Marine Pollution Bulletin 106 (2016) 323–328

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Assessment of factors enabling halite formation in a marsh in a humid temperate climate (Ajó Marsh, Argentina)

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ARTICLE INFO

Article history:
Received 30 November 2015
Received in revised form 14 March 2016
Accepted 16 March 2016
Available online 25 March 2016

Keywords:
Evaporites
Coastal wetland
Water balance
Samborombón Bay
Argentina

ABSTRACT

The formation of evaporites associated with the final stages of the precipitation sequence, such as the case of halite, is frequent in marshes in arid areas, but it is not to be expected in those humid climates. This work, by means of the study of the hydrological, climatic and land use conditions, identifies the factors that allow the formation of saline precipitations in a marsh located in a humid climate area. The results obtained show that the exclusion of the marsh as a result of the embankment is the main reason for the presence of halite. It is to be expected that in the future the growth of the embanked marsh areas, together with the climatic and tidal condition tendencies recorded, will favour a higher rate of formation of evaporite salts. The identification of these factors makes it possible to set basic sustainable management guidelines to avoid soil salinisation.

Salt marshes occur worldwide, particularly in middle to high latitudes. Thriving along protected shorelines, they are a common habitat in estuaries. The formation of salt precipitates in marshes is controlled by the tidal flows, which contribute saline water, and the characteristics of the climate; the latter are related to the predominance of evapotranspiration over rainfall in the water balance. This is the reason why the formation of evaporites associated with the final stages of the precipitation sequence, such as halite, is restricted to marshes developing in arid areas (Butler, 1969; El-Omla and Aboulela, 2012; Aref Mahmoud et al., 2014; Alvarez et al., 2015).

The littoral of the outer Río de la Plata estuary (Argentina) constitutes an area which has a humid temperate climate (Carol et al., 2013) and in which there is an extensive marsh that reaches its greatest extent at the southern end (Fig. 1). In this sector, the tide enters the marsh along a large tidal channel referred to as Ajó River, which also receives the contribution of continental water from groundwater discharge and surface runoff; the latter is regulated by floodgates. Even though the estuary has a semidiurnal microtidal regime, the low topography of the marsh makes it possible for the tide to reach the most continental sectors periodically (Carol et al., 2012). Within the marsh, there are approximately ten farms whose main activity is livestock farming. The development of this activity modifies the marsh hydrologically, due to the construction of embankments for internal access roads to the farms and to contain the tidal flow in order to reclaim land for livestock (Carol et al., 2014).

Salt precipitates are frequently found covering the surficial sediments in different sectors of the marsh. Although their spatial development is not important, their presence in a marsh within a humid climate area is noteworthy. The objective of this work is to identify the composition of the salt precipitates, their source and the factors conditioning their formation, in order to set basic sustainable management guidelines to avoid soil salinisation.

QuickBird satellite images from 2014 (Software Google Earth) were used in order to identify areas with similar hydrological patterns, which were then verified in field surveys. The hydrological characterisation of the area was carried out taking into consideration climate and tidal data. The annual and seasonal variations in the rainfall and temperature regime, as well as their influence on the real estimated evapotranspiration as suggested by Thornthwaite and Mather (1957), were analysed using historical climate data of the General Lavalle station from the 1956–2014 period. The tidal regime was studied on the basis of the hourly observed tidal heights (astronomical tide plus weather effects) of the General Lavalle port recorded by the Prefectura Naval Argentina (Argentine Coast Guard). Salt precipitates samples were extracted from the most surficial sediments, stored hermetically in order not to alter the humidity conditions and examined under a binocular magnifying glass, an X-ray diffraction (Philips X'Pert PRO diffractometer) and a scanning electron microscope (JEOL JSM 6360 LV microscope). In order to assess the hydrological and climatic conditions in which the

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http://dx.doi.org/10.1016/j.marpolbul.2016.03.031
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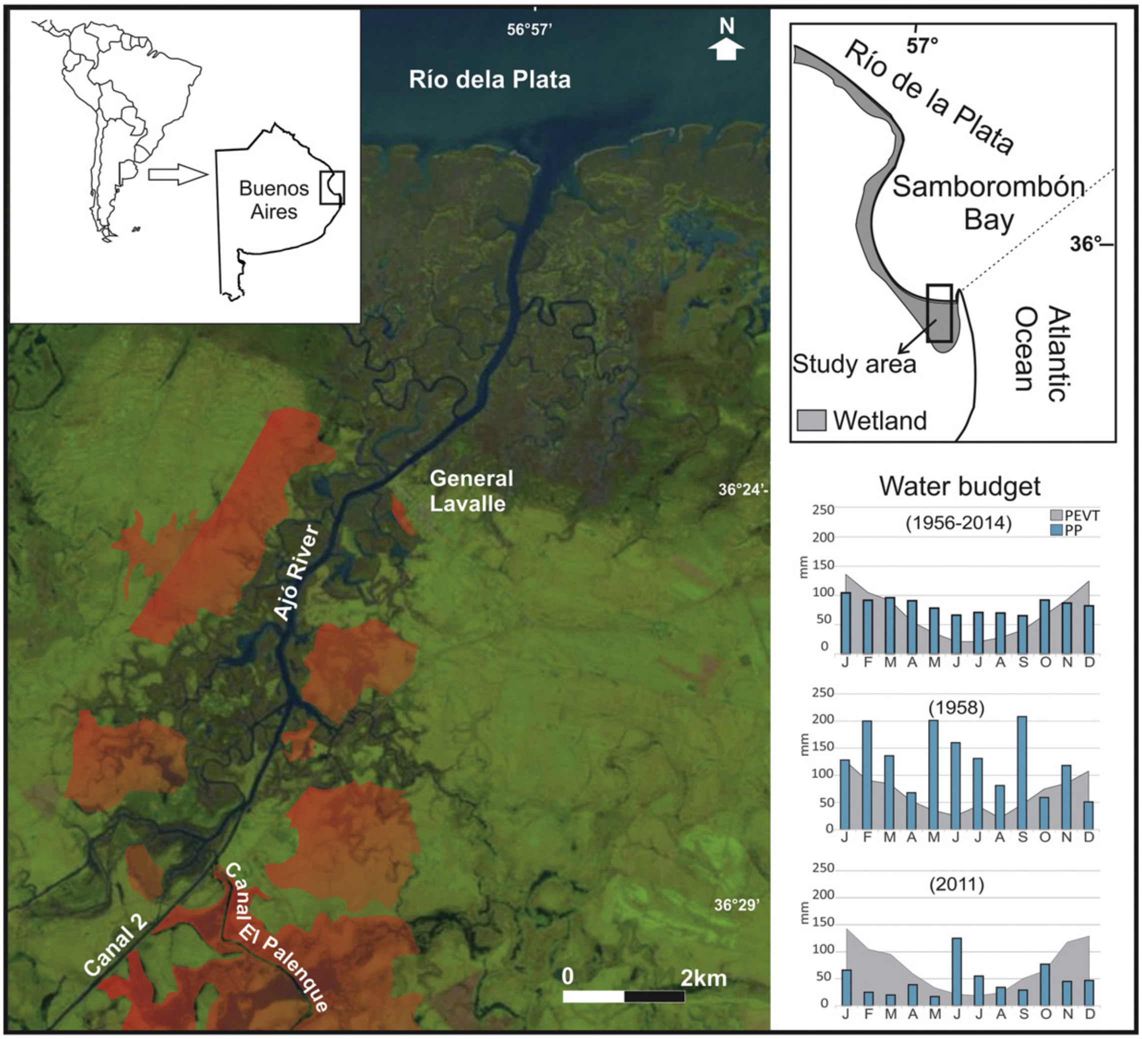

Fig. 1. Location and water balances of the study area. In the map, sites affected by anthropogenic modifications are shown in red. Balances correspond to the historical mean (1956–2014), wettest year (1958) and driest year (2011) of the entire period analysed. PP: Precipitation; PEVT: Potential evapotranspiration.

salt precipitates were formed, tide time, daily precipitation, relative humidity and mean daily temperature data from the days prior to the sampling were analysed. Besides, tidal water samples were obtained from the Ajó River to determine the major ion concentration (Fig. 1). The hydrochemical data were used to estimate the possible salts that may precipitate due to tidal water evaporation by modelling using PHREEQC (Parkhurst and Appelo, 1999). In order to do so, a total evaporation of the tidal water sample of a sequential type was modelled and the ion activities and saturation indices of the evaporites were estimated.

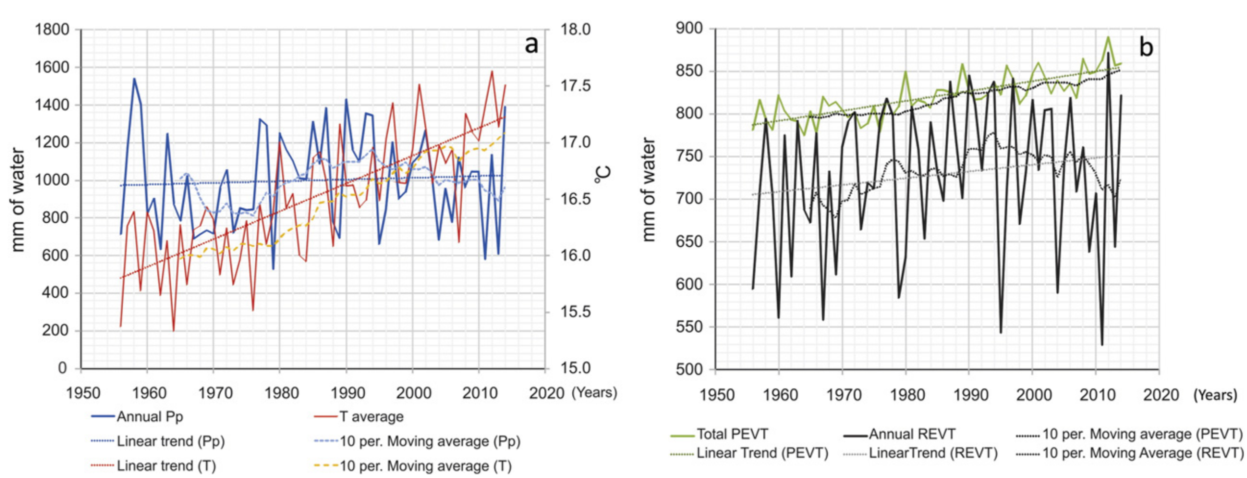

Fig. 2. Historical trend for (a) precipitation and temperature, and (b) potential (PEVT) and real evapotranspiration (REVT) during the last 60 years.

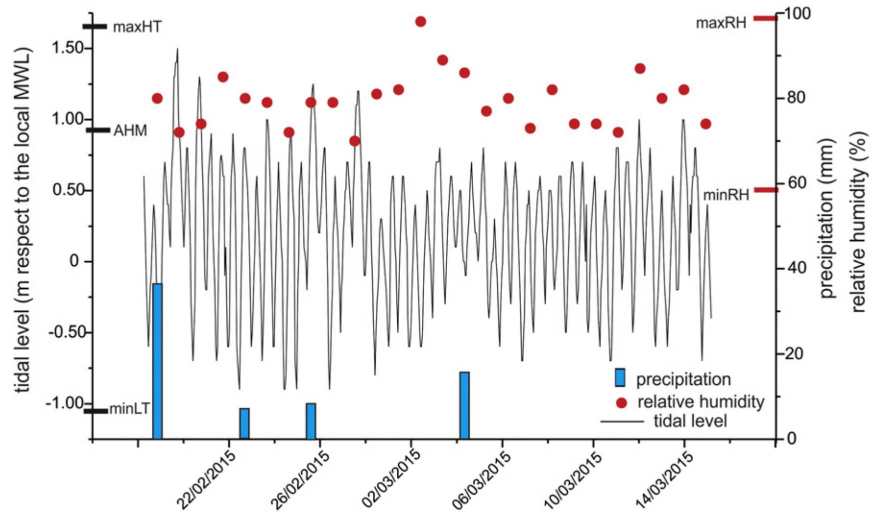

Fig. 3. Tidal height, precipitation and relative humidity for the month prior to sampling. Along the tidal level axis, the minimum low tide (minLT) and maximum high tide (maxHT) values recorded that year, as well as the average height of the marsh (AHM), are indicated. Along the relative humidity axis, the minimum (minRH) and maximum relative humidity (maxRH) values recorded that year are indicated.

The historical precipitation records (1956–2014) show that the area of the marsh under study has mean annual precipitation (Pp) of 994 mm with alternating dry and wet years (Fig. 2a). The Pp tendency, interpreted on the basis of moving averages, suggests that since the 1950s until the 1990s the precipitations increased, but then decreased slightly towards the end of the series. On the other hand, the tendency of the mean annual temperature (T), even though it fluctuated, was always rising (Fig. 2a).

The water balances show that potential evapotranspiration (PEVT) for the 1956–2014 period is 817 mm (82% of the mean annual rainfall) and that it predominates between November and March. In the wettest year (1958), the PEVT is 794 mm and it represents 51% of the rainfall, with the PEVT being higher than precipitation only for two months of the year. Considering one of the most driest years (2011), the PEVT exceeded the Pp in ten months of the year (Fig. 1), reaching an annual value of 862 mm, which represents approximately 149% of the annual rainfall (Fig. 2). The analysis of the annual balances undertaken as a whole shows that the PEVT has a rising trend (Fig. 2b). This is owing to the fact that it is a variable which does not depend on precipitation but on temperature, apart from other conditioning variables (such as hours of insolation, heliophany, winds, and plant cover).

On the other hand, the real evapotranspiration (REVT) is limited by the amount of water available in the soil to be transpired by plants or evaporated. Therefore, the variations in time concerning this variable depend mainly on Pp, which is why the REVT moving averages trend in the period under study follows the same pattern as rainfall, starting with an upward trend and ending in a downward trend (Fig. 2b). This deviation from the PEVT and REVT trend lines indicates that there is an increase in atmospheric demand, a situation that generates more favourable conditions for the formation of evaporites. In turn, the daily relative humidity values oscillate most of the year between 70% and 85%, with minimum values of 59% and maximum values of 100% (Fig. 3).

The tidal flow is the main contribution of surface water to the marsh, since the continental drainage is controlled by floodgates. The high tide from the Río de la Plata estuary enters through the Ajó River and the numerous tidal channels that flow towards it, with the tidal propagation reaching a distance close to 25 km from the estuary coastline. The analysis of the hourly water level records taken from the Ajó River shows that the heights fluctuate between −1.0 and 1.5 m, respect to the local mean water level (MWL) (Fig. 3). Moreover the high tides reaching a height of 0.9 m with respect to local MWL, which is the average height of the marsh, show a high recurrence meaning that the marsh is flooded by high tides most of the year.

The analysis of the satellite images and field observations shows that there are numerous embankments that cut across the tidal channels, leaving sectors of the marsh out of the tidal cycle (see coloured areas in Fig. 1). In the digitalisation of the affected areas it can be observed that at present about 42 km^2 of the marsh are out of the tidal cycle as a result of the embankments. Most of the embankments have an average height of 0.50 m above the height of the adjacent marsh. All of the embankments are made of mounded earth and generally lack drains or, if present, they are broken or blocked by sediments. During extraordinary high tides greater than 1.50 m a MWL, the tide overtops the embankments and floods the isolated marsh areas. Subsequently, at low tide, the embankments prevent the tidal flow from draining, causing the area to remain waterlogged until the water infiltrates or evaporates completely.

The tidal water entering the Ajó River has a salinity averaging 13,770 mg/L with a composition that is mainly sodium chloride type, followed in order of concentration by sulphate and magnesium ions

Table 1
Hidrochemical data (in mg/L).

Sample	TDS	pH	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
Ajó river 1	12,790	8.10	151	1040	6182	75	178	367	3410	65
Ajó river 2	14,745	7.80	272	1184	7273	120	222	432	4100	89

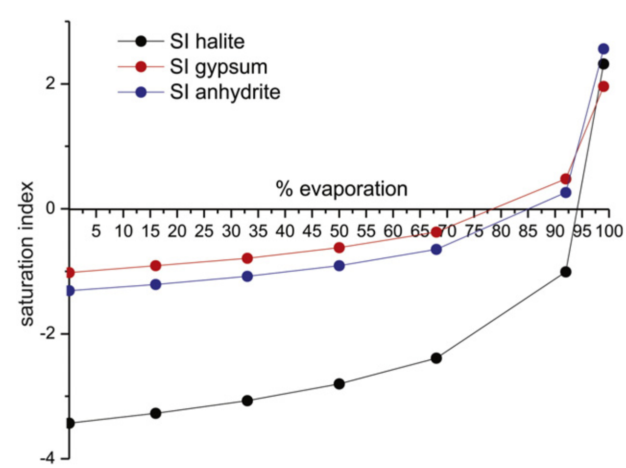

Fig. 4. Evaporation percentages vs. saturation indices.

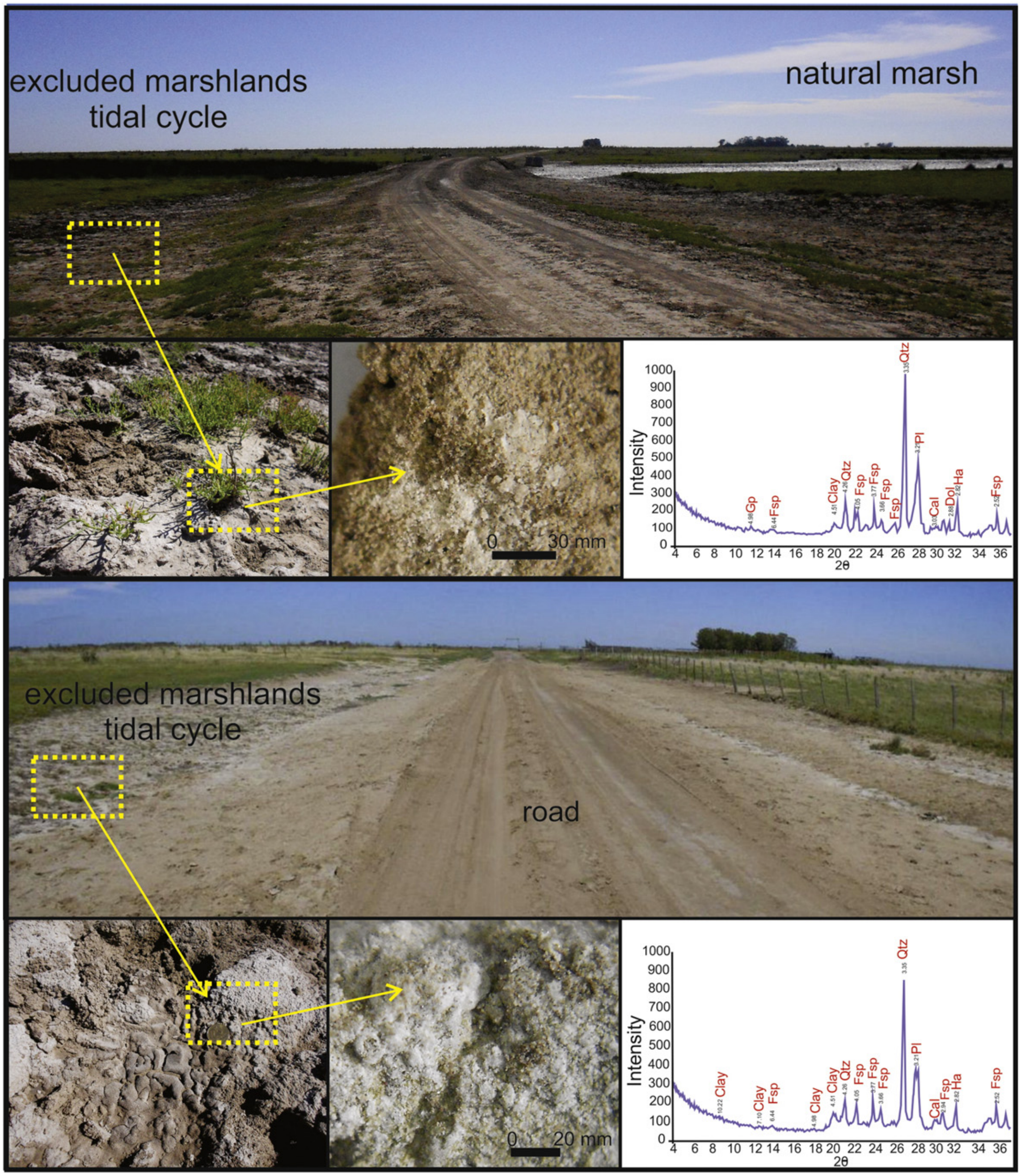

Fig. 5. Photographs showing the formation of saline precipitates in embanked marsh areas and diffractograms.

(Table 1). The total evaporation estimates obtained for tidal water show that the evaporites that could precipitate are gypsum, anhydrite and halite. The first two start forming when the percentage of evaporated water is close to 77 and 85% respectively, whereas the precipitation of halite is only produced when 94% of the water has evaporated (Fig. 4).

In field surveys carried out in March 2015, the formation of evaporites was observed in a large portion of the embanked marsh areas. The precipitates of the evaporite salts form crusts over clayey sediments, showing abundant desiccation cracks, as well as over sandy sediments in the form of a patina, producing agglomerates due to the cementation of the grains (Fig. 5). In turn, in the natural marsh areas, no saline precipitates were observed.

The mineralogical determinations by XRD indicate that in the sandier areas of the marsh, the surficial sediments are mainly composed of quartz grains (Qtz), plagioclases (Pl), feldspars (Fsp) and carbonates of the calcite and dolomite types (Cal and Dol). In the sectors in which fine textures predominate, illite (Ill) and kaolinite (Kln) type clays and interstratified layers were determined. In the samples with a presence of saline precipitates associated with the embanked marsh areas, gypsum (Gp) and halite (Ha) evaporites were registered in most of the samples (Fig. 5).

The SEM observations of the surficial sediments of the embanked marsh areas also show the presence of detrital minerals composed of Qtz and Pl associated with gypsum and halite evaporites. In the photographs obtained (Fig. 6), it can be observed that halite and gypsum precipitate, coating the detrital minerals of the sediment. Halite occurs as crystals of cubic habit, with crystals whose faces fail to develop completely and that coat the detrital minerals as a patina (Fig. 6a–b), as well as cubic crystals with all of their faces developed forming over the surface of feldspars (Fig. 6c). In certain samples, gypsum precipitates abound and they occur in a rose-like form (also called *desert roses*), as well as in pseudotabular and irregular forms (Fig. 6d).

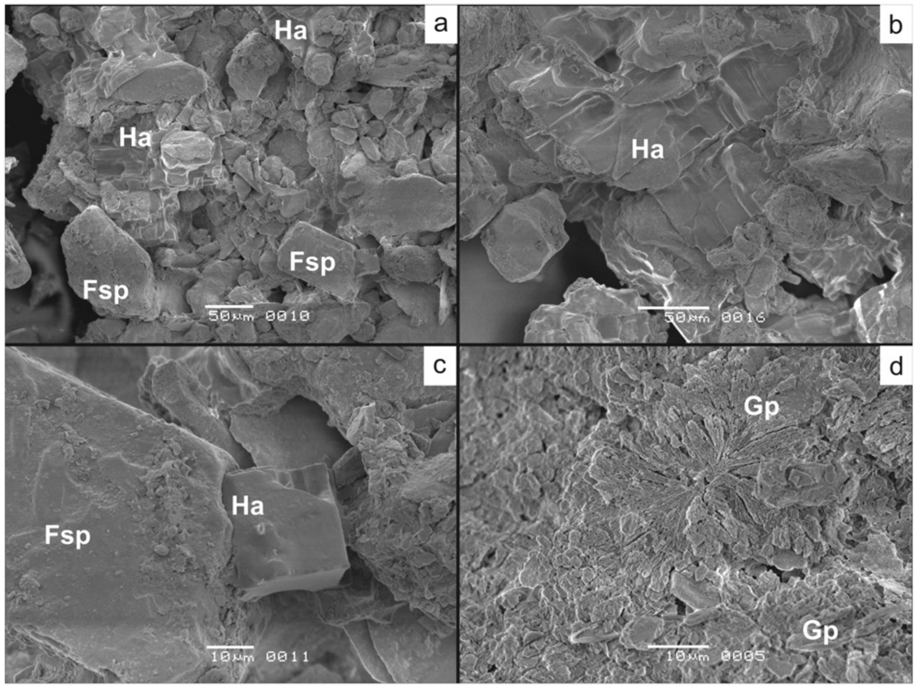

Fig. 6. SEM-acquired photographs.

The presence of saline precipitates in the surficial sediments exclusively in the marsh areas excluded from the tidal cycle by the embankments shows that these anthropogenic modifications are the main cause for the presence of halite in the marsh. When the high tide exceeds the height of the embankments, it floods both the natural areas and the embanked marsh areas (Fig. 7a). Subsequently, at low tide, in the natural marsh area the tidal water is drained, whereas in the anthropised area the embankment prevents runoff (Fig. 7b). The tidal water accumulated in the embanked marsh evaporates (Fig. 7c) and its chemical composition with predominating Cl^- and Na^+ ions and SO_4^{2-}, Mg^{2+} and Ca^{2+} in a smaller proportion determines the prevalence of the formation of halite (NaCl) and gypsum/anhydrite ($CaSO_4$ $nH_2O/CaSO_4$). For this precipitation to occur, it is necessary for more than 77% of the tidal water to evaporate in the case of gypsum/anhydrite and for almost total evaporation to occur (94%) for the formation of halite (Fig. 4). No evaporites composed of Mg^{2+} were observed, as this ion occurs in the sediment as dolomite and it may replace the Ca^{2+} in calcite by means of a dolomitisation process (Butler, 1969). In turn, the release of Ca^{2+} ions from the carbonates increases their concentration in solution, causing a greater precipitation of

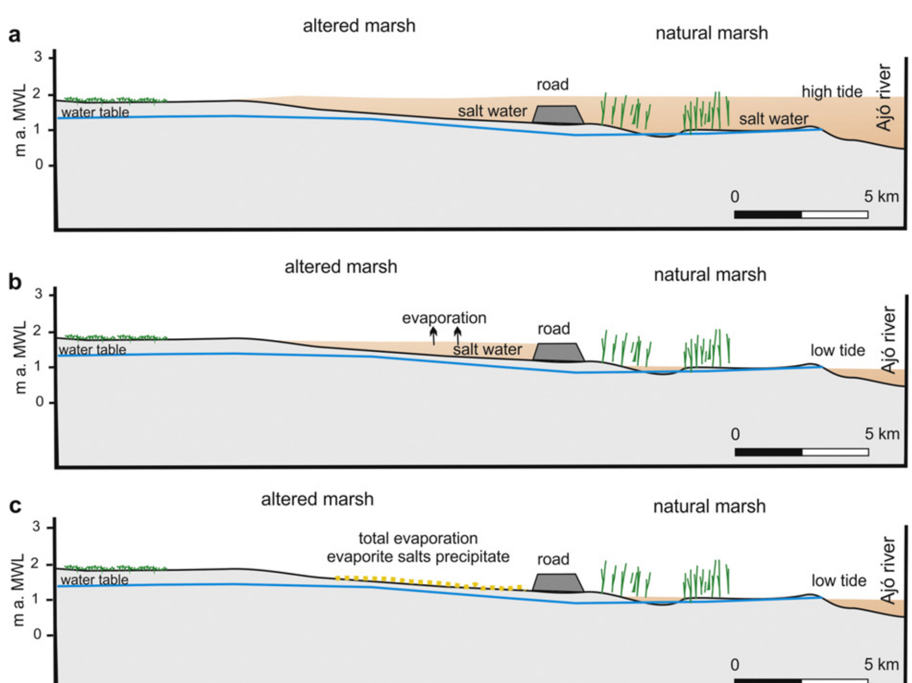

Fig. 7. Diagram showing the conceptual model of evaporite salt formation.

gypsum/anhydrite (Curtis et al., 1963; Illing et al., 1965). The gypsum/anhydrite and halite crystals formed tend to coat the grains of the detrital sediment or to associate with the desiccation cracks in the clayey areas, not forming evaporite layers within the sediment. These processes contribute to soil salinisation as well as to alterations in the marsh vegetation, which is sensitive to hydrological and environmental changes (Burchett et al., 1999; Idaszkin et al., 2014).

The precipitation of halite due to the evaporation of the shallow sodium–chloride groundwater that dominates in the marsh is another possible process (Schreiber and El Tabakh, 2000). In the marsh under study, the presence of halite has only been registered on the surface of sediments and not in the unsaturated zone close to the water table, which is why such a formation process is rejected. This is due to the fact that in the current climatic conditions the percentages of groundwater evaporation are three times lower than those of surface water (Carol et al., 2015).

As regards the natural factors regulating the occurrence of precipitates, the ones with the highest incidence are the recurrence of high tides that exceed the height of the embankments and the climatic conditions. The tidal factors are associated with extraordinary high tide events that make it possible for the tide to overtop the height of the embankments. These extraordinary high tides are caused by the action of positive storm surges owing to strong southeast winds that lead to severe flooding. Studies undertaken on the basis of tidal heights of the last 100 years show that the ten-year averages of frequency and duration of positive surges have increased in the last three decades (D'Onofrio et al., 2008). Besides, the rise in the relative level of the estuary, which has increased to 17 cm in the last century (D'Onofrio et al., 1999), would favour a higher flooding frequency, as predicted for the marsh under study (Tosi et al., 2013).

As regards the climatic factors, the formation and permanence of evaporites require that, in the water balance, evapotranspiration dominates over precipitation. This occurs during the months with water deficit (mainly between November and March) or in the dry years in which the potential evapotranspiration exceeds the precipitation (Fig. 1). Besides, the analysis of the historical trend of these variables indicates that the favourable conditions for the formation of evaporite salts have intensified in the last few years with the increase in temperature and PEVT (Fig. 2). This indicates that, regardless of the soil moisture, the atmospheric conditions for the formation of evaporites have been on an upward trend for the last 60 years.

Relative humidity is also an important factor in controlling evaporite formation. In particular, laboratory studies show that halite formation requires a relative humidity below 65% for the precipitates formed to be preserved in the sediments (Kinsman, 1976). The marsh area under study has an annual mean relative humidity of 75%, with occasional daily values below 65% (statistics by the Servicio Meteorológico Nacional [National Weather Service]). Under these conditions, the formation of halite would be possible though in an unstable process. However, field observations show that evaporite precipitates are preserved in the surficial sediments, possibly in metastable equilibrium.

Rainfall also conditions the amount of evaporite precipitates that may form and their dissolution. In embanked areas where ponds are formed, due to the accumulation of the tidal flow, total evaporation rarely occurs before receiving the contribution of rainwater. This rainfall contribution dilutes tidal water, leading to a lower percentage of evaporite precipitates in relation to the total volume of water that evaporates. Besides, halite dissolution takes place when the area is flooded once again by tidal flows or is dissolved by rainfall. When the dissolution occurs, the Cl^{-} and Na^{+} ions enter the shallow subsurface layer with the infiltration of the tidal or rain water, increasing the salt content (Carol et al., 2009).

Finally, it is concluded that the main factor that controls the halite formation in the marsh are the man-made embankments. Management guidelines such as performing drains with floodgates in the embankments will allow the evacuation of the accumulated tidal flow and therefor will help to reduce soil salinisation and thereby preserve the environment of the marsh.

Acknowledgements

The authors are very indebted to the Agencia Nacional de Promoción Científica y Tecnológica (National Agency for Scientific and Technological Promotion) and the Consejo Nacional de Investigaciones Científicas y Técnicas (National Council for Scientific and Technological Research) of Argentina for financially supporting this study by means of their grants, PICT 2013–2248 and PICT 2012–687.

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