2-} concentrations, which are higher in sea samples, and HCO_3^- and CO_3^{2-} content, which is higher in lagoon samples (Fig. 4). Finally, significantly lower concentrations of nutrients, such as PO_4^{2-}-P total phosphorus (TP), total nitrogen (TN) and organic nitrogen (Norg), are detected in sea samples, and no differences between NH_4^+-N, NO_2^--N, NO_3^--N and TOC were found (Table 3 and Fig. 4).

To assess the temporal hydrochemical characteristics and evolution of La Pletera lagoons, five sampling points were selected: one point in LFA and LFC, and three points in LFB. Due to its heterogeneous shape, two points were selected in LFB close to its surface

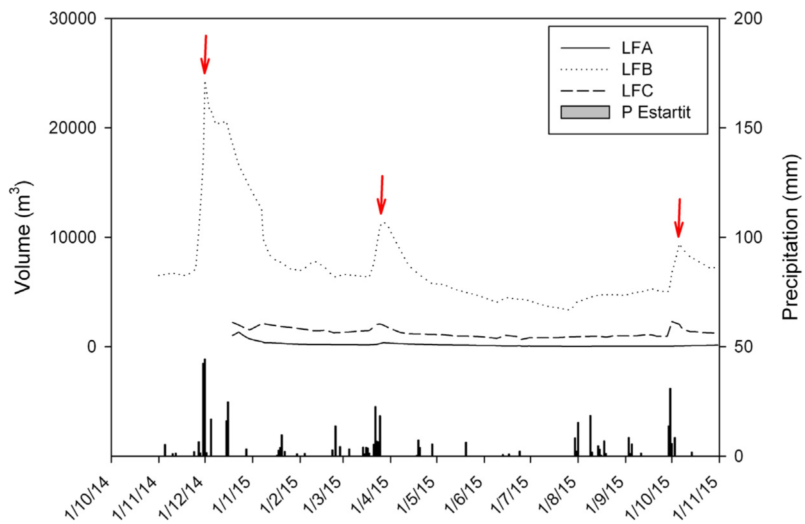

Fig. 2. Precipitations (P) in the Estartit weather station (in mm) and water volume evolution (in m^3) during the study period in LFA, LFB, and LFC lagoons. Legend: red arrows indicate cyclonic storm events. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2a
General Lake Model results, in a monthly basis, for LFA lagoon (in m^3). Legend: Vin, initial volume; Vfin, final volume; Evap, evaporation output as total volume (in m^3), and as percentage (%); Rain, rain water input; Inflow, water input as surface, subsurface and groundwater; Outflow, water output as surface, subsurface and groundwater; In-Out, difference between Inflow and Outflow.

Period	Vin (m^3)	Vfin (m^3)	Vfin-Vin (m^3)	Evap (m^3)	Evap (%)	Rain (m^3)	Inflow (m^3)	Outflow (m^3)	In-Out (m^3)
Nov14–Dec14		1295.83							
Dec14–Jan15	1295.83	386.17	−909.66	−92.28	−7.12	4.52	314.50	830.06	−515.56
Jan15–Feb15	386.17	251.77	−134.40	−39.90	−10.33	4.47	0.00	90.01	−90.01
Feb15–Mar15	251.77	209.90	−41.87	−28.25	−11.22	7.06	0.00	20.83	−20.83
Mar15–Apr15	209.90	265.83	55.93	−57.41	−27.35	27.75	184.50	102.93	81.58
Apr15–May15	265.83	154.03	−111.80	−39.92	−15.02	0.00	0.00	70.81	−70.81
May15–Jun15	154.03	80.99	−73.04	−28.91	−18.77	3.29	8.38	53.53	−45.15
Jun15–Jul15	80.99	34.20	−46.78	−26.05	−32.16	0.00	27.22	48.17	−20.95
Jul15–Aug15	34.20	33.47	−0.73	−12.62	−36.90	10.40	14.32	10.03	4.29
Aug15–Sep15	33.47	32.01	−1.46	−5.02	−15.00	6.26	6.21	5.83	0.38
Sep15–Oct15	32.01	87.24	55.23	−7.23	−22.58	10.49	58.05	2.50	55.55
TOTAL	1295.83	87.24	−1208.59	−337.60	–	74.22	613.17	1234.69	−621.52

Table 2b
General Lake Model results, in a monthly basis, for LFB lagoon (in m^3). See Table 2a for legend.

Period	Vin (m^3)	Vfin (m^3)	Vfin-Vin (m^3)	Evap (m^3)	Evap (%)	Rain (m^3)	Inflow (m^3)	Outflow (m^3)	In-Out (m^3)
Nov14–Dec14	8036.22	19793.35	11757.12	−813.41	−10.12	2330.10	16143.74	4562.63	11581.11
Dec14–Jan15	19793.35	10288.42	−9504.93	−627.41	−3.17	69.60	53.87	9244.97	−9191.10
Jan15–Feb15	10288.42	8847.39	−1441.02	−804.41	−7.82	69.58	445.98	1041.99	−596.02
Feb15–Mar15	8847.39	7378.09	−1469.31	−1013.69	−11.46	258.61	182.80	992.75	−809.94
Mar15–Apr15	7378.09	7888.53	510.44	−1441.28	−19.53	806.40	5201.12	4030.05	1171.07
Apr15–May15	7888.53	5465.33	−2423.20	−1251.68	−15.87	0.00	0.00	1230.00	−1230.00
May15–Jun15	5465.33	4222.86	−1242.46	−950.78	−17.40	85.22	355.00	771.93	−416.93
Jun15–Jul15	4222.86	2812.80	−1410.06	−787.14	−18.64	0.00	10.73	701.92	−691.20
Jul15–Aug15	2812.80	3867.09	1054.28	−562.10	−19.98	136.04	1458.94	224.54	1234.40
Aug15–Sep15	3867.09	4162.91	295.83	−443.42	−11.47	119.21	674.08	175.66	498.41
Sep15–Oct15	4162.91	7106.57	2943.66	−568.02	−13.64	272.45	4376.30	1292.71	3083.60
TOTAL	8036.22	7106.57	−929.65	−9263.33	–	4147.21	28902.57	24269.15	4633.41

in western and eastern positions (LFB-01s and LFB-02, respectively), and one additional point close to its bottom in the western position (LFB-01p), where the lagoon is deeper than 2 m (Table 1). For the sake of simplicity, only one of the three different sampling points in LFB (LFB-01s) has been represented in Fig. 5a–c, where the evolution of some of the most representative parameters has been also plotted for LFA and LFC. In addition, the evolution of the same representative parameters for the three sampling points in LFB (LFB-01S, LFB-01P and LFB-02) have been represented in Fig. 5d–f.

Although LFA is the most inner lagoon, it shows the highest EC values (60,300 ± 39,400 μS/cm), together with the highest ionic concentrations (Fig. 5, SM1 and SM2). Its concentrations are similar to those detected in the deeper layers of LFB during stratification (from October to April, approximately), with mean EC values in LFB-01P of 52,800 ± 8,750 μS/cm. In contrast, LFC is the lagoon with the lowest EC values (with a mean value of 33,300 ± 12,800 μS/cm), similar in some campaigns to those detected in sampling points close to the surface in LFB (LFB-01S and LFB-02). However, this lagoon may also present higher EC than sea water, reaching up to

Table 2c
General Lake Model results, in a monthly basis, for LFC lagoon in m^3. See Table 2a for legend.

Period	Vin (m^3)	Vfin (m^3)	Vfin-Vin (m^3)	Evap (m^3)	Evap (%)	Rain (m^3)	Inflow (m^3)	Outflow (m^3)	In-Out (m^3)
Nov14–Dec14		1970.73							0.00
Dec14–Jan15	1970.73	1828.34	−142.39	−77.35	−3.92	9.89	587.07	663.07	−76.00
Jan15–Feb15	1828.34	1487.99	−340.34	−102.30	−5.60	9.85	35.76	280.77	−245.01
Feb15–Mar15	1487.99	1470.99	−17.00	−102.04	−6.86	31.10	199.01	147.79	51.23
Mar15–Apr15	1470.99	1385.64	−85.35	−143.16	−9.73	115.84	598.37	646.00	−47.63
Apr15–May15	1385.64	1117.82	−267.83	−153.67	−11.09	0.00	7.32	128.41	−121.09
May15–Jun15	1117.82	1049.65	−68.16	−181.79	−16.26	15.11	267.38	150.86	116.52
Jun15–Jul15	1049.65	828.09	−221.56	−137.28	−13.08	0.00	163.76	256.19	−92.43
Jul15–Aug15	828.09	897.83	69.74	−78.95	−9.53	67.37	142.73	59.88	82.86
Aug15–Sep15	897.83	1027.51	129.68	−36.73	−4.09	37.53	244.86	121.59	123.27
Sep15–Oct15	1027.51	1715.73	688.22	−60.38	−5.88	60.68	1347.76	654.93	692.83
TOTAL	1970.73	1715.73	−255.00	−1073.63	–	347.38	3594.02	3109.48	484.55

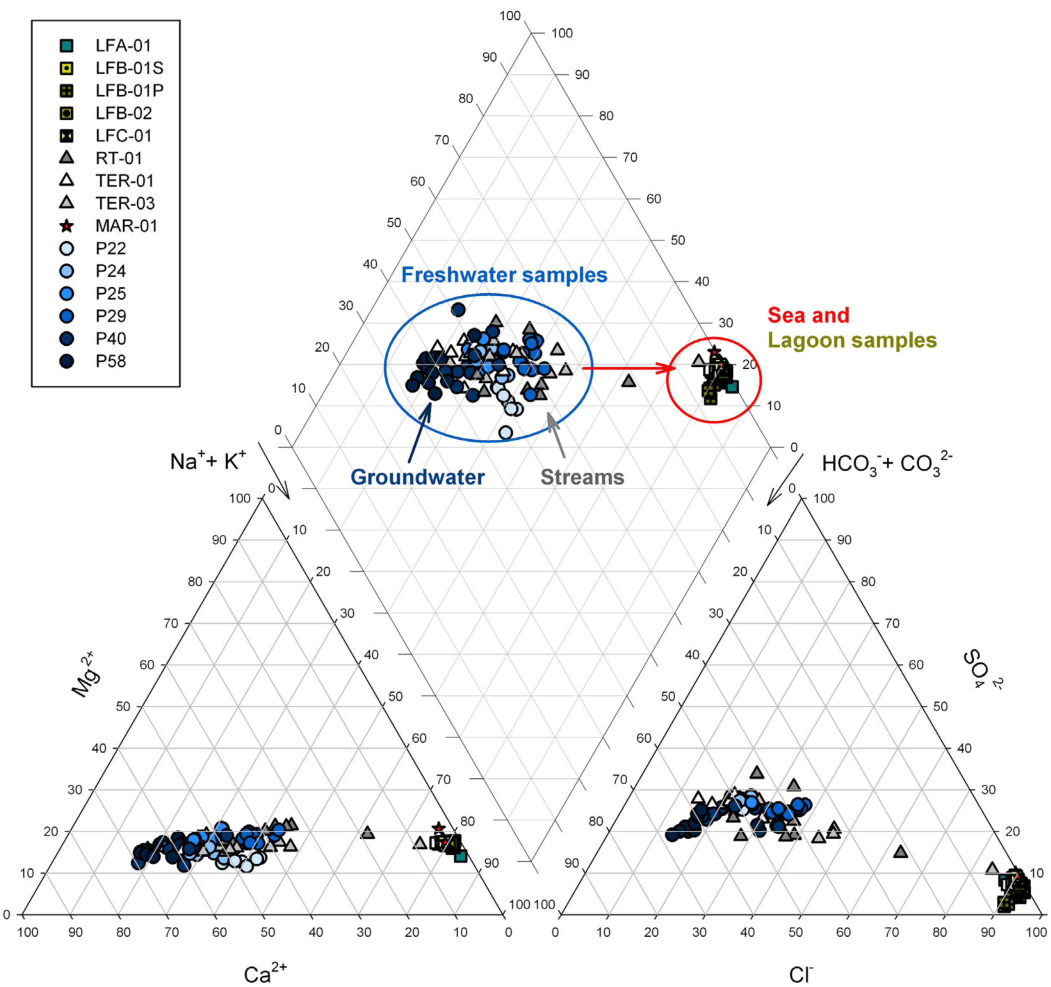

Fig. 3. Piper plot of the collected samples. Sample codes as in Fig. 1. LFB-01S, surface water sample; LFB-01P, 2 m deep water sample.

60,000 μS/cm values in summer campaigns. In addition, LFA, and more usually LFB-01P, shows low DO values (<0.01 mg/L) during part of the summer, testifying for the presence of a reducing environment.

When temporal variations are considered, a common decrease in Cl^- concentration has been detected in December 2014 and in March, April, August and October 2015, while in the rest of the sampling campaigns Cl^- tends to increase in all the lagoons (Fig. 5a). This behavior has been also observed in EC values, as well as in Na^+, Mg^{2+}, K^+, Br^- and SO_4^{2-}, which show high correlations with Cl^- (ranging 0.92–0.99, with p-values <0.001). In December 2014 the lowest concentrations of all of these parameters have been detected, showing lower concentrations than sea samples. However, due to the stepped increase of these ions (with some occasional breaks caused by the previously described storms and rainy periods), these concentrations may exceed twice or even more than three times the values observed in sea samples.

There is a second group of parameters composed of HCO_3^-, TP, TN, and NH_4^+, which present high and significant correlations between them (ranging 0.91–0.98, with p-values <0.001), and lower correlations with the first group of parameters described before. These parameters show an increase of their concentrations in sampling campaigns where in the first group a decrease is detected (Fig. 5b and e).

Table 3
Hydrochemical and isotopic data of the study area. Results of the same row followed by the same letter are not significantly different ($p < 0.05$).

Water types	Sea	Lagoons	Aquifer	Streams
EC (μS/cm)	45,096 ± 9,412 (a)	44,679 ± 22,779 (a)	1,200 ± 265 (b)	999.71 ± 890.39 (b)
pH	8.21 ± 0.31 (a)	8.32 ± 1.19 (a)	7.19 ± 0.14 (c)	8.00 ± 0.40 (a)
pE	2.43 ± 1.41 (a)	1.75 ± 1.13 (b)	5.24 ± 1.48 (c)	1.92 ± 0.49 (a)
DO (mg O_2/L)	8.44 ± 3.33 (a)	5.45 ± 4.28 (b)	1.64 ± 1.77 (c)	6.25 ± 2.54 (d)
T (°C)	18.3 ± 4.5 (a)	17.9 ± 6.1 (a)	17.9 ± 2.5 (a)	16.4 ± 5.6 (a)
HCO_3^- (mg/L)	162.9 ± 22.0 (a)	449.7 ± 546.5 (b)	419.9 ± 52.0 (c)	264.1 ± 107.5 (d)
CO_3^{2-} (mg/L)	0.2 ± 0.8 (a)	12.0 ± 19.2 (b)	0.0 ± 0.0 (c)	0.3 ± 1.1 (a)
Cl^- (mg/L)	19,161.6 ± 3,737.6 (a)	19,033.9 ± 10,543.7 (a)	129.3 ± 59.6 (b)	192.6 ± 406.9 (c)
SO_4^{2-} (mg/L)	2,717.8 ± 538.1 (a)	2,083.2 ± 1,143.6 (b)	171.9 ± 46.7 (c)	121.6 ± 70.5 (d)
Br^- (mg/L)	68.4 ± 13.7 (a)	67.5 ± 36.9 (a)	0.2 ± 0.1 (b)	0.5 ± 1.4 (b)
F^- (mg/L)	1.17 ± 0.18 (a)	0.90 ± 0.26 (b)	0.17 ± 0.06 (c)	0.19 ± 0.06 (c)
Na^+ (mg/L)	10,776.3 ± 2,115.8 (a)	10,698.4 ± 5,849.7 (a)	96.5 ± 41.2 (b)	121.9 ± 227.57 (c)
K^+ (mg/L)	398.17 ± 81.04 (a)	398.69 ± 214.67 (a)	6.01 ± 2.46 (b)	9.01 ± 9.23 (c)
Mg^{2+} (mg/L)	1,308.2 ± 260.6 (a)	1,232.3 ± 667.8 (a)	28.0 ± 8.3 (b)	26.6 ± 28.7 (c)
Ca^{2+} (mg/L)	404.2 ± 70.5 (a)	314.8 ± 115.2 (b)	149.6 ± 26.0 (c)	93.8 ± 26.2 (d)
NH_4^+-N (mg/L)	0.14 ± 0.20 (a)	3.74 ± 12.02 (a)	0.07 ± 0.13 (a)	0.08 ± 0.19 (a)
NO_2^--N (mg/L)	0.00 ± 0.00 (a)	0.34 ± 2.83 (a)	0.02 ± 0.03 (b)	0.04 ± 0.03 (c)
NO_3^--N (mg/L)	0.20 ± 0.34 (a)	0.13 ± 0.29 (a)	5.36 ± 6.04 (b)	1.81 ± 1.20 (b)
PO_4^{2-}-P (mg/L)	0.01 ± 0.02 (a)	0.37 ± 1.17 (b)	0.01 ± 0.02 (c)	0.11 ± 0.15 (d)
TP (mg P/L)	0.05 ± 0.07 (a)	0.66 ± 1.48 (b)	0.02 ± 0.02 (c)	0.18 ± 0.19 (d)
TOC (mg C/L)	15.5 ± 13.1 (a)	55.0 ± 43.7 (a)	1.8 ± 0.9 (b)	8.3 ± 4.2 (c)
TN (mg N/L)	1.5 ± 1.6 (a)	9.8 ± 16.4 (b)	5.8 ± 6.3 (c)	2.6 ± 0.9 (c)
N_{org} (mg/L)	1.21 ± 1.56 (a)	5.63 ± 8.11 (b)	0.36 ± 0.58 (a)	0.73 ± 0.33 (a)
$\delta^{18}O$ (‰VSMOW)	0.34 ± 1.51 (a)	1.86 ± 3.17 (a)	−6.31 ± 0.37 (b)	−6.11 ± 0.70 (b)
δD (‰VSMOW)	0.90 ± 9.19 (a)	1.26 ± 12.46 (a)	−41.27 ± 1.89 (b)	−40.75 ± 3.98 (b)

Finally, there are a third group of parameters that show low or no significant correlations with the rest of the parameters. This is the case of nutrients such as NO_3^- and NO_2^- that show correlations lower than 0.4 with the rest of the parameters (SM2).

As regards LFB lagoon, stratification is observed throughout December 2014 to April 2015 campaigns (Fig. 5d–f), since significantly higher concentrations in most of the parameters analyzed are detected in the deepest point (LFB-01P). From May to August 2015 mixing occurs, and the concentrations close to the surface are similar to those of the deepest parts of the lagoon. However, an increase in HCO_3^-, PT, NH_4^+ and TN concentrations in LFB-01P is detected, when in the rest of the sampling points a decrease in all of them has been reported.

In Fig. 6, the stable isotopic composition ($\delta^{18}O$ and δD) of water has been plotted. According to this Figure, three main groups of samples can be distinguished:

- A first one is composed of freshwater samples, with an isotopic composition ranging −7.17 to −4.83‰ for $\delta^{18}O$ and −46.1 to −33.0‰ for δD.
- A second group is constituted by sea samples, some of them affected by mixing with stream water during storm events. Despite these disturbances, their values showed lower variations, ranging −3.95 to 1.85‰ for $\delta^{18}O$ and −25.7 to −8.17‰ for δD.
- Finally, the group of lagoon samples is located in intermediate positions between freshwater and sea water in Fig. 6. However, part of them is affected by evaporation, since they are displaced from the mixing line following a slope of around 4 (Clark and Fritz, 1997).

Going into detail to this last group of samples, it is possible to depict different characteristics among the lagoons and sampling campaigns. In December 2014 and January 2015 campaigns, the isotopic values of the lagoons are situated in the mixing line between freshwater and seawater. After this campaign, a stepped increase in their isotopic composition is observed, with some isolated breaks, until June 2015, when the most enriched isotopic values are detected. After this maximum, a return to the initial positions, close to those of November 2014, progressively occurs. In spite of this general trend, there are some differences between lagoons, and sampling points. On the one hand, the lagoon with the highest variation in its isotopic composition is LFA, which shows the most enriched values in summer ($\delta^{18}O$ of 12.2‰ and δD of 35.5‰). These values are similar to those observed in the deepest parts of LFB (that is in LFB-01P), which presents isotopic compositions of 7.3‰ of $\delta^{18}O$ and 21.5‰ δD in summer. In contrast, the lagoon with a lower enrichment caused by evaporation is LFC, which its maximum content is 5.08‰ of $\delta^{18}O$ and 11.0‰ of δD. Although the same behavior is observed in this lagoon, the range of variation is the lowest (SM2).

4.3. Hydrochemical and evaporation models

The mixing and evaporation models have been conducted taking as the main endmembers a sample of a well (P-25) and a sea sample (MAR-01). P-25 has been selected since this is the well located closest to the Pletera lagoons (Fig. 1), following the natural groundwater flow paths in the alluvial plain (Montaner, 2010), and its isotopic values are closer to the mean freshwater isotopic composition in this area (especially during the 11th campaign). Besides, the selected sea sample is the closest to the mean values of sea samples for this period (sample of the 2nd campaign).

In Fig. 7 the results obtained for the mixing between P-25 and MAR-01 have been plotted, together with the solutions for the evaporation process considering two different pathways, one starting at 20% mixing with sea water, and a second one at 80%. According to Fig. 7, different situations can be distinguished:

- There is a group of ions, such as Cl^-, Na^+, Br^- and Mg^{2+}, which do not seem to be affected by other processes than mixing and evaporation. An example of this situation can be observed in Fig. 7a and b, where all the samples of the lagoons are located following the both models and it is not possible to distinguish which one is more influencing the chemistry of the lagoon samples. Most of these ions have been previously considered in group 1 in the hydrochemical description. In addition, processes that usually affect alluvial aquifers with sea water intrusion or

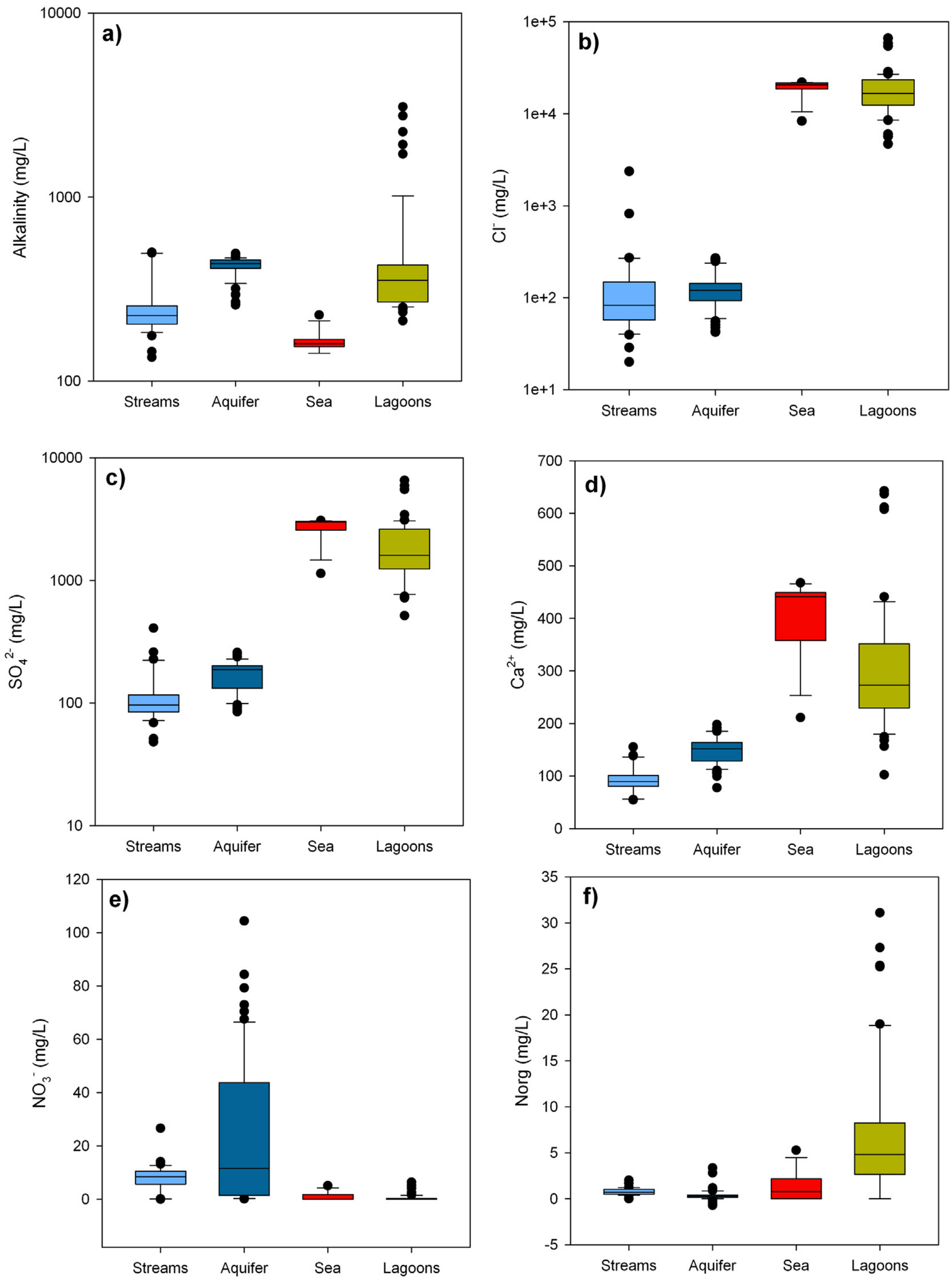

Fig. 4. Box-plots of some of the most representative parameters, representing the median, 10th, 25th, 75th and 90th percentiles as vertical boxes with error bars, and closed symbols as extreme values: a) alkalinity as mg HCO_3^-/L; b) Cl^-; c) SO_4^{2-}; d) Ca^{2+}; e) NO_3^-; and f) N_{org}.

refreshing, such as cation or inverse exchange, do not seem to be affecting this system, since all the samples in Fig. 7a and b follow the sea ratio 1:0.55 for Na:Cl.

– A second group of ions includes those that may be affected by some hydrochemical reactions. This is the case of SO_4^{2-}, Ca^{2+}, HCO_3^- and CO_3^{2-} (Fig. 7c and d), which may be affected by SO_4^{2-}, reduction, or even gypsum and calcite precipitation and dissolution. Samples especially affected by SO_4^{2-} reduction are those located in the deepest part of LFB (LFB-01P; Fig. 7c), but most of the rest of the lagoons samples also seems to be affected by this process.

In the case of gypsum and, especially, calcite precipitation and re-dissolution, they affect the lagoons depending on the season.

In order to determine the magnitude of the hydrochemical processes occurring in the lagoons, an inverse model has been conducted (with the assistance of PhreeqC) between two characteristic campaigns of the lowest and the highest evaporation observed in the lagoons (January 2015 and June 2015, Figs. 5 and 6, and Tables 2a, 2b and 2c). In particular, January 2015 was chosen for being the last sampling campaign characteristic of the most depleted isotopic signature (for $\delta^{18}O$ and δD) in the lagoons; and June 2015 was the last sampling campaign with the most enriched

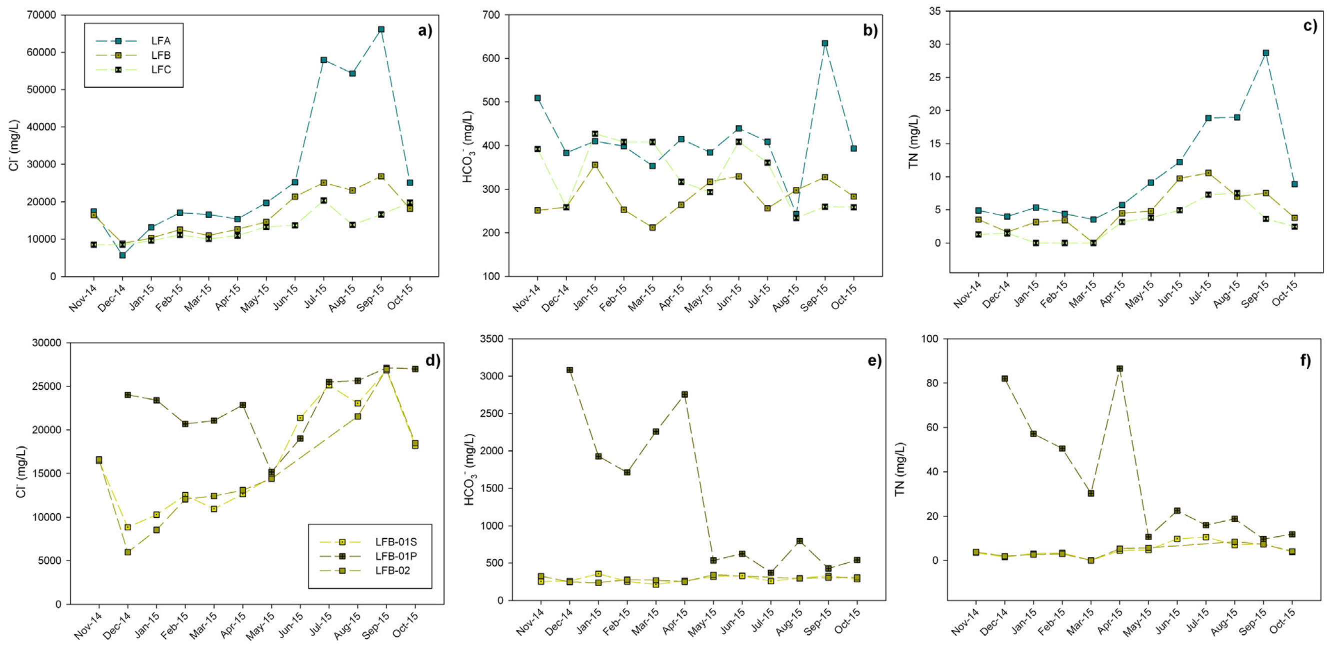

Fig. 5. Temporal evolution of the most representative hydrochemical parameters in the three lagoons (LFA-01, LFB-01s and LFC-01): a) Cl^- in mg/L; b) HCO_3^- in mg/L; and c) TN in mg/L for LFA, LLFB and LFC lagoons; and d) Cl^- in mg/L; e) HCO_3^- in mg/L; f) TN in mg/L for all sampling points in LFB (LFB-01S, LFB-01P and LFB-02).

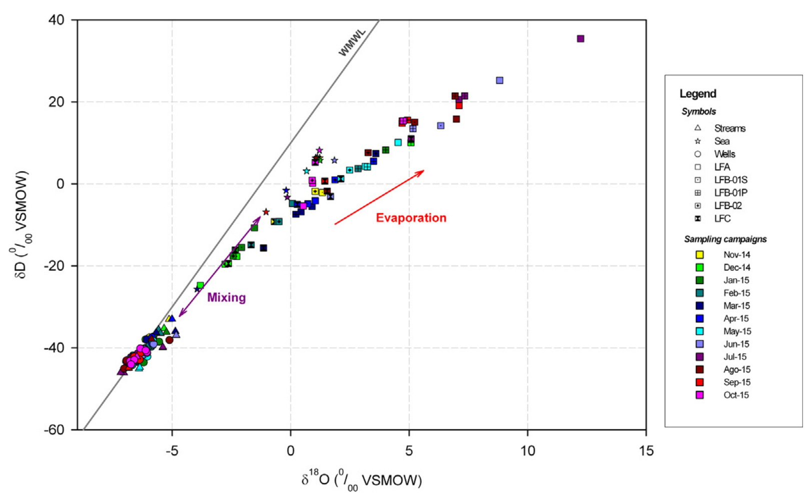

Fig. 6. Isotopic composition of the studied samples. Legend: GMWL, global meteoric water line.

isotopic values that could be also used to determine the percentage of evaporation through the Gonfiantini's model. According to the obtained results (Table 4), one of the main processes affecting these lagoons is evaporation, showing maximum values of 78.7% in LFA, 60.8% in LFB and 50.5% in LFC. Other processes observed are carbonate precipitation (as calcite, dolomite or aragonite) that account for 0.81–2.66 mmoles/kg of water; and sulfate concentration decrease, which is attributed to gypsum precipitation (with 1.18–3.65 mmoles/kg) or sulfate reduction to HS^- (with values ranging 0.07–0.13 mmoles/kg).

Finally, in Fig. 8, results of Gonfiantini (1986) evaporation model have been represented, together with the described mixing models. In the first campaign, conducted in November 2014, samples were affected by evaporation, but this effect was not observed in December 2014 and January 2015 campaigns, when lagoon samples shifted to positions closer to the mixing line between fresh groundwater and sea water. In these campaigns the proportion of seawater in La Pletera lagoons ranged between 30 and 65% due to the cyclonic storm events occurred at the beginning of December. In the following campaigns, a progressive increase of evaporation is observed, being the proportion of seawater in the lagoons maintained around 40–60% until July 2015. This behavior is observed in all the lagoons, but the total percentage of evaporation differs. While in LFC the largest evaporation was around 40% in July (the 9th campaign), in LFB was around 60%, and in LFA, was even higher (Table 5 and Fig. 8). In this last lagoon, the high $\delta^{18}O$ and δD values recorded in July campaign did not allow to determine the percentage of evaporation. After this survey, a decrease in the percentage of evaporation occurred in all the lagoons, together with a shift to higher proportions of sea water, until the last campaign (October 2015), when a return to positions closer to the initial campaign is observed. In the shift observed during the summer campaigns, the proportion of sea water reached values around 70–80%, or even higher, in all the lagoons.

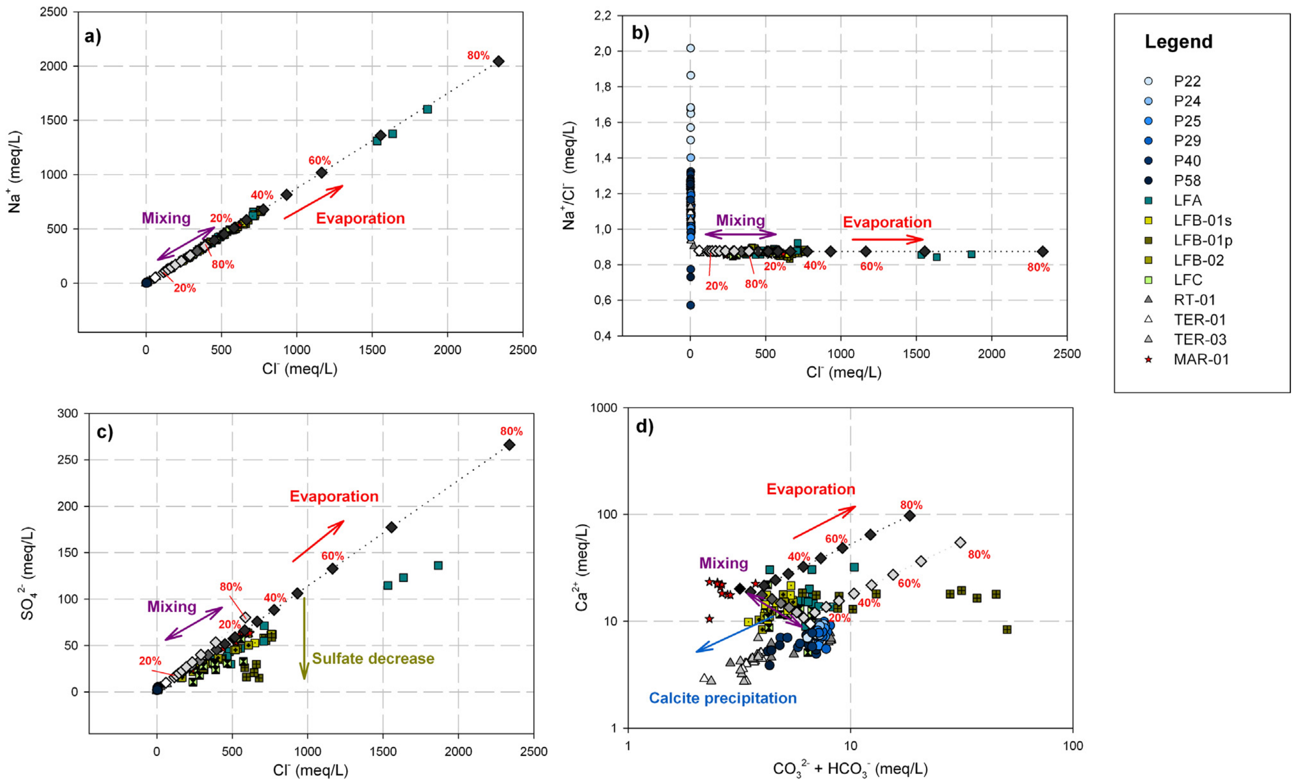

Fig. 7. Mixing and evaporation evolutions obtained with PhreeqC models, with results for the evaporation model of samples with a 20% and a 80% composed of sea sample: a) Cl^- vs. Na^+; b) Cl^- vs. Na^+/Cl^-; c) Cl^- vs SO_4^{2-}; and d) $CO_3^{2-} + HCO_3^-$ vs Ca^{2+} (in meq/L).

Table 4
Results of the inverse models conducted between sampling campaigns 3 and 9 (January and June 2015). Legend: negative values represent precipitation or diminution, and positive values, dissolution or increase.

Lagoon		LFA			LFB			LFC
		Model 1	Model 2	Model 3	Model 1	Model 2	Model 3	Model 1
Tranfers (mmol/kg)	H_2O (g)	−43,725	−43,561	−43,561	−33,783	−33,459	−33,459	−28,062
	CO_2 (g)	−4.41	−4.27	−4.27	2.81	2.82	2.82	−3.04
	H_2S (g)	0.07	0.07	0.07	0.13	0.13	0.13	0.11
	Calcite	0.00	−2.66	0.00	0.00	0.00	−1.61	0.00
	Dolomite	−1.33	0.00	0.00	−0.81	0.00	0.00	−1.04
	Gypsum	−3.65	−2.32	−2.32	−2.03	−1.18	−1.18	−2.54
	Aragonite	0.00	0.00	−2.66	0.00	−1.61	0.00	0.00
Redox processes (mmol/kg)	O_2	0.27	0.33	0.27	0.50	0.50	0.50	0.43
	HS^-	0.07	0.08	0.07	0.13	0.13	0.13	0.11
% Evaporation		78.71	78.42	78.42	60.82	60.23	60.23	50.52

5. Discussion

The interpretation of the isotopic data and the use of the Gonfiantini's model do not permit to determine whether evaporation is taking place in the lagoons, when an isotopic depletion between successive campaigns occurs. This situation has been especially detected in summer, in August, September and October of 2015 surveys (campaigns 10, 11 and 12), when in each of them a lighter isotopic composition was obtained than in the previous campaign (Fig. 8, Table 5). This decrease in the isotopic composition could be caused by mixing with water not affected by evaporation, which could mask the evaporation occurring in the lagoons. In this season, however, the most likely source of water inputs was groundwater (Tables 2a, 2b and 2c).

When evaporation is determined using the GLM, significantly higher values, compared to those achieved with the isotopic model (especially in LFC), are obtained. In GLM, the percentage of evaporation is calculated based on the meteorological data, and considering the extension and volumes of La Pletera lagoons. Thus, the relationship with the aquifer does not alter the results, and the values calculated are only dependent on meteorological factors. These higher values achieved with the GLM and hydrochemical models, confirm the high evaporation occurring during summer, which was masked by the presence of groundwater inflows when the isotopic composition was analyzed. In addition, when the percentage of inflows are determined with the GLM on monthly basis, mean annual values obtained are higher than 25%, being around 40% of the total water mass in the lagoons during the summer months.

Hydrochemical data indicated that the main processes affecting La Pletera lagoons were mixing of freshwater and sea water, and evaporation. These mixing processes could take place within the lagoons during storm events, due to mixing of surface, subsurface and groundwater flows; but they could also occur within the aquifer, due to the presence and the seasonally movement of the

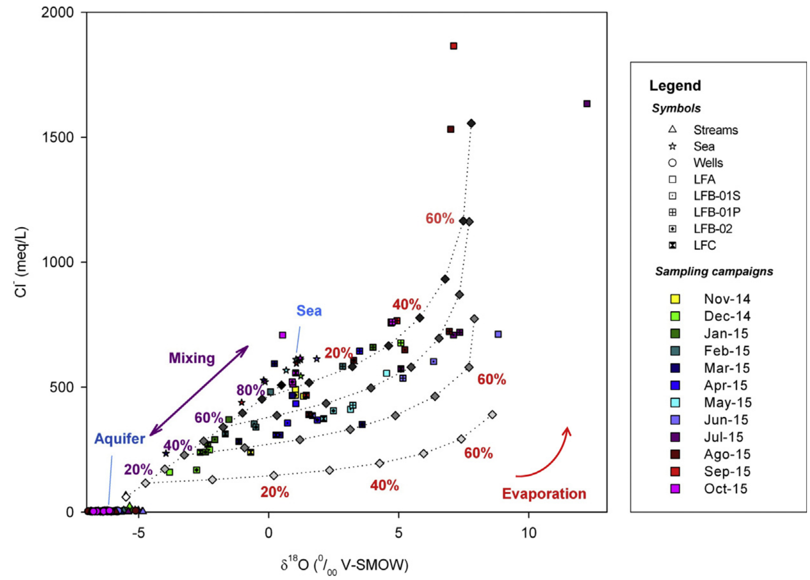

Fig. 8. Mixing and evaporation results obtained comparing $\delta^{18}O$ vs. Cl^- concentrations, considering an air humidity of 65%.

Table 5
Summary of the % of evaporation obtained for with the different models between sampling periods 2 to 9 (December 2014–July 2015) and 3 to 9 (January 2015–July 2015). Legend: GLM, results of General Lake Model normalized; PhreeqC, results of the inverse model; Gonfiantini $\delta^{18}O$ and δD, results of the evaporation model.

Lagoon	LFA		LFB		LFC	
Period	2–9	3–9	2–9	3–9	2–9	3–9
GLM	74.85	72.92	64.04	62.87	50.65	48.63
PhreeqC	90.92	78.71	64.90	60.82	55.70	50.52
Gonfiantini-$\delta^{18}O$	–	–	61.83	61.34	42.13	41.36
Gonfiantini-δD	–	–	58.98	57.71	40.18	37.84

saltwater wedge under natural conditions. While in sampling surveys conducted from December 2014 to July 2015 the proportion of sea water in the lagoon was around 40–60% (Fig. 8), the shift to proportions higher than 60–80% of sea water in the summer season, unrelated to important cyclonic storm events (and thus the arrival of surface and subsurface flows to the lagoons), pointed out the occurrence of groundwater inputs in the lagoons during this season with a higher proportion of sea water, caused by the movement of the saltwater wedge to more inland positions (Fig. 9).

Some other secondary processes, such as sulfate reduction or gypsum and calcite precipitation and dissolution may be also occurring in these lagoons. However, hydrochemical processes that usually affect alluvial aquifers where sea water intrusion or refreshing occurs, such as cation or inverse exchange, do not seem to be affecting this system.

Furthermore, some of the nutrients and ions analyzed could be used as indicators of groundwater inputs in the lagoons. This is the case of TN, TP, NH_4^+, and HCO_3^- that presented some picks in their concentration, especially in the deepest parts of LFB lagoon, coinciding with the highest inflow values determined with the GLM.

Finally, when the three lagoons are compared, the percentage of evaporation is significantly higher in LFA than in the rest of the lagoons (Table 5). This behavior may be caused by the highest ratio between surface and volume (S/V) obtained in this lagoon (Table 1). In contrast, although LFB and LFC show a similar S/V ratio, the values of evaporation seem to be significantly lower in LFC. This lower percentage of evaporation may be caused by two different situations: 1) a more efficient relationship with the aquifer, with a higher groundwater inputs in this lagoon that would maintain its isotopic values in lighter values; 2) a lower evaporation affecting

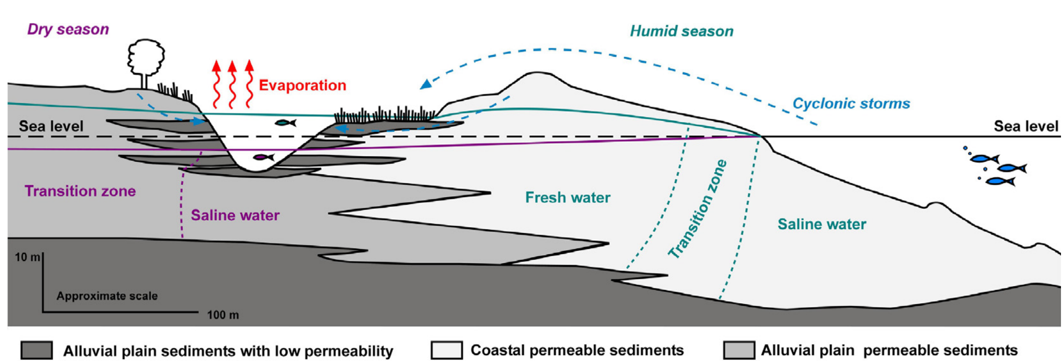

Fig. 9. Evolution of surface water-groundwater interactions and aquifer saltwater wedge dynamics in a coastal lagoon area.

this lagoon. Considering the evaporation results obtained with the GLM, the second hypothesis seems to be more likely, since the mean monthly evaporation value obtained for LFA is 19.6% (24.8% in summer season), for LFB is 13.9% (15.0% in summer) and for LFC is 8.5% (6.5% in summer). This lower percentage of evaporation is caused by the different shape of the lagoons, since all the lagoons show the same evaporation/area ratio (with monthly mean values ranging 36.5–39.5 mm), but when evaporation is determined considering the volume of the lagoons, the final value is the one previously obtained.

6. Conclusions

During the studied period only three cyclonic storms occurred, coinciding with important rainfall events (in November 2014, March 2015 and September 2015). In these events, surface, subsurface and groundwater inputs in the lagoons were detected and considered as total inflow in the GLM. However, water inputs were also detected in other sampling campaigns (especially in summer season), not affected by these important storms or rainfall events.

Using the hydrochemical and isotopic models, together with the GLM, the influence of groundwater in La Pletera lagoons has been proved. This contribution is particularly significant during the dry season, when it accounts for 15–80% of the water in the lagoons.

Therefore, water salinity in La Pletera lagoons depended on two main processes, 1) mixing of fresh and sea water occurring within the lagoons or in the aquifer, and 2) evaporation. In the case of mixing in the aquifer, the proportion of sea water varies throughout the year, being more important during the summer season, when the saltwater wedge in coastal aquifers is naturally located in more inland positions. In the case of evaporation, its percentage depends on morphological features of the lagoons, being more important in LFA, which S/V ratio was significantly higher.

From a management perspective, the goal of preserving such lagoons as a rich natural environment implies maintaining groundwater fluxes towards the ocean, to control salinization of the lagoons. Since groundwater inputs are paramount to keep these lagoons as permanent and with adequate hydrochemical characteristics, their morphological evolution must be controlled to maintain the hydraulic connection with the underlying aquifer.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2017.07.034.

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