Characterization of tirsification soil weathering processes: The case of Los Lirios wetland, Guadalquivir basin, Seville, Spain

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ABSTRACT

The "Andalusian Black Lands" (Chromatic Vertisols) are soils of great ecological and productive importance, emphasizes their fertility, however, their formation is still a reason for discussion. The main objective of this work was to analyze the most recent geomorphological and environmental evolution and the physical-chemical behavior of some parameters along its profile (Chromatic Vertisols). This study was conducted in Los Lirios wetland of the Guadalquivir basin (Seville, Spain). In addition, samples were obtained in an exploration of the bottom of this wetland for a study on pollen. Samples were obtained to a depth of 260 cm every 6 cm in the 120 cm upper soil layer. Physicochemical characteristics of samples were determined in the laboratory. A total number of 20 samples were evaluated, 11 of which correspond to the 65 cm of compact horizons submitted to tirsification. Radiocarbon dating (C^{14}) was performed by Beta Analytic (Miami, Florida, USA). The results indicate the formation of a cumulative glacis and a subsequent environmental change towards more hydromorphic conditions might account for the surface and physical-chemical processes that characterize this alterological process, which generates soils of high ecological significance and agricultural productivity.

Key words: Black soil forming, wetland Andalusia, Spain.

INTRODUCTION

Tirsification (from the latin '*tirs*', meaning 'clay' or 'compact') is a complex pedological process that results from a number of ecological processes, such as the presence of substrates rich in smectite clays and the existence of flat or slightly low-lying lands (depression) intensely affected by seasonal hydromorphism . Because of this, organic matter evolves differently, and significant descarbonation and desalinization of the soil profile occur. Additionally, pH values in the soil are slightly acid, dissolving Fe and Mn (Fe^{2+} and Mn^{2+}). The intense black color, which is typical of this type of soil (Schwertmann, 1993; Nguetnkam et al., 2007; Borja et al., 2010; Porta et al., 2013). Besides these conditions lead to the formation of Vertisols (Duchaufour, 1984; Nordt et al., 2004; Nordt and Driese, 2010), Typic Cromoxerets according to Soil Conservation Service (1975), Chromic Vertisols (FAO, 1989), or Andalusian Black Earths (González-García et al., 1962; CEBAC, 1971; Verheye and de la Rosa, 2005), which correspond to soils with high agrological capacity locally called 'bujeos'. These authors and classification systems describe two different influences in their genesis: one predominantly lithological (lithomorphs) and another that corresponds to topo-lithomorphs, which in turn depend on the geomorphological conditions given by the topographical relief (surface processes and slope).

Due to their intense black color, these soils resemble Ukrainian Chernozems, but both formations show very significant differences (Núñez et al., 1997). Similar formations can be also found in the north of Morocco (Bouabid et al., 1996; Moujahid and Bouabid, 2015), where they are known as 'tirs' because of this edaphogenetic process (Real Sociedad Española de Historia Natural, 1914; Huguet del Villar, 1950).

Studies conducted during the early and mid-1900s considered that the formation of these soils was associated with old rainy climates and/or related to the bottoms of extensive wetland areas (Hernández-Pacheco, 1915; Dantín Cereceda, 1929; Huguet del Villar and Robinson, 1937; Fischer et al., 2008; Nordt and Driese, 2010). The presence of Paleolithic industry incorporated into the edaphic mass was described at that time (Breuil, 1917), and it has been also discussed in more recent studies conducted by Martínez (2012) and Araque (2014). According to Díaz and Recio (1991), these paleosoils might be related to the Holocene Climatic Optimum (post glacial climatic optimum), which coincides with the Atlantic period (7450-4450 BP).

All the necessary pedological requirements for the formation of this type of soil seem to be met in Los Lirios wetland (Fuentes

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de Andalucía, Seville, Spain). Therefore, this location constitutes a study site where the geomorphological and environmental evolution of the soil can be studied, and the physical-chemical behavior of some parameters along the soil profile can be analyzed. The objective of this work was the study of the process of tirsification, in the formation of the Chromic Vertisols, analyzing geomorphological, climatic and vegetation environmental change necessary for its formation.

MATERIALS AND METHODS

The place of the studio is located in Los Lirios wetland (37°26'9" N; 5°17'49" W), Guadalquivir basin, Seville, Spain. The climate of the province of Seville is continental Mediterranean with a clear oceanic hue. The annual average temperature oscillates between 18 and 20 ºC. Winters are mild, spring and autumn are warm and summers are dry and very hot, reaching max 40 °C during July and August. Rainfall, with an average of 650 mm per year, occurs mainly between October and April, with December being the rainiest month. Samples were obtained to a depth of 260 cm using a percussion hammer (HM1800, Makita, La Mirada, California, USA) and taking samples every 6 cm in the 120 cm upper soil layer. Physicochemical characteristics of samples were determined in the laboratory. A total 20 samples were evaluated (Table 1).

Data provided by the cartography of the Geological Map of Spain (Magna series, scale 1:50.000, nr 986) were interpreted and modified (IGME, 1977), using the topographic map of Andalusia at a scale 1:10.000 and interpreting the aerial photograph from the American flight in 1956. Google satellite images were also used.

Table 1. Physicochemical characterization of studied samples (n = 20).

Depth	C	P	Cal. act.	EC	Wet.	CO_3	Fe	Mn
cm	%	mg 100 g^{-1}	%	mmho cm^{-1}	—— % ——		mg 100 g^{-1}	
0-2	1.44	3.96	1.68	2.12	8.71	9	124	21
4-6	1.02	4.38	1.44	2.42	8.69	8	104	27
10-12	1.02	4.14	1.68	2.64	8.80	10	104	18
16-18	1.26	3.76	1.92	4.08	9.54	8	111	20
22-24	1.32	3.02	1.20	4.12	8.55	12	102	19
32-34	0.90	3.32	1.80	5.44	8.40	9	91	15
38-40	0.60	3.84	1.44	6.10	8.70	10	85	14
44-46	0.66	3.22	1.32	4.96	9.80	17	84	14
50-52	0.66	3.46	1.44	6.54	8.53	5	83	13
58-60	0.78	6.74	2.16	9.94	8.41	10	84	12
62-64	1.02	3.76	1.68	10.68	7.92	16	100	7
66-68	0.84	2.86	2.28	9.46	8.46	16	130	17
72-74	0.72	10.72	2.52	14.30	7.68	16	139	11
78-80	0.42	2.38	2.76	15.36	8.15	18	114	16
84-86	0.30	2.50	3.48	11.40	7.79	22	81	11
90-95	0.54	14.78	2.64	11.72	9.20	12	94	8
99-101	0.30	7.16	2.04	9.86	7.53	16	90	3
101-103	0.48	9.32	2.88	13.72	6.96	15	106	6
107-109	0.24	4.40	6.60	9.90	3.89	59	41	9
113-115	0.60	4.36	2.88	13.70	6.98	18	129	6

Cal. act: Activated limestone; EC: electrical conductivity; Wet.: water content.

The following parameters were studied in the laboratory: color (with Munsell); pH in water; electrical conductivity (EC); soil moisture; organic C and mineralized organic matter (OM; Sims and Haby, 1971); P Olsen; total carbonates ($CO_3^{=}$) and active limestone (Duchaufour, 1975); texture (pipette method); magnetic susceptibility (MS; Dearing, 1999); clay mineralogy (Brindley and Brown, 1980); and determination of Fe and Mn forms (Mehra and Jackson, 1960). Radiocarbon dating (C^{14}) was performed by Beta Analytic (Miami, Florida, USA).

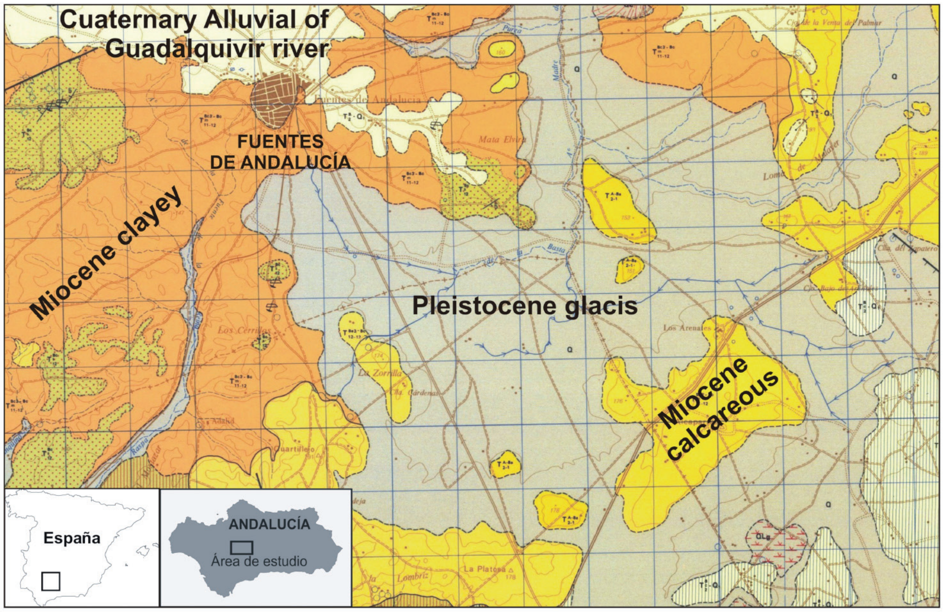
The pollen samples used were taken from the lower part of the wetland. Laboratory treatment for pollen samples, pollen isolation, and soil debris separation were performed according to the conventional methodology (Girard and Renault-Miskovsky, 1969; Dupré, 1979; Moore et al., 1991; Saa Otero et al., 1996). The pollen zones were visually determined on the basis of the variation of the preponderant taxa at the percentage level and with emphasis on the trends observed, the plant dynamics is discussed by virtue of climatic, historical and edaphic conditions and in the context of previous studies in the regional scope and in the Mediterranean basin (Yll et al., 2003), and the reference library of the Department of Botany Ecology and Plant Physiology of the University of Cordoba, Spain.

The design directed to a selection of sites, taking 20 randomly sub-samples, the study site was centered on a 10 ha area. Results were subjected to an analysis of correlation (Pearson) considered significant $P \leq 0.05$.

RESULTS Y DISCUSSION

Figure 1 shows the location and geological-geomorphological context of the study area. The higher areas of relief around 170 m a.s.l. are made up of hard white Miocene limestones (10YR 8/2), rich in carbonates (97%) and smectites in their insoluble residue (97%), this characteristic last of Vertisols (Coulombe et al., 1996; Ray et al., 2006). Miocene layers, which are stratigraphically located above them but lying on the bottom of the relief at 140 m a.s.l., are brown to yellowish brown color (10YR 6/(s) and 10YR 4/(h)), containing 84% clay and 90% smectites in their clay fraction. The interaction of the iron oxides with the clays depends on the pH; at low pH, the oxides precipitate on the surface of the clay minerals and, once these coatings are formed, they are stable at elevated pH (Peacock y Rimmer, 2000). Climate and depth of deposition of smectite in sedimentary environments is directly related to the high level of water, as well as warm and mode rate climates conditions with alternating grey and wet seasons that it changes frequently (Adatte et al., 2002). Iron oxides are useful field indicators of pedogenic environments for three reasons: (i) they include several minerals, (ii) these minerals have different colors, and (iii) the type of mineral formed is influenced by the environment. Therefore, recognizing the Fe-oxide mineral in the field by its color has a potential to yield information about pedogenesis (Schwertmann, 1993). When soil is

Figure 1. Location and geological context of studied area.



waterlogged, Fe^{3+} is reduced to Fe^{2+}, and this is reflected in an increase in Fe solubility. Overall, ion Fe^{2+} is moderately mobile in the secondary environment, whereas Fe^{3+} has a very low mobility. It is noted that the mobility of Fe in soil is largely controlled by the solubility of Fe^{3+} and Fe^{2+} amorphous hydrous oxides, although the formation of other Fe compounds, such as phosphates, sulfides and carbonates, may greatly modify Fe solubilities. The reactions of Fe in weathering processes are dependent largely on pH-Eh, and on the oxidation state of the Fe compounds involved. In general, oxidizing and alkaline conditions promote Fe precipitation, whereas acid and reducing conditions favor the solution of Fe compounds; therefore, acid soil tends to have higher levels of soluble inorganic Fe compounds than neutral and calcareous soil types (Kabata-Pendias and Pendias, 2000). Based on these lithologies, Figure 2 outlines the existing cumulative glacis from the Pleistocene chronology according to IGME (1977), which forms the entire depression. This deposit presents values of 30%-40% carbonates and 75% clay (75% is expansive clay). It is located in the interfluvial zone between the courses of the Guadalquivir and Corbones rivers; it presents limestone reliefs that surround the depression but no slopes are found. A number of streams that flow to the main fluvial artery barely affect the area.

Figure 2. Glacis accumulative and tirsified zone.

All these features make drainage of seasonal rainwater difficult, so that a whole network of canals has been constructed to prevent this autumn-winter hydromorphism, and allow for the agricultural use of these soils, mainly for the production of wheat and/or sunflower crops (Figure 3). Slow lateral surface drainage causes intense tirsification on the surface of the glacis up to 65 cm depth (10YR 4/1 'dark gray'), resulting in carbonated (contents of 10%) and with more detritus material (31.4% sand), but rich in clay material (57.6%), of which 73% corresponds to expansive clay (Figure 4).

Brownish colors (10YR) correspond to the lower part of the initial vertisolized glacis and the presence of a calcic Vertisol (FAO, 1989) (Figure 5). These colors evolved into 10YR 4/1, which is the typical 'dark gray' of the hydromorphism that affects the 65-cm surface layer of the Chromic Vertisol (FAO, 1989). There is no uniformity in the color of its different layers or horizons, which vary from brown to even redder tones (7.5YR) in some areas of this Vertisol (Figure 5).

Figure 5 shows the depth evolution of total carbonates and active limestone. Decarbonation occurs with contents ranging from 60% at 110 cm depth to 10% at 55-60 cm, which coincides with the lower limit of the tirsified zone. These values are constant along the profile, same as finely divided carbonate (active limestone) with values around 1.5%.

Figure 3. Core location and network canals in tirsified zone.

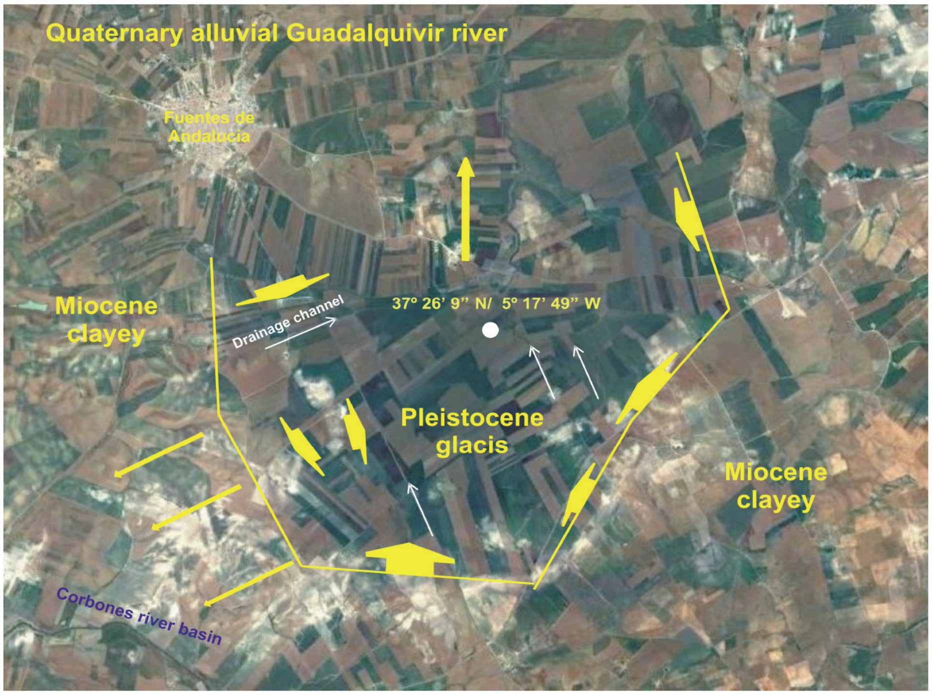
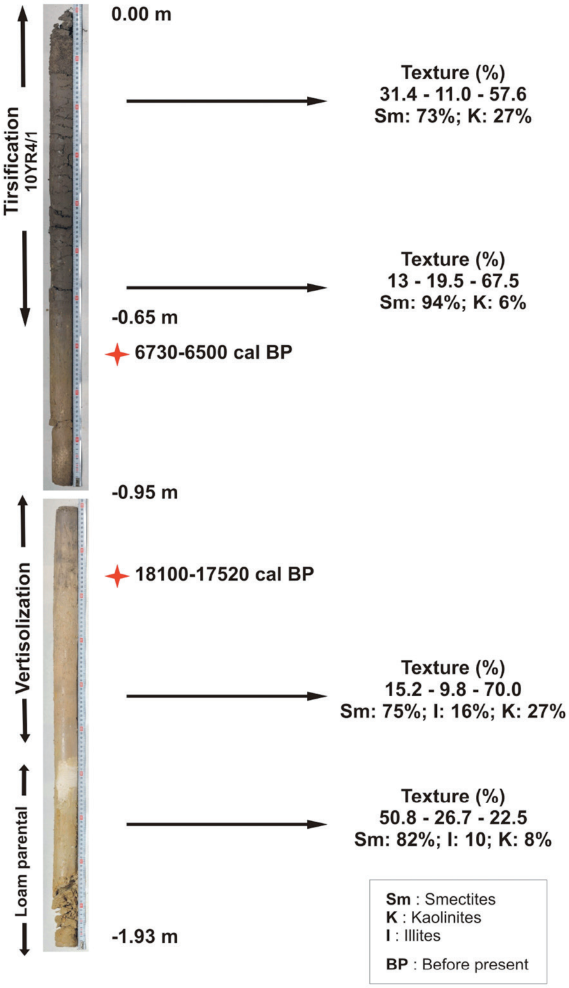


Figure 4. Texture, clay mineralogy and radiocarbon dating.



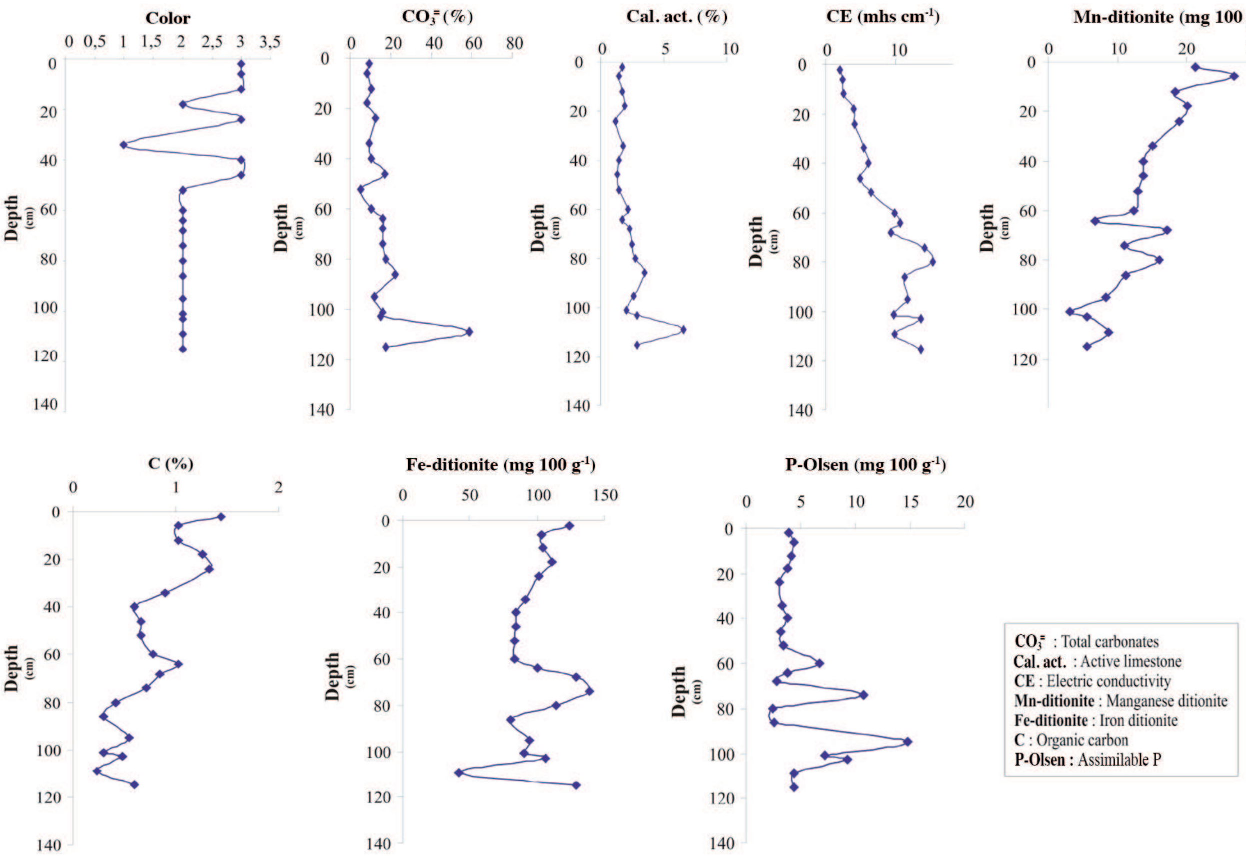
Soil desalination occurs gradually towards the surface layers, ranging from 15-16 mhs cm^{-1}, which coincide with the base of the tirsification, to 2 mhs cm^{-1} on the surface (Figure 5). Manganese content (Mn-dithionite) also increases towards the surface layers as the hydromorphism acts and penetrates the more subsurface layers of the profile, reaching levels of 25 mg 100 g^{-1}.

A similar behavior is observed with Fe levels (Fe-dithionite), reaching values of 120 mg 100 g^{-1} on the surface (Figure 4). Therefore, Fe amount is higher than that of Mn as described by Huguet del Villar and Robinson (1937), while the maximum levels are reached at depths in which tirsification begins. This seems to indicate a greater degree of alteration in this area, and it might be related to the presence of an old horizon buried in the calcareous paleo-Vertisol (FAO, 1989) developed on the glacis that is not tirsified.

This assumption is supported by the behavior of C content (C%) at different depths (Figure 5). Values of 1.02% found in the base of the tirsification, and the morphology of the curve that represents its distribution in depth provide evidence of the existence of this paleohorizon. Values range from 1.4% to 1.32% on the surface at a depth of about 25 cm, which might be related to possible surface vertic movements.

The values of assimilable P (P_2O_5-Olsen) (Figure 5) also support this assumption. Levels recorded throughout the tirsified zone are lower than those on its vertisolized base, with values of 4 and 10-12 mg 100 g^{-1}, respectively. Therefore, the great agricultural capacity of these tirsified soils seems to be more related to its geomorphological condition more than its chemical fertility, as the former favors a greater availability of water throughout the year

Figure 5. Evolution of soil parameters in tirsified zone.



the amount of phosphorus present in the soil solution depends on the extent to which it is adsorbed or desorbed by iron oxides, which may be influenced by interactions with organic matter (Almeida et al., 2003; Fink et al., 2016). Therefore, systems for fertilizer recommendation based on methodologies considering interactions between soil components such as oxides and organic matter. The phosphorus sorption capacity resulting from such interactions (e.g. residual P analysis), may be more reliable to ensure efficient, rational use of phosphate.

The weathered data and the distribution of the studied parameters at different depths suggest the existence of a polyphasic glacis with at least two formation phases. A first non-hydromorphism is found 150 cm apart from an earlier edafogenetic process (calcic vertisolization), and a second one with the formation of a tirsified soil (Chromic Vertisol; FAO, 1989) resulting from a less intense drainage network and under a wetland environment. Radiocarbon dating indicates that formation of this tirsified layer dates to 6730-6500 BP, while formation of the initial glacis corresponds to 18100-17520 BP (Figure 4).

The study of pollinic sequence provided evidence of this key environmental change (Table 2), as suggested by the great pollen load presented in this last phase compared to the first, the disappearance of *Olea europaea* and *Echium* spp. in the hydromorphic environment created, appearance of *Chenopodium* spp. and absence of phreatophyte plants in an environment of bodies of non-stagnant water. Palynology is a valuable tool when it comes to tackling climate change. The analysis of the pollinic content of a sediment allows an approximation to the existing plant landscape in an area, to define the observed changes and to translate them into climatic terms.

The correlation matrix between parameters defines the dynamics of the alterological process mentioned above (Table 3). Values for Fe and Mn are highly correlated (0.68); the presence of these elements is not compatible with the presence of carbonates ($CO_3^=$), active limestone (-0.43 and -0.40) or salts (EC), particularly Mn (-0.71). The hygroscopic moisture is related to the OM and controls Mn levels (0.49), while the presence of carbonates affects moisture content negatively (-0.85). Organic matter (C) controls almost all other soil parameters, except Olsen P, which is positively dependent on salinity and Mn (0.68), and negatively dependent on carbonate and active limestone levels.

Table 2. Pollen analysis of plant present in sediment in depth profile.

(+/-) 50 cm zone tirsification processes	(+/-) 150 cm zone vertisolation processes
Olea europaea (disappearance)	*Olea europaea* (presence)
Chenopodium spp. (appearance)	*Pinus* spp. (appearance)
Echium spp. (disappearance)	*Cistus* spp. (disappearance)
Non-hydrophytics plant (presence)	Maximum *Pinus* forest
Maximum pollen charge	Pollen present

Table 3. Correlation coefficients in soil parameters (n = 20).

	C	P	Cal. act.	EC	Wet.	$CO_3^=$	Fe	Mn
C, %	-	-0.24	**-0.59**	**-0.68**	**0.52**	**-0.52**	**0.44**	**0.68**
P, mg 100 g^{-1}	-	-	0.12	**0.40**	-0.04	-0.04	0.11	**-0.43**
Cal. Act., %	-	-	-	**0.48**	**-0.86**	**0.91**	**-0.43**	**-0.40**
EC, mmho cm^{-1}	-	-	-		**0.46**	0.33	0.13	**-0.71**
Wet %	-	-	-			**-0.85**	**0.37**	**0.49**
$CO_3^=$, %	-	-	-	-	-	-	**-0.52**	-0.35
Fe, mg 100 g^{-1}	-	-	-	-	-	-		**0.68**
Mn, mg 100 g^{-1}								

Bold numbers: 99% significance.

Cal. Act: Activated limestone; EC: electrical conductivity; Wet.: water content.

CONCLUSIONS

The tirsification process occurring in Los Lirios wetland presents the typical features of this pedological process, such as a special transformation of organic matter, decarbonation processes as well as desalination and solubilization of Mn and Fe.

The soil presents a topo-lithomorphic genesis, with the polyphasic formation consisting of a clay-cumulative Holocene glacis made up of smectites. It presents a slight slope that prevents stagnation, facilitates subsurface flows and results in a weak runoff, as required for the lateral movement of water and removal of soluble products.

A buried paleohorizon serves to separate this tirsified surface glacis from a lower one, which is older and affected by a calcic vertisolization. These environmental conditions and vegetation have guided both edafogenetic processes.

Tirsification does not imply the formation of deep vertic movements to homogenize the profile. The content of soluble Fe always exceeds that of Mn, while both Fe and organic C play a key role in the process. The neosynthesis of smectites is nonsignificant, while the geomorphological position seems to account for its agricultural capacity.

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