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Soil-geomorphology relationships and landscape evolution in a southwestern Atlantic tidal salt marsh in Patagonia, Argentina

Ileana Ríos*, Pablo José Bouza, Alejandro Bortolus, María del Pilar Alvarez

Instituto Patagónico para el Estudio de los Ecosistemas Continentales (IPEEC-CONICET), Boulevard Brown 2825, CP U9120 ACF, Puerto Madryn, Chubut, Argentina

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A B S T R A C T

Salt marshes in Patagonia ecosystem are nowadays fully recognized by ecological, pollution and phytoremediation studies but a soil genesis and geomorphology approach is currently unknown. The aim of this study was to establish the soil-geomorphology relationship in Fracasso salt marsh and to determine the successional vegetation dynamics associated with the landscape evolution. This work was carried out in Fracasso salt marsh sited in Peninsula Valdés, Argentina, where an integrated study on soil-geomorphology relationship and landscape evolution was performed along with sedimentological analysis and vegetation changes (C3 photosynthesis pathway vs. C4 photosynthesis pathway plants). This last was determined through the δ13C composition from soil organic matter (SOM). Soil descriptions and laboratory analysis of soil samples were performed. A marked relationship between the vegetation unit, the dominant landform and the type of associated soil was found. *Limonium brasiiliense* (Lb) and *Sarcocornia perennis* (Sp), both C3 plants, are dominant in levees associated with tidal creeks, and soils were classified as Typic Fluvaquents, while *Spartina alterniflora* (Sa) soils were classified as Sodic Endoaquents and Sodic Psammaquents. Although no sulfidic materials were identified by incubation test, they were identified by hydrogen peroxide treatment in Sa soils, and now are considered potential acid sulfate soils (PASS). Sedimentological analysis from deepest sandy C horizons indicates a beach depositional environment. On the other hand, the δ13C stable isotope composition of SOM preserved into these buried soil acting as parent materials shows the dominance of C4 plants presumably belonging to *Spartina* species, suggesting a possible colonization and stabilization as the pioneer salt marsh.

1. Introduction

Tidal salt marshes are peculiar environments placed in the highest part of the intertidal zone where a muddy substrate generally supports a wide range of halophyte vegetation (Allen and Pye, 1992). These environments are formed according to the variations of sea level occurred during the Holocene and they are frequently flooded and subjected, not only to marine action, but also to the influence of water and continental sediments, either from estuary system or from surface runoff. This is why salt marsh soils have a very weak profile development, most of them belonging to Entisols Order and Aquents Suborder in places where aquic moisture regime prevails (Soil Survey Staff, 2014).

Anoxia and salinity conditions would be both sufficient to produce sulfidic materials (potential acid sulfate soils; Soil Survey Staff, 1999) due to the buildup and stability of sulfides, mainly pyrite, which comes from the biological reduction of sulphate dissolved in seawater and Fe²⁺ from marine sediments. This Fe²⁺ and SO₄²⁻ reduction is responsible for pH increase (Van Breemen, 1993; Konsten et al., 1994, Eqs. (1) and (2)). Therefore, sulfidic materials soils are classified as Sulfaquents (Great Group level, Soil Survey Staff, 1999).

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + \frac{1}{2} \text{H}_2\text{O} + 4\text{H}^+ & \rightarrow 2\text{Fe}^{2+} + \frac{1}{2} \text{CO}_2 + \frac{5}{2}\text{H}_2\text{O} \\
\text{SO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ & \rightarrow \text{H}_2\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Salt marsh soils are closely related with landforms, sedimentation processes and vegetation (Redfield, 1972; Fagherazzi et al., 2004). A first complete description of the main salt marsh landforms was made by Benito and Onaindia (1991) on the Mundaka-Urdaibai salt marsh (Basque Country, Northeastern Spain). They considered tidal channels as one the most important salt marsh landforms because of the exchange of matter and energy between the salt marsh and the ocean (Mitsch and Gosselink, 2000). In this way, linear channels are typical of the first stages of salt marsh evolution and, over the time, they evolve to more complex forms such as dendritic or meandriform-dendritic forms (Pye and French, 1993). Levees are another important salt marsh landform formed in the edge of the tidal channels as a consequence of

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sea water flow. In this way, during the flooding, a rapid sand sedimentation occurs showing a pattern of grain size decreasing with the distance from the channel to the inner marsh (Friedrichs and Perry, 2001). As regards vegetation, Zedler et al. (1999) established a relationship between this variable and marsh elevation in California salt marshes. Therefore, Otero and Macias (2001) related the physiographic position with the dominant vegetation in order to characterize the main salt marsh soils.

Particularly, botanical zonation is the most common salt marsh characteristic worldwide which can be observed in a generalized cross-section of the salt marsh coastline, where soil conditions such as salinity, saturation, immersion and anoxia are highlighted by a pattern roughly parallel to the coast (Pennings and Callaway, 1992; Silvestri et al., 2005). This pattern could reflect ecological succession assuming that bare soils of the tidal flats are colonized by typical low marsh species that promote soil accretion by trapping sediment and producing land elevation. This would enable the colonization of other species and eventually, the first colonizing plants would disappear, possibly settling in the lower levels of the marsh (Leeuw et al., 1993; Steers, 1977). However, changes in vegetation may also be due to changes in sea level, continental water and sediment discharges or any other possible event (e.g. storminess) or geomorphological and sedimentological processes (e.g. changes on depositional regimes and sediment autocompactation) which took place during Holocene (Allen et al., 2006; Choi et al., 2001; Goman et al., 2008; Lamb et al., 2006, 2007).

One way to determine past changes in the vegetation and the geomorphology is by assessing the proportion of plants C4/C3 through δ13C isotopic compositions from soil organic matter (SOM) which is recorded in the soil profile (Chmura and Aharon, 1995; Choi et al., 2001; Lamb et al., 2006, 2007). This is based on the discrimination of plants with respect to CO2 during the process of photosynthesis, which is due to the biochemical properties of primary enzymes that fix carbon and to the diffusion process that controls the CO2 entrance in leaves (Farquhar et al., 1989). This type of discrimination varies according to the photosynthetic cycles C3, C4 and CAM of the terrestrial plants. C3 plants reduce CO2 to phosphoglycerate (3C) via the ribose bisphosphate/oxigenase enzyme (Rubisco). That is why the plants with this type of photosynthesis have a δ13C of −32% to −22% with an average of −27% (Boutton, 1991). They are best adapted to cool and wet environments. Unlike C3 plants, C4 plants reduce CO2 to aspartic or malic acid (4C) via the enzyme phosphoenolpyruvate carboxylase (PEP). These plants discriminate less 13CO2 so they have higher values in δ13C than the C3 plants. The isotopic range for this plant type is −17% to −9% with an average of −13% (Boutton, 1991). They are best adapted to hot, sunny environments which implies an evolutionary advantage on C3 plants regarding to global warming. For example, in a northern Patagonia salt marsh, in the low position, where waterlogging conditions prevail almost permanently, Spartina alterniflora (C4 pathway) species is dominant and tolerant to salt stress (Mendelsohn and Morris, 2002; Bortolus et al., 2015) and soil anoxia (Bertness, 1991; Idaszkin et al., 2011). Whereas in the high marsh position, where the water table is about tens centimeters deep, Sarcocornia perennis (C3 pathway) are dominant (Bortolus et al., 2009; Idaszkin et al., 2011).

In addition, in order to determine if the SOM is autochthonous (i.e. it contains terrestrial components such as lignin, cellulose and humic substances) or allochthonous (it contains marine components), the weight ratio of organic carbon to total nitrogen (C:N) is used. Lamb et al. (2006) established that C:N ratios higher than 12 suggest that organic matter is from terrestrial sources. On the contrary, the allochthonous component coming from aquatic organisms tends to balance at a C:N ratio ranging from 4 to 10, indicative of organic matter without cellulosic structures from algae and phytoplankton.

In view of the foregoing, research on salt marshes on Extra-Andean Patagonian coast has focused mainly on ecological, pollution and phytoremediation aspects (Bortolus et al., 2009; Idaszkin and Bortolus, 2011; Idaszkin et al., 2011, 2014, 2015, 2017). As regards the pedology and geomorphology approach, Bouza et al. (2008) carried out a preliminary study describing salt marsh soils and classified the main Patagonian salt marshes. In addition, Playa Fracasso, a salt marsh of great ecological interest (Bala et al., 2008; Idaszkin et al., 2011), has only been focused from multi-disciplinary studies such as soil-plant relationship, hydrological-geomorphological relationship, and salinization processes (Ríos, 2015; Alvarez et al., 2015, 2016). Moreover, integrated studies on soil – geomorphology relationship and geo-ecology are scarce, mainly those aimed at elucidating landscape evolution, ecological processes (e.g. ecological succession) and geochemical processes. Considering all the above mentioned, the aim of this study was to establish the soil-geomorphology relationship in Playa Fracasso salt marsh and to determine the successional vegetation dynamics associated with the landscape evolution. The results will substantially increase the knowledge about salt marsh soils and eco-geomorphology, and will be useful to apply successful conservancy strategies for these environments in the protected area of Peninsula Valdés.

1.1. Study area

Peninsula Valdés (PV) is a 3600 km² area located on the Patagonia east coast between parallels 42°05′ and 42°53′S and meridians 63°05′ and 64°37′W connected to the mainland by the Istmo Carlos Ameghino (Carlos Ameghino Isthmus) which is only 11 km wide and less than 30 km long (Fig. 1). That is the reason why PV is almost an island that belongs to the Patagonian steppe, a cool semi-desert environment which surrounds it. It has a dynamic coastal zone with active sand dunes, numerous cliffs, spits, bays and coastal lagoons. The inside land is a desert steppe with dry climate and strong winds. UNESCO designated PV as a World Heritage Site list in 1999 because its coast and gulfs have global significance for the conservation of marine mammals (e.g. southern right whale). And following the ecological approach, PV is considered a transition area between two bathygeographic provinces (Monte and Patagonia) and two marine biogeographic regions (Argentina and Magallanica) which results in the richest diversity of marshes with both, muddy and rocky bottoms. In particular, the Spartina-dominated muddy bottom marshes are found in PV northern area (<42°S) and the Sarcocornia-dominated muddy marshes in the south (>42°S) (Bortolus et al., 2009).

The study area corresponds to the so-called Playa Fracasso (PF) salt marsh, northeast of the Istmo Carlos Ameghino (Fig. 1) on the Golfo San José (San José Gulf) margins. This gulf splits longitudinally into two hydrographic domains (east and west) by a climatic frontal system. The west circulation domain of the current is driven by well-defined vortices at the edge of the mouth whereas in the east domain -where the present study was performed-the conditions are more stagnant (Amoroso and Gagliardino, 2010). Fracasso salt marsh had a muddy plain built up by deposition of very fine grains produced by decantation and retention of halophyte plants. This salt marsh was protected by high sand bars, presumably due to both an exceptional storm and an extraordinary tide. The salt marsh was dominated by tides and exhibits a pattern of accretion. This pattern was largely controlled by the distribution of tidal channels and creeks and ephemeral alluvial sediment inputs from the mainland. The surrounding salt marsh geologic units are represented mainly by tertiary marine rocky sediments of Puerto Madryn Formations (Middle Miocene), and by the sandy-gravel deposits called “Rodados Patagónicos” (RP) of Plio-Pleistocene age (Haller, 1981; Haller et al., 2001). These Neogene-Quaternary units outcrop both on active cliffs and on erosion scarps of the littoral piedmont. The Holocene, which partially covered these geologic units, is formed by colluvial, alluvial, aeolic, and coastal marine deposits. In the study area the average annual precipitation is 246 mm and the average annual temperature is 12.5 °C. The tidal regime is semi-diurnal with an average value of amplitude between 7.01 and 4.57 m.a.s.l. (SHN, Servicio de Hidrografia Naval Argentino, 1983). Considering that Playa Fracasso in PV has been identified as one of the
main wetlands of the Patagonian coast, it has been declared one of the Wetlands of International Importance by the RAMSAR Convention on Wetlands and has been included in the Hemispheric Reserve Network for Shorebirds.

2. Materials and methods

2.1. Field work

To determine the relationship between landforms, soils and vegetation, three communities of the most dominant vegetation -S.
alterniflora (Sa), L. brasiliense (Lb) and S. perennis (Sp) – were described and associated with landform elements (Fig. 2). The term landform element is used in this study to define different geomorphic processes observed in the salt marsh (e.g. shallow pans, sand bars, dunes, alluvial fans, tidal creek, levees of the tidal creeks, point bars of the tidal creeks, mud flats). The landform elements (with relatively homogeneous vegetation patterns) were delimited by aerial photographs (1:20,000; SHN) and Google Earth® satellite images. Two topographic transects (P1 and P2) were drawn along the tidal creeks.
and P2, Fig. 2) perpendiculars to the shoreline were performed by an optical level Kern GK1-AC in order to identify the plant zonation and soil landform distribution. The 0-level was estimated considering an annual maximum extraordinary low tide according to the tide table provided by the National Hydrographic Service (Fig. 2). A soil pit was made in the most representative area for each mappable landform element traversed by topographic transects. The designation of soil horizons, morphological description and soil sampling was performed according to Schoeneberger et al. (2012). Soil classification was made according to Soil Survey Staff (2014). Initial pH and Eh of each soil horizon was determined according to Faulkner et al. (1989) using an electrode of a portable digital pH/Eh-meter. The soil samples were zipped, taken to the laboratory and stored in hermetic containers at ∼4°C. A monitoring network was performed where the groundwater wells (piezometers) were positioned over the topographic transects and near the soil pits in order to analyze the groundwater ionic composition and to study the geochemical reactions that take place at the saturated zone. The wells were drilled with a hand auger up to a depth of 3m and with 2.5-inch PVC tubes sealed at the bottom. A gravel filter was placed between the borehole and the casing, facing the permeable section, and then a layer of bentonite was added over the gravel pack to avoid a preferential vertical flow around the piezometer. Water samples were taken with bailers and water sample collection, preservation, and chemical analysis of major ions were carried out in accordance with the standard methods proposed by the American Public Health Association (APHA, AWWA and WPCF, 1997).

### 2.2. Laboratory processes and analytical determinations

At the laboratory, the soil samples were separated in two fractions: one was stored in freezer to −20°C and another was used to perform the analytical determinations. This last, was air-dried and sieved (2 mm mesh size) in order to separate the gravel and estimate its percentage. This fraction was stored in freezer to avoid a preferential vertical flow around the piezometer. Water samples were taken with bailers and water sample collection, preservation, and chemical analysis of major ions were carried out in accordance with the standard methods proposed by the American Public Health Association (APHA, AWWA and WPCF, 1997).

The CPSDI is derived as follows:

\[
\text{CPSDI} = \sum_{i=1}^{n} m_i
\]

Where \( n \) is the number of fractions and \( m_i \) is the lower weight percentage for each fraction \( i \).

A CPSDI of 94–100 does cover the sampling and analytical errors. Consequently, an index of 94 or more attests for an extremely high similarity. Between 90 and 94 the index points samples are very similar and between 85 and 90 the similarity is high (Langooh and Van Vliet, 1979).

In order to characterize and classify the hydromorphic soils and their relationship to bearing capacity, the n-value was determined (Soil Survey Staff, 2014). For this index determination, the field capacity (FC) was estimated from soil texture according to Bodman and Mahmud (1932) procedure (FC (%)) = 0.023 sand + 0.25 silt + 0.61 clay). Soil samples were dried and screened through to 2 mm mesh size. For each subsample < 2 mm, soil pH was measured from 1:2.5 soil-water extract previously treated with hydrogen peroxide 30% (peroxide pH, pHp; Ahern et al., 1998). A 1:2.5 soil-water extract was prepared from the fine earth and after 24 h the solution was vacuum pumped and its pH and electrical conductivity (EC) measured. The Ca\(^{2+}\) and Mg\(^{2+}\) contents in the soil solution were determined by EDTA titration, the Na\(^+\) and electrical conductivity (EC) measured. Total nitrogen was determined by micro-Kjeldahl method, and soil organic matter (SOM) was determined by ignition at 430°C (Davies, 1974) after dehydration at 105°C for 12 h. Soil organic carbon (C) was determined by dividing the organic matter content by the factor 1.72 (Page et al., 1982). Calcium carbonate equivalent was determined by gravimetric method (U.S. Salinity Laboratory Staff, 1954).

In order to determine the presence of sulfidic materials, incubation soil pH was measured once a week until stabilization, setting out soils under moist aerobic conditions (field capacity) at room temperature (initial pH, pHI; incubation pH, pHinc; Soil Survey Staff, 2014).

Cation-exchange capacity (CEC) was determined by saturating samples with 1 N Na-acetate at pH 8.2. Retained sodium in the exchange sites was extracted with 1 N NH\(_4\)\(^+\)-acetate at pH 7.0 and measured by flame photometry (Bower et al., 1952) after discarding the exchangeable cations. Total nitrogen was determined by micro-Kjehldal method and soil organic matter (SOM) was determined by ignition at 430°C (Davies, 1974) after dehydration at 105°C for 12 h. Soil organic carbon (C) was determined by dividing the organic matter content by the factor 1.72 (Page et al., 1982). Calcium carbonate equivalent was determined by gravimetric method (U.S. Salinity Laboratory Staff, 1954).

The isotopic compositions of δ\(^{13}\)C of soil organic carbon (bulk soil sample) and leaf plant tissues were determined by putting between 2000 and 8000 μg sample grounded at 0.5 mm sieve (40-mesh) and pretreating with HCl to remove inorganic carbon in tin capsules. Leaf plant tissues of Spartina alterniflora, Sarcocornia perennis and Limonium brasiliense were field harvested and laboratory cleaned in ultrasonic bath and oven-dried at 40°C. The grounded samples were analyzed in an elemental analyzer (Carlo Erba EA1108) coupled to a mass spectrometer continuous flow isotope ratio (Thermo Scientific Delta V Advantage) through a ConFlo IV interface. The δ\(^{13}\)C values were normalized in L-SVEC-NBS-19 scale, according Coplen et al. (2006).

C3 and C4 proportions of each sample were estimated according to Carvajal et al. (2013) as follows:

\[
C_{C3} = \left( \frac{(\delta^{13}C_{C3} - \delta^{13}C_{C4})}{(\delta^{13}C_{C3} - \delta^{13}C_{C4})} \right) \times 100 \%
\]

\[
C_{C4} = \left( \frac{(\delta^{13}C_{C4} - \delta^{13}C_{C3})}{(\delta^{13}C_{C3} - \delta^{13}C_{C4})} \right) \times 100 \%
\]

Where δ\(^{13}\)C\(_{C3}\) is the natural abundance of C in soil corresponding to C3 plants; δ\(^{13}\)C\(_{C4}\) is the natural abundance of δ\(^{13}\)C in the soil corresponding to C4 plants; δ\(^{13}\)C\(_{C3}\) and δ\(^{13}\)C\(_{C4}\) is the natural abundance of δ\(^{13}\)C in leaf plant tissues of C3 plants (δ\(^{13}\)C average of Sarcocornia perennis and Limonium brasiliense) and C4 plants (Spartina alterniflora), respectively, and C is the soil carbon content.
3. Results

3.1. Landforms and landscape characteristics

According to Pye and French (1993), Fracasso salt marsh was classified as open marsh coast, since it is affected by the predominant influence of marine action, which is principally protected both by sand bars which stand parallel to the coastline and by a small modern recurved spit developed towards the west of the marsh. The restrictive effect of wave action to develop the salt marsh was produced by a series of parallel sand bars, which were formed by sediment accretion from the mainland to the sea due to the influence of waves and the littoral drift. This littoral drift was mainly manifested from SW to NE and was recorded by a small modern recurved spit towards the west of the study area (Fig. 3). However, a paleo spit (small and recurved) was observed towards the east of the salt marsh with NE-SW direction indicating another current component. Return currents at low tide were those that produced the perpendicular channels to the coast cutting the bars almost completely; then, these channels in turn were connected by inter-bars channels.

The low position of the salt marsh was colonized by Spartina alterniflora (Sa), where the waterlogged conditions were almost permanent due to daily tides. In this sector the upper limit of the saturated zone was near to the surface, registering anoxic conditions throughout the soil profile. The tidal channels that cross the tidal plain had a meandering habit. Erosion occurred on the concave (internal) face with formation of levees at the top. On the convex face (external) sedimentation occurred (point bars) at the lower physiographic level (colonized also by Spartina alterniflora). The tidal channel levees were a few meters wide which were highlighted by the dominance of Limonium brasiliense accompanied with S. perennis. The inner marsh, the tidal flat was dominated mainly by Sarcocornia perennis, while at the higher marsh, where it was only reached by syzygy tides (towards the continental sector), the S. perennis community was accompanied by L. brasiliense and a few isolated S. densiflora plants. In these sectors, the drainage network in this landform that resulted from the flat slope and the preexisting microtopography, showed a dendritic or meandriform-dendritic pattern.

Fig. 3. Geomorphological sketch of the Fracasso salt marsh showing the topographic transects (P1 and P2), groundwater piezometres, soil sampling profiles and its associated vegetation units.
3.2. Soil-geomorphic relationship

The morphological soil descriptions (Table 1) show sedimentological discontinuities, which delimit successive depositional units, occurred during marsh landscape evolution. The n-values were < 0.7 in all soil horizons. The Sa soils occurred in sand bars environments; Sa1 soil developed in the inter-bar area, where clay and silt particles were deposited, evolving to the sequence Ag1-Ag2 horizons. This horizon sequence overlaid the 2Cg horizon with sandy texture corresponding to the foot-slope of the sand bar. The main redoximorphic feature found in this soil was constituted by a depleted matrix in the Ag horizons (value ≥ 4 and chroma ≤ 2, Munsell soil color chart; Schoeneberger et al., 2012), with few pore linings (root channels) in the upper part of the Ag1 horizon (Fig. 4a). On the other hand, Sa2 soil developed at the top of a sandy bar and the soil horizon sequence was Ag-Cg. (Fig. 4b). The redoximorphic features were represented by a reduced matrix (value ≥ 4 and chroma ≤ 2, Munsell soil color chart), which smells of rotten eggs, indicating the occurrence of sulfurates and sulfides, and therefore, strongly reduced conditions (Mitsch and Gosselink, 1993, Fig. 4b). Lb soils developed on the highest topographic position of the salt marsh. The horizon sequence of Lb1 prole was: A-C-2Cg1-3Cg2. It was also observed in water-table fluctuation zone (Fig. 4d).

The water tables at the time of sampling were from 63 to 76 cm deep. The Sp1 soil was developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil developed on levee deposits, but the Lb2 soil was developed on levee deposits, while the Lb1 soil 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3.3. Analytical determinations

The pH field increased with depth in Sa1 and Sa2 soils while it decreased with depth in Lb1, Lb2 and Sp2 soils. On the other hand, the Eh values decreased with depth, except in Lb1 soil, where a slight increase in potential redox with depth was observed in the sandy 3Cg2 horizon (Table 1). In Sp1 soil potential redox remained practically constant with depth. The decrease incubation pH values (Table 1) was not enough to diagnose sulfidic materials; only the deep horizons of Sp2 and Lb2 soil reached values of pH 3.7 and 4.2, respectively. In superficial horizons of Lb and Sp soils, a slight rise of incubation pH was recorded. The pH values fell drastically in the deepest horizons Sa1, Lb2, and Sp2 soils after hydrogen peroxide treatment, which denoted the presence of sulfidic materials (pyrite) and therefore the occurrence of potential acid sulfate soils (PASS; Ahern et al., 1998; Alsemgeest et al., 2005). The SEM-EDS analysis (Fig. 5) indicated the presence of sulfidic material registered by framoidal pyrite (from French word: framboise, raspberry-patterns) composed of spheroidal aggregates of octahedral pyrite microcrystals, which reached from 0.2 to 0.5 μm long. There were also isolated octahedral pyrite microcrystals. The EDS analysis showed the S-Fe relation (2:1) indicating the pyrite formula.

The carbonate contents reached the maximum value (1.7%) in Ag1

Fig. 4. Fracasso soils profiles and classification. a Sodic endoaquent (Sa1,a) and Sodic Psammaquent (Sa2,b) in Spartina alterniflora and Typic fluvaquent in Limonium brasiliense (Lb1,c; Lb2,d) and Sarcocornia perennis (Sp1,e; Sp2,f). bm black mottled; rm red mottled; gm grey mottled, sl sand lens. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
horizon of Sp1 soil, probably due to shell fragments observed in the field and during soil sieving. As regards to macronutrients, total soil nitrogen values did not exceed 0.4% in the studied soils, while organic carbon reached 6% in Ag1 horizon of Sa1 soil. The C and N contents indirectly varied with sand fraction contents (Table 1).

The pH values in the 1:2.5 soil-water extract (Table 1) were neutral to moderately alkaline in the surface and subsurface soil horizons but they decreased with depth to extremely acidic (pH 4) in 2Cg2 horizon of Sp2 soil. Both sodium and chloride were the dominant ions (Table 2) followed by sulfate and magnesium because the chemistry of the water table and soil solution was influenced by the sea water. The dominance of Na⁺ versus Ca²⁺ and Mg²⁺ (ESP > 15%) and a high value of EC (> 4 dS m⁻¹), met the conditions of saline-sodic soils (U.S. Salinity Laboratory Staff, 1954). The CEC in these soils reached maximum values of 67.3 cmol(c) kg⁻¹ in the Ag1 horizon of Sp1 soil, while a minimum value of 2.5 cmol(c)kg⁻¹ was recorded in the deepest C horizons of Lb1 and Sa2 soils.

Regarding the groundwater characteristics, the samples obtained from monitoring network (Fig. 3) showed soluble salt contents higher than the marine water in all piezometers, with fluctuations associated mostly with the evapotranspiration process and the inflow frequency. The sample located near the upped edge of the salt marsh was also influenced by continental groundwater flow. The groundwater pH values ranged from 6.7 to 7.3 and the Eh values were positive in most of the samples. The major ions contents indicated that the groundwater type that dominates was the Na-Cl type (Table 5).

Table 2: Chemical composition of soil solutions from Fracasso salt marsh soils extracts.

<table>
<thead>
<tr>
<th>Horizons (cm)</th>
<th>pH</th>
<th>CE (dS/cm)</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>SO₄²⁻/Cl⁻</th>
<th>ESP (%)</th>
<th>CEC (cmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Sa1) Sodic Endoquent</td>
<td></td>
<td></td>
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</tr>
<tr>
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<tr>
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<td>12.2</td>
<td>126.4</td>
<td>4.7</td>
<td>10.1</td>
<td>33.2</td>
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<td>10.5</td>
<td>0.08</td>
<td>27.9</td>
<td>10.3</td>
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<tr>
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Fig. 5. a SEM Mycrophotography of a pyrite framboid composed of octahedral microcrystals (center) and a few isolated microcrystals (bottom left and top right) and, b EDS spectrum showing sulphur and ferrum dominance (2:1); both obtained from the Sarcocornia perennis deepest soil horizon (2Cg2, Sp2) in Fracasso salt marsh.
occurrence. became richer as depth increase while in Sa soils this tendency did not occur.

In general, the isotope composition of leaf plant tissues of S. alterniflora, L. brasilense and S. perennis were 14.4‰, 28.8‰ and 25.6‰, respectively. In general, the δ13C of soil organic carbon (Table 1) varied between −17.9‰ and −24.0‰. In Lb and Sp soils, the isotope compositions dominated with the increase in depth showing an abrupt drop in the last horizon dominated by C4 (Fig. 7f). Finally, Sp2 soil presented a marked isotopic enrichment with increasing depth where the C4 was dominant in the deepest two horizons (Fig. 7f).

Even though isotopic impoverishment was observed in Sa1 as the depth increased, C4 dominated most of the Sa1 profile (Fig. 7a). But in Lb1, an inversion of the values of δ13C was observed in the first two horizons, corresponding to an increase in C3 plants and a decrease δ13C as the depth increased (Fig. 7b). In the case of Sp1 an isotopic enrichment was observed with the increase in depth, increasing the proportion of C4 (Fig. 7c). The same isotopic fluctuation was observed in the described soils corresponding to the P2 topographic transect (Table 1). In the case of Sa2 soil, an isotopic enrichment was observed in most of the profile and a slight isotopic impoverishment in depth with a clear dominance of C4 plants in most of the profile (Fig. 7d). Lb2 soil presented similar δ13C values throughout the profile where the C3 plants dominated with an increase in depth showing an abrupt drop in the last horizon dominated by C4 (Fig. 7e). Finally, Sp2 soil presented a marked isotopic enrichment with increasing depth where the C4 was dominant in the deepest two horizons (Fig. 7f).

### 4. Discussion

#### 4.1. Salt marsh geomorphology, soil development and classification

The results obtained in soil analysis showed a strong interrelationship among edaphic variables, mainly between texture and EC. For instance, the great permeability of sandy soils did not retain the salts in the soil solution and were washed by subsurface drainage. On the other hand, silts and clays had a larger specific surface area, which allowed

<table>
<thead>
<tr>
<th>Soil/horizon</th>
<th>Sa1/2Cg</th>
<th>Lb1/C</th>
<th>Lb1/3Cg2</th>
<th>Sp1/2Cg2</th>
<th>Sa2/Ag</th>
<th>Sa2/Cg</th>
<th>Lb2/3C</th>
<th>Lb2/3Cg</th>
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<tr>
<td>Folk and Ward method (φ)</td>
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<td>2.75</td>
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<td>2.92</td>
<td>2.69</td>
<td>2.69</td>
<td>2.85</td>
<td>2.73</td>
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<td>0.40</td>
<td>0.33</td>
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<tr>
<td>Kurtosis</td>
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<td>7.87</td>
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Table 3: Folk and Ward parameters of Fracasso salt marsh sandy soil horizons.

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<tr>
<th>Soil/horizon</th>
<th>Sa1/2Cg</th>
<th>Lb1/C</th>
<th>Lb1/3Cg2</th>
<th>Sp1/2Cg2</th>
<th>Sa2/Ag</th>
<th>Sa2/Cg</th>
<th>Lb2/3C</th>
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Table 4: Comparative particle size distribution index of the sand fractions, between C horizons of the studied soil profiles.

#### 3.5. Stable carbon isotope analysis of soil organic matter

The results obtained in soil analysis showed a strong interrelationship among edaphic variables, mainly between texture and EC. For instance, the great permeability of sandy soils did not retain the salts in the soil solution and were washed by subsurface drainage. On the other hand, silts and clays had a larger specific surface area, which allowed

#### 3.4. Grain-size distribution analysis of buried sandy soil horizons

The mean grain-size ranges (in phi values) varied from 2.915 to 2.689 phi (sand fine), and the standard deviation values ranged from 0.508 to 0.298 phi (Table 3). This sorting grade corresponds to the well sorted to very well sorted, except for the 2Cg horizon of Sa soils, corresponding to an increase in C3 plants and a decrease δ13C as the depth increased (Fig. 7b). In the case of Sp1 an isotopic enrichment was observed with the increase in depth, increasing the proportion of C4 (Fig. 7c). The same isotopic fluctuation was observed in the described soils corresponding to the P2 topographic transect (Table 1). In the case of Sa2 soil, an isotopic enrichment was observed in most of the profile and a slight isotopic impoverishment in depth with a clear dominance of C4 plants in most of the profile (Fig. 7d). Lb2 soil presented similar δ13C values throughout the profile where the C3 plants dominated with an increase in depth showing an abrupt drop in the last horizon dominated by C4 (Fig. 7e). Finally, Sp2 soil presented a marked isotopic enrichment with increasing depth where the C4 was dominant in the deepest two horizons (Fig. 7f).
In this case, the sand fraction was utilized because this relationship can be expressed by the following solution and the adsorption of electrolytes on the surface of the colloids favoring the retention of the soil. 

The slight rise in pH after the incubation test registered in surficial horizons of Sp and Lb soils could indicate a destruction of organic acids by oxidation (Alsemgeest et al., 2005). The inhibition of pyrite oxidation during aerobic incubation could be due to buffering properties, as carbonates contents (shell fragments) and high soil cation exchange capacity provided by clay minerals and/or by organic matter (Table 1). The rapid-acidification process generated by hydrogen peroxide treatment could be producing a breakdown of the buffering mechanism when a quick oxidation is produced (Van Breemen, 1975). In addition, this delay in the pyrite oxidation rate may be in part due to the formation of oxy-hydroxide of Fe and Al and silica coatings (Zhang and Evangelou, 1996, 1998; Alsemgeest et al., 2005).

The following equation shows the acidification process that occurs during the peroxide test:

\[ \text{FeS}_2 + 15 / 4 \text{O}_2 + 7 / 2 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2 \text{SO}_4^{-2} + 4 \text{H}^+ \]  

And if the pH < 3 implies that there is Fe\(^{3+}\) in the soil solution, the oxidation processes occurs without presence of O\(_2\) [Eq. (4)].

\[ \text{FeS}_2 + 14 \text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 16\text{H}^+ + 2\text{SO}_4^{-2} \]  

The slight rise in pH after the incubation test registered in surficial horizons of Sp and Lb soils could indicate a destruction of organic acids by oxidation (Alsemgeest et al., 2005). The inhibition of pyrite oxidation during aerobic incubation could be due to buffering properties, as carbonates contents (shell fragments) and high soil cation exchange capacity provided by clay minerals and/or by organic matter (Table 1). The rapid-acidification process generated by hydrogen peroxide treatment could be producing a breakdown of the buffering mechanism when a quick oxidation is produced (Van Breemen, 1975). In addition, this delay in the pyrite oxidation rate may be influenced by the formation of oxy-hydroxide of Fe and Al and silica coatings (Zhang and Evangelou, 1996, 1998; Otero and Macías, 2001).

In general, the pH-Eh relationship measured at the field (Table 1) is commonly associated with anoxia intensity in depth (Patrick and Delaune, 1972). However, the slight increase in redox potential in the 3Cg2 horizon of Lb1 soil can be related to oxygenate and nutrient-rich seawater that easily flows across the sandy deposits that underlie silt loam 2Cg1 horizon. This redox potential pattern was observed in the deepest gravelly deposits (buried Holocene beach ridges) of other marine environments along the Patagonian coast (Esteves and Varela, 1991; Bouza et al., 2008, 2017).

The decrease in depth of pH 1:2.5 soil-water extract could be due to acid sulfurous generation by oxidation of sulfides during air drying. This process was determined by the \(\text{SO}_4^{2-}/\text{Cl}^-\) ratio, which is 0.105 in seawater (Giblin, 1988; Hounslow, 1995; Araújo et al., 2012). Also, this ratio was similar to groundwater sampled in piezometers located next to Sp1, Sp2, Lh1 and Lb2 soil profiles (Table 2), and from seawater in the study site, with values around 0.1 (Alvarez et al., 2015); lower values of \(\text{SO}_4^{2-}/\text{Cl}^-\) ratio suggest the occurrence of sulfate reduction and the synthesis of metal sulphides, whereas a higher value suggests their oxidation. The \(\text{SO}_4^{2-}/\text{Cl}^-\) ratio is higher than in seawater in the Sa1 and Sa2 soils and deepest soil horizons of Lb2 and Sp2 soils. These soil horizons also have Eh values < 0 and sulfidic materials identified by peroxide treatment.
4.2. Sedimentation units and isotopic values relationship

The CPSDI and the cumulative frequency diagrams of the grain size distribution indicate the relative high similarity grade between horizons from actual sand bars (Sa soils) and the soil parent materials of sandy C horizons developed on the high-level salt marsh (Lb and Sp soils), thus showing a common sedimentary deposition environment. Also the mean grain-size of all samples analyzed is sand fine, indicating a high homogeneity grade and a beach sedimentary environment (Mazzoni, 1978). This beach environment is characterized by the standard deviation, which measures the sorting of sediments and indicates the fluctuations in kinetic energy or velocity conditions of depositing agent (Sahu, 1964). Thus, the range between moderately well sorted to very well sorted (values < 0.50 phi) of the studied samples, suggests the continuous action of the waves by the ebb and flow action, and a negative to slightly positive skewed sediment would indicate a beach sedimentary environment (Friedman, 1961; Andrews and van der Lingen1969).

The organic carbon preserved in soil horizons is mainly of terrestrial origin (C:N > 12), and thus could be associated with vascular vegetation developed in the salt marsh. On the other hand, the δ13C composition of the soil organic matter, both in surficial and buried sandy horizons (old beach levels) could be an indicator of vegetation shift, succession processes and salt marsh evolution (e.g. sea-level indicators).

As expected, the C4 provenance in soil organic matter of surficial horizons in low marsh level soils derived from actual Spartina alterniflora (Sa soils), while the C3 provenance derived from actual Limonium brasiliense and Sarcocornia perennis at low and high levels. However, the isotopic signature in soil organic matter of subsurfiicial and deepest C horizons indicates a dominance of C4 plant; so if this soil parent material corresponds to old beach levels, the original installed vegetation could be Spartina species (Ainouche et al., 2004) constituting a pioneer marsh. The presence of salt marsh plant with C4 photosynthetic metabolism such as S. densiflora, could be interfering with these determinations since the isotopic values corresponding to gender Spartina are practically the same for both species found in these marshes but in different topographic levels which is present in topographically high isolated areas in Fracasso. Nevertheless, the sedimentological component of the deepest sandy C horizons indicates a low tide area or beach levels that would belong to Spartina species. In this case, the grain-size analysis was useful to determine the sedimentary environment, as skewness is environment dependent (Friedman, 1961).

The C4 plant dominance was detected in the deepest high salt marsh soil profiles from 40 to 75 cm deep and considering that the total accretion rate in Fracasso salt marsh was estimated in 0.24 cm/year (Ríos, 2015), it could be inferred that a C4 plant was present since 200–300 years old which is consistent with the S. alterniflora colonization hypothesis proposed by Bortolus et al. (2015). According to these authors there are no records of the S. alterniflora presence on the South American Atlantic coast until approximately two to three centuries ago. These studies are mainly based on a review of herbarium collections, on historical floristic descriptions and on extensive literature that supports the controversial hypothesis that the plant was introduced accidentally on the South America Atlantic coast by the water from ballast or wood from merchant vessels.
5. Conclusion

Fraccaso salt marsh soils were classified as Entisols, Suborder Aquents. Particularly, Spartina alterniflora soils (Psamments and Sodic Endoaquents) were associated to sand bars environments. These soils were also considered potential acid sulfate soils (PASS) because of the presence of sulfide materials (Pyrite). On the other hand, Limonium brasiliense and Sarcocornia perennis (both Typic Fluvaquents) were associated to tidal channel levees and intertidal plains, respectively. For all from above we conclude that at great group level, a strong relationship between soil, landform and vegetation could be established. The challenge for future studies will be integrate these relationships in ecological studies (e.g. competition) in order to understand better these complexes interactions.

As regard salt marsh landscape evolution, our results indicate the presence of old sandy intertidal plains corresponding to ancient or pioneer salt marsh which is consistent with the Holocene salt marsh development, when geomorphological and sedimentological processes took place to perform the current Fraccaso salt marsh. Further studies, such as $^{14}C$ radiocarbon dating of soil organic matter (e.g. accelerator mass spectrometry, AMS) should be done in order to establish precisely when these processes occurred. Furthermore, C4 plant species identification (e.g. phytolites analysis) is necessary to corroborate S. alterniflora invasion.

Finally, this study constitutes an important contribution to the salt marsh knowledge in the protected area of Península Valdés and should be extended to other Patagonian salt marshes.

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