University of São Paulo
"Luiz de Queiroz" College of Agriculture

Pedogenesis and geochemistry of saltmarsh soils from the Brazilian coast

Danilo Jefferson Romero

Thesis presented to obtain the degree of Doctor in Science. Area: Soil and Plant Nutrition

Piracicaba
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Pedogenesis and geochemistry of saltmarsh soils from the Brazilian coast

versão revisada de acordo com a resolução CoPGr 6018 de 2011

Advisor:
Prof. Dr. **TIAGO OSÓRIO FERREIRA**

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1. Áreas úmidas costeiras 2. Pedologia 3. Geoquímica de ferro 4. Classificação I. Título

To my grandmothers Wilma and Anazira, who have proud of their PhD grandson; To my grandfathers José Jefferson and Sebastião, who supported my studies.

Às minhas avós Wilma e Anazira, que tem orgulho do seu neto Doutor; Aos meus avôs José Jefferson e Sebastião, que apoiaram meus estudos.

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Calvin and Hobbes (Billy Watterson)

SUMMARY

RESUMO

Pedogênese e geoquímica de solos de marisma da costa brasileira

As marismas são ecossistemas de transição entre a terra seca e os ambientes costeiros e tem características de ambos. Além disso, sua biota é adaptada para períodos de anaerobiose com saturação da água e alterações na salinidade. Além disso, são responsáveis por vários serviços ecossistêmicos, direto ou indiretamente associados aos solos. Apesar do aumento das pesquisas sobre o assunto, os solos de marismas ainda são pouco estudados no mundo, e não existem estudos no Brasil que descrevam a morfologia e classificação desses solos. Para isso, é necessário (1) analisar os estudos de marismas no mundo e suas relações com o solo; (2) avaliar as características morfológicas, químicas e físicas desses solos no Brasil; (3) Relacionar a geoquímica do ferro aos processos pedogenéticos nesses solos; (4) Discuta a relação entre a dinâmica do ferro na transição entre manguezais e marismas em clima tropical. Para isso, foram analisadas duas regiões contrastantes de marismas no Brasil (clima tropical e subtropical). Análises químicas (cátions, pH, Eh, C.E.), tamanho de partícula e análises sequenciais de ferro foram realizadas em ambas as áreas. Assim, as publicações de marismas estão mais relacionadas ao uso da terminologia de "sedimentos" do que "solo", com 794 (65%) e 437 (35%) publicações, respectivamente. No entanto, o solo de Bragança foi classificado como Gleissolo Tiomórfico órtico sódico, e os solos de Laguna foram Gleissolo Tiomórfico órtico sódico e Gleissolo Tiomórfico órtico típico. Suas diferenças foram relacionadas ao maior teor de ferro no Pará que o de Santa Cataria, e às formas de ferro, onde no Pará são mais óxidos (baixa e alta cristalinidade), e em Santa Catarina está na forma de sulfeto. Os processos relacionados ao ferro de sulfurização e sulfidização foram observados no Pará e Santa Catarina, respectivamente. Em Bragança, os solos das marismas se diferem dos manguezais devido à elevação das marismas, o que reduziu a inundação e favoreceu a oxidação da pirita (processo de sulfurização), enquanto no manguezal parte do ferro é retida como pirita (sulfidização), pela presença de matéria orgânica e sulfetos.

Palavras-chave: Solos de áreas úmidas costeiras, Pedologia, Processos pedogenéticos

ABSTRACT

Pedogenesis and geochemistry of saltmarsh soils from the Brazilian coast

Saltmarshes are transitional ecosystems between dry land and coastal environments and have characteristics of both environments. Also, their biota is adapted for periods of anaerobiosis with water saturation and changes in salinity. Furthermore are responsible for several ecosystem services directly or indirectly associated with soils. Despite the increase in research on the subject, the saltmarshes soils are still poorly studied in the world, and there are no studies in Brazil that describe the morphology and classification of these soils. For that, it is necessary (1) to analyze the studies of saltmarshes in the world and their relations with the soil; (2) to evaluate the morphological, chemical and physical characteristics of these soils in Brazil; (3) Relate the geochemistry of iron to the pedogenetic processes in these soils; (4) Discuss the relationship between iron dynamics in a transition between mangroves and saltmarshes in a tropical climate. For this, two contrasting regions of salt marshes in Brazil (tropical and subtropical climate) were analyzed. Chemical analyzes (cations, pH, Eh, C.E.), particle size and sequential iron analyzes were performed in both areas. Thus, saltmarsh publications are more related to the use of the terminology of "sediment" than "soil", with 794 (65%) and 437 (35%) publications respectively. However, Bragança saltmarsh soil was classified as Gleissolo Tiomórfico órtico sódico, and Laguna soils were Gleissolo Tiomórfico órtico sódico and Gleissolo Tiomórfico órtico típico. Their differences were related to the higher iron content on Pará than Santa Catarina, and to the iron forms, wherein Para it is more oxide forms (low and high crystallinity), and in Santa Catarina is in sulphate form. The iron-related processes of sulfuricization and sulfidization were observed in Pará and Santa Catarina respectively. In Bragança the saltmarsh soils differ from mangroves due to the elevation of saltmarsh, which reduced the inundation and has favoured to pyrite oxidation (sulfuricization process), while in mangrove soil portion of iron is retained as pyrite, once organic matter and sulphates are available.

Keywords: Coastal wetland soil, Pedology, Pedogenetic process

1. INTRODUCTION

Saltmarshes are responsible for providing a great variety of ecosystem services (Barbier et al., 2011). Recent studies have highlighted their abilities to act as an efficient sink for CO2 (Beaumont et al., 2014; Chmura et al., 2003), metals (Williams et al., 1994) and an important ecosystem to the maintenance of biodiversity (Deegan et al., 2002; Greenberg et al., 2014). These functions are, to some extent, directly or indirectly related to their soils. One example of the importance of saltmarsh soils in providing ecosystem services is the fact that the largest organic carbon pool in coastal ecosystems lies buried belowground, which contain more organic carbon than the aboveground biomass (Grimsditch et al., 2013; Kauffman et al., 2018).

It is underestimated there is 5,500,000 ha of saltmarsh worldwide (Mcowen et al., 2017), mainly in North America and Europe. Duarte et al. (2008) estimate a worldwide area of 140 Mha of saltmarshes, been the largest coastal wetland, while seagrasses (18 Mha) and mangroves (15 Mha) cover smaller areas. Despite its widespread occurrence, saltmarshes are being rapidly degraded around the world; losses are between 25% and 50% of their global historical coverage (Crooks et al. 2011, Duarte et al. 2008). In response to degradation, saltmarshes may lose their ability to act as sinks for metals or C but instead may be a source.

To understand that saltmarshes soils are essential to maintain their ecological services, it is pivotal to understand how these soils function, with respect to its formation, overall characteristics, chemical elements dynamics and behaviour to assess its responses under different stress situations (Kelleway et al., 2017). For this reason, studies about soil genesis (pedogenesis), soil formation, soil morphology and also pedology (the study of soil) are important.

Saltmarshes are coastal wetlands formed mainly by herbaceous vegetation and shrubs under the influence of saline or brackish water. Saltmarshes differ from mangrove forests mainly by the absence of trees (Adam, 1990). Both, mangroves forests and saltmarshes grasslands can occur at similar physiographic positions, however, each ecosystem has its optimum development under different climate regimes; temperate and sub-tropical climate usually favour saltmarshes; and sub-tropical to tropical climates mangroves (Perillo et al. 2009).

As mangroves, saltmarshes are transitional ecosystems located between drylands and the ocean, which present a biota adapted to long periods of water saturation, anoxic soil and salinity (Adam, 1990).

Saltmarshes have a high primary production both in the aboveground and belowground (Perillo et al. 2009). The higher production associated with the anaerobic environment (water-saturated), slows the rate of organic matter decomposition, promoting the accumulation of high contents of organic matter in its soils (i.e. paludization process). Hence, saltmarshes are an effective ecosystem in promoting carbon sequestration. Thus, when this ecosystem is impacted (e.g. land-use change), it may work as sources for CO_2 due to the increase in organic matter decomposition (Howard et al., 2014).

In response to the tidal action, saltmarshes soils are subjected to a redox-oscillating environment where different respiration processes act in an alternating fashion (anaerobic and aerobic respiration). Following the thermodynamic sequence, after oxygen (O_2), nitrate (NO_3^-) is the most avid electron acceptor, being reduced to nitrite (NO_2^-). Subsequently, manganese and iron oxides are used and then, sulphate is reduced to sulphite (Reddy et al., 1986).

The iron oxides (Hematite Fe_2O_3 and Goethite FeOOH) are the main pigmenting agent in soils. Iron reduction in oxygen-depleted environments drastically increases its solubility and produces low chroma and values colours in response to a process called gleyzation. Oxic microenvironments within the soil (produced by root and fauna activity) may favour the reoxidation of Fe producing mottled patterns with reddish or yellowish colours (redoximorphic features).

Under anoxic conditions (Eh $<$ 0 mV) sulphate reduction may be the main organic matter decomposition pathway (Baas Beccking and Moore, 1961; Connel and Patrick, 1969). In saltmarshes, sulphate is maintained by seawater, which allows the formation of both mono and di iron sulphites (mackinawite and pyrite). The formation of pyrite is called sulfidization (Fanning and Fanning, 1989; Ferreira et al., 2007). This process alters several chemical and morphologic properties (Griffin and Rabenhorst, 1989).

Sulfidization can contribute to the unavailability of potentially toxic metals by the coprecipitation of these metals with pyrite (Otero et al., 2000). Moreover, pyrite oxidation produces sulfuric acid, which can decrease soil pH to values as lower than 3.0 triggering the sulfuricization process (Fanning et al., 2017).

Despite the recent recognition of coastal wetland soils for several key ecosystem services (e.g. carbon sequestration and contaminant immobilization), pedological studies are still scarce in some of these environments. Saltmarsh soils have been mostly studied in temperate countries despite the fact that these ecosystems cover vast areas of tropical coastlines.

Thus, the present study aimed to:

1. Assess the pedological studies on saltmarshes worldwide;
2. Assess the main chemical and morphological characteristics of saltmarshes soils from Brazil;
3. Identify the iron dynamic related to pedogenetic processes active in these soils;
4. Study iron and sulphur geochemistry in tropical and subtropical saltmarsh soils.

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2. A BIBLIOMETRY APPROACH OF SALTMARSH SOILS

ABSTRACT

Saltmarshes are responsible for providing a great variety of ecosystem services such as sink of metals, atmospheric carbon, and important to the maintenance of biodiversity. Bibliometry consists on the quantitative and qualitative study of trends, subjects, based on data such as word frequency, co-occurrence, and could be used to understand research trends, scientific progression and dispersion Also, this technique provides an understanding of the scientific performance local and global, and the soil science. Nowadays, despite the rise of the number of scientific papers worldwide, there is an increase of works about saltmarshes, however, pedological studies about saltmarsh soils are still scarce. In this way, a bibliometric analyse was done to quantify studies about (1) saltmarsh, (2) saltmarsh soils and (3) pedology on saltmarsh; for this, was used Scopus scientific database and search about these topics. All searches focused on author keywords, title, author's countries, the total frequency of words, co-occurrence of keywords and title were analysed. The number of publications about saltmarshes until 2018 was 11,097. Among these publications, 2,021 involved saltmarshes and soils (18%), and 26 publications about saltmarsh and pedology (0.23%). The main countries with publications about saltmarshes are USA (5,045), UK (1,267) and China (675). Saltmarsh publications are more related to the use of the terminology of "sediment" than "soil", with 794 (65%) and 437 (35%) publications respectively.

Keywords: Coastal wetlands, Soil science, Scientometry; Estuarine soils

2.1. Introduction

Saltmarshes are responsible for providing a great variety of ecosystem services (Barbier et al., 2011). Recent studies have highlighted their abilities to act as an efficient sink for CO_2 (Beaumont et al., 2014; Chmura et al., 2003), metals (Williams et al., 1994) and an important ecosystem to the maintenance of biodiversity (Deegan et al., 2002; Greenberg et al., 2014). These functions are, to some extent, directly or indirectly related to their soils. One example of the importance of saltmarsh soils in providing ecosystem services is the fact that the largest organic carbon pool in coastal ecosystems lies buried belowground, which contain more organic carbon than the aboveground biomass (Grimsditch et al., 2013; Kauffman et al., 2018).

It is underestimated there is 5,500,000 ha of saltmarsh worldwide (Mcowen et al., 2017), mainly in North America and Europe. Duarte et al. (2008) estimate a worldwide area of 140 Mha of saltmarshes, been the largest coastal wetland, while seagrasses (18 Mha) and mangroves (15 Mha) cover smaller areas. Despite its widespread occurrence, saltmarshes are being rapidly degraded around the world; losses are between 25% and 50% of their global historical coverage (Crooks et al. 2011, Duarte et al. 2008). In response to degradation, saltmarshes may lose their ability to act as sinks for metals or C but instead may be a source.

To understand that saltmarshes soils are essential to maintain their ecological services, it is pivotal to understand how these soils function, with respect to its formation, overall characteristics, chemical elements dynamics and behaviour in order to assess its responses under different stress situations (Kelleway et al., 2017). For this reason, studies on soil genesis (pedogenesis), soil formation, soil morphology and pedology (the study of soil) are important.

Bibliometry is the application of indexes and statistical analyses to study publications, such as book, magazines and journals (Pritchard, 1969). Librarians and journals have used statistics on library systems for a long time, such as the Journal Impact Factor (Hood and Wilson, 2001), to understand the dispersion of publications. However, bibliometry consists on the quantitative and qualitative study of trends, subjects, based on data such as word frequency, co-occurrence, citations and co-citations, which, could be used to understand research trends, scientific progression and dispersion (Cox et al., 2019) in different areas of the scientific knowledge (Aksnes et al., 2019; Huang et al., 2012; Sun et al., 2012; Zhi and Ji, 2012). This technique also provides an understanding of the scientific performance both in local and global scales, and soil science is an outstanding and developing field among environmental sciences (Cancian et al., 2018).

As showed by Chen and Xiao (2016), it is possible to use different approaches based on the publications keywords: using all keywords to explore the structural characteristics of the domain of knowledge at the macro-level; or/and use some “selected” keywords (such as those with higher frequency) to analyse the details of a domain’s major research topics and their relation at the micro-level.

Nowadays, despite the rise of the number of scientific papers worldwide, there is an increase of works about saltmarshes, however, pedological studies are still scarce. Thus, a bibliometric analyse was done to quantify studies about (1) saltmarsh, (2) saltmarsh soils and (3) pedology approach on saltmarshes; and also, to verify which nomenclature was used to refer to saltmarsh substrate; highlighting pedological features (as chemical elements and taxonomy).

2.2. Data source and Methodology

Scopus® (Elsevier) and Web of Science (Clarivate Analytics) are the most commonly used scientific databases worldwide, and both are daily improving their system. The use of one or another depends on what item will be analysed, the scientific field and also the period of analysis (Chadegani et al., 2013). Indeed, even with differences between them, there is a high correlation between data obtained in both databases (Archambault et al., 2009; Vieira and Gomes, 2009). In this work, the data for analysis was obtained from the Scopus® database.

Three types of searches were carried out on Scopus. The first was done to comprehend the totality of saltmarsh studies by searching the following keywords: "Salt Marsh" OR "Saltmarsh" with plural forms. The second search was focused on soil studies and, thus, it was used "Salt Marsh" OR "Saltmarsh" AND "Soil" also with the corresponding plural forms. The third search was done to assess the pedology approach in the studies of saltmarshes, by using "Salt Marsh" OR "Saltmarsh" AND "Soil Morphology" OR "Soil Genesis" OR Soil Classification" OR Pedology OR Pedogenesis, and the corresponding plural forms. These words were searched on Titles or Abstracts or Keywords of each work. The search was performed for all period on the Scopus database, until 2018.

Data were analysed on Scopus® website, VOSViewer (van Eck and Waltman, 2010), and also on R (R Core Team, 2019). The words were grouped in singular forms, misspelt words were revised, meaningless words and prepositions were excluded, and keywords with the same meaning were grouped into a standard form (e.g. sulphate and sulfate; saltmarsh plants and saltmarsh vegetation).

All searches focused on Author Keywords, Title, Author's Countries, the total frequency of words and co-occurrence of keywords were analysed. Authors keyword was used instead of title or index keyword because they can represent the paper's main concepts and there are substantial implications for the understanding of the knowledge structure (Yi and Choi, 2012).

Three chemical elements are important on coastal wetlands pedogenetic processes: iron (Fe), carbon (C) and sulphur (S). They are related to the core soil processes in coastal wetland soils such as gleyzation, paludization and sulfidization, sulfuricization. Not only these three chemical elements were select, but also the most frequent as a keyword was select to be analysed among the saltmarsh studies.

Discriminant analysis is a multivariate analysis able to determine a better linear function to discriminate groups, which maximizes the variance between groups and reduces the variance inside the different groups. It is used when there are knowledge groups and it is necessary to check if the groups to which observations belong are distinct, it also shows the properties of the groups using explanatory variables (Manly, 2008).

On “Saltmarsh” search, were create two groups: (1) keywords related to soil and (2) keywords related to sediments. These keywords carefully analysed and were classified by kind of process as physical, chemical, biological or none. Thus, trying to understand how these processes are related to each substrate (soil and sediment), was performed discriminant analyses between soil and sediments, using the frequency of keyword and its process kind. In addition, discriminant analyse was check with Wilk’s lambda test.

2.3. Results and Discussions

Until 2018, the number of publications about saltmarshes was 11,097. Among these publications, 2,021 are related to saltmarshes and soils (18% of the total saltmarshes studies), and only 26 publications involved saltmarsh and pedology, which represents 0.23% of the total saltmarshes studies.

Our results show that saltmarsh ecosystems have been continuously studied since the 19th century. However, until 1964 it was a research topic with a rather low number of scientific publications (1114 publications). There was a significant difference between the number of publications from the research topics “saltmarsh”, “saltmarsh and soils”, and “saltmarsh and pedology”. For “saltmarsh and pedology”, the period of publications was not continuous, with many gaps between the years (Figure 2.1). In recent years, research topics such as carbon sequestration and blue carbon, are between the most studied (Kristensen and Rabenhorst, 2015), which increased the number of publications.

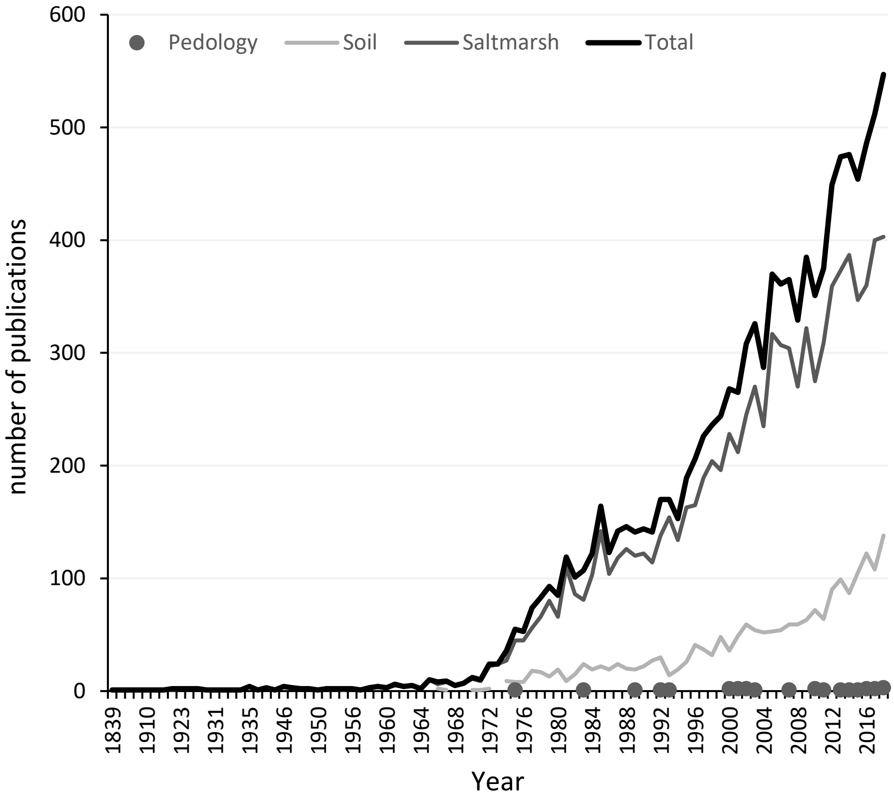

Figure 2.1. The number of publications by year of studies related to (●) saltmarsh and pedology; (▬) saltmarsh and soil; (▬) only saltmarsh; and (▬) the total of publications.

Because it is an ecosystem usually found under temperate/subtropical climate, it was expected that the studies would be concentrated in these locations and not worldwide. Countries with most publications about saltmarshes are of temperate climate or beyond the tropics, such as Australia (Figure 2.2). The countries with more publications about saltmarshes are USA (5,045), UK (1,267) and China (675). However, regarding the studies of "saltmarsh soils", the UK lost its position and Spain advances with 162 publications. USA, Italy and Spain hold more than 50% (14) of the studies regarding "saltmarsh and pedology" (Figure 2.2).

Brazil is essentially a tropical country; indeed, most of its coastline falls within the tropics, with the exception of the south of the country, which is below the tropic of Capricorn and is marked by a subtropical climate. This is probably a reason why Brazil has a reduced number of studies about saltmarshes (151 publications, 15th position) and saltmarsh soils (21 publications, 16th position).

Coastal wetlands substrates are treated either as soil or as sediments in the literature which mostly depends on the authors' background. However, the use of these terms shows a different approach toward these substrates.

There is a similar use of the term "sediment" and "soil" by scientists from different areas, like marine or earth scientists (Kristensen and Rabenhorst, 2015). Aiming to understand the difference between soil and sediment on saltmarsh researches, a discriminant analysis was used. Also, the significance of the discriminant analyses was checked with Wilk's lambda test.

When authors use the term "soil", the keywords of the works are mostly associated with biological and chemical processes (Figure 2.3). On the other hand, when the term "sediment" is used, the keywords are mostly related to physical processes (Figure 2.3). Our results evidence a clear difference between the terms soil and sediment, which is evidenced by the distance of the centroid areas on discriminant analyses (tested with Wilk's Lambda test), defining different groups (Figure 2.3).

In this context, saltmarsh publications use more the terminology of "sediment" than "soil", with 794 (65%) and 437 (35%) publications respectively. This pattern is similar to that found by Kristensen and Rabenhorst (2015) within a smaller period (1970-2014) not only for saltmarshes but also to mangroves.

The difference in the used terminology could be related to the evolution of soil science, since, for many years, coastal wetlands were not considered as soils in many soil classification systems. For this reason, mangrove's, saltmarsh, hypersaline tidal flat and seagrasses soils were called and understand as sediments. Until today, sediment is the background for some disciplines. On the other hand, soil science is evolving and is being more multidisciplinary. Subaqueous soils, for example, were included in the USDA definition of soil in 1999 (twenty years ago), on the World Reference Base for Soil Resources (WRB – IUSS Working Group, 2014), subaqueous soils were added only in 2006. In Brazil, mangrove soils were called "indiscriminate mangrove soils" until 1999 before the first edition of the Brazilian Soil Classification System (SiBCS - Santos et al., 2018) was released, when the Gleissolos (Gleysols) or Organossolos (Histosols) incorporated these wetland soils. Nowadays, on the fifth edition of the Brazilian Soil Classification System (2018), soil definition included soils under 2 m of the water column; however, SiBCS still does not has a subaqueous class or specific diagnostic properties for these soils.

Gradually, soil science has broadened its horizons and has aimed wetland soils in its most recent studies. Moreover, wetland soils have received great due to its key role in providing ecosystem services. In this way, more studies are expected using the term soil to refer to coastal wetland substrates in the next years.

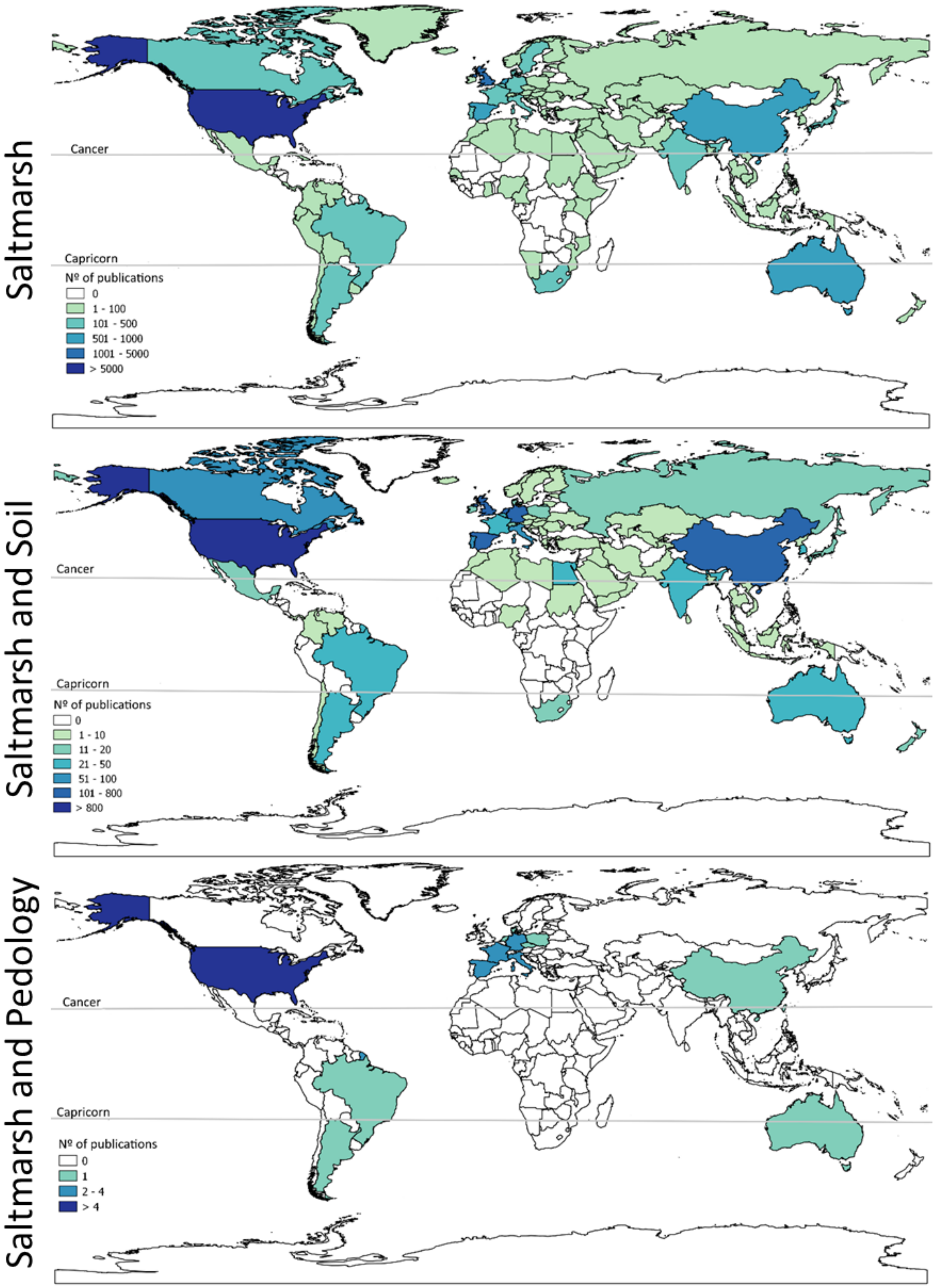

Figure 2.2. The number of publications for countries for each search. Unknown data was not considered.

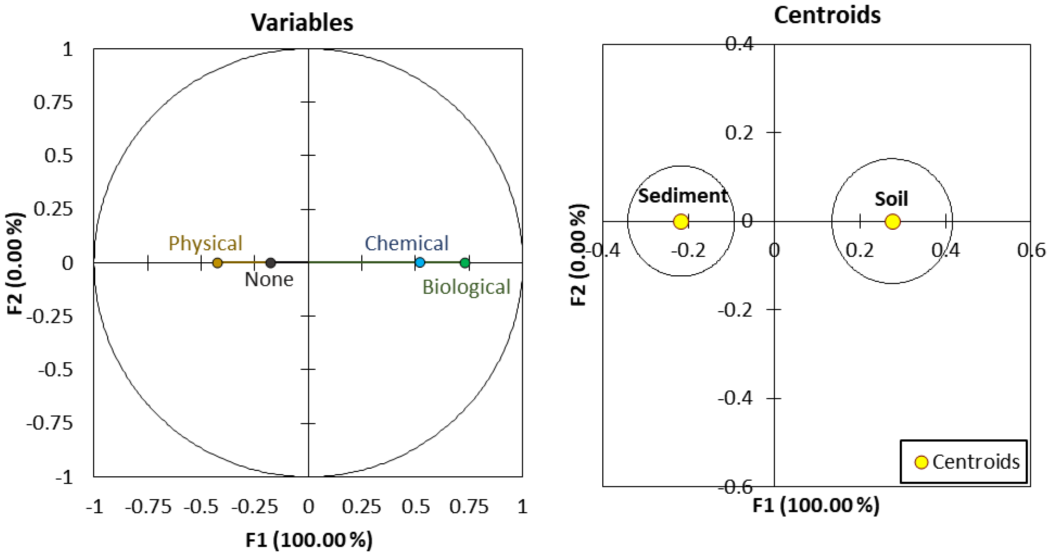

Figure 2.3. Discriminant analyses between "*Soil*" and "*Sediment*" based on the frequency of each kind of process (Chemical, Biological, Physical or none).Soil and Sediment have different centroid areas, thus, they are different groups tested with Wilk's Lambda.

Science focus changes over the years and new trends affect the researches and new "hotspots" are discovered and affected the studies about saltmarshes. During the 90s, the focus of saltmarsh studies was the "community structure", "succession" and plant species "zonation" (Figure 2.4), and, thus, functional ecology. With time, functional ecology was replaced by the "ecosystem services" approach and the "climate change" related issues, also including "phytoremediation", "carbon sequestration" and "blue carbon" (Figure 2.4).

Studies on saltmarsh soils also have changed over the last 100 years. On the 90s and beginning of 00s, the major keywords were related to "community structure", "nitrogen fixation" and "germination". During the 10's, soils studies also have been focused on "climate change", including "soil organic carbon", "carbon sequestration' and "blue carbon" appeared as the major keywords (Figure 2.5).

Saltmarshes vegetation are typically represented by *Spartina alterniflora* species and there is a strong keyword co-occurrence with the plant *Phragmites australis* species (Figure 2.4 and 2.5). Mangroves and seagrasses have a strong keyword co-occurrence with saltmarsh studies, showing that despite the differences between these ecosystems, these three coastal wetlands are spatially or functionally related.

In the soil studies at saltmarshes, climate changes are not only a current research topic but also has a co-occurrence with mangroves, indicating that "climate changes", "saltmarshes" and "mangroves" have been studied together (Figure 2.4).

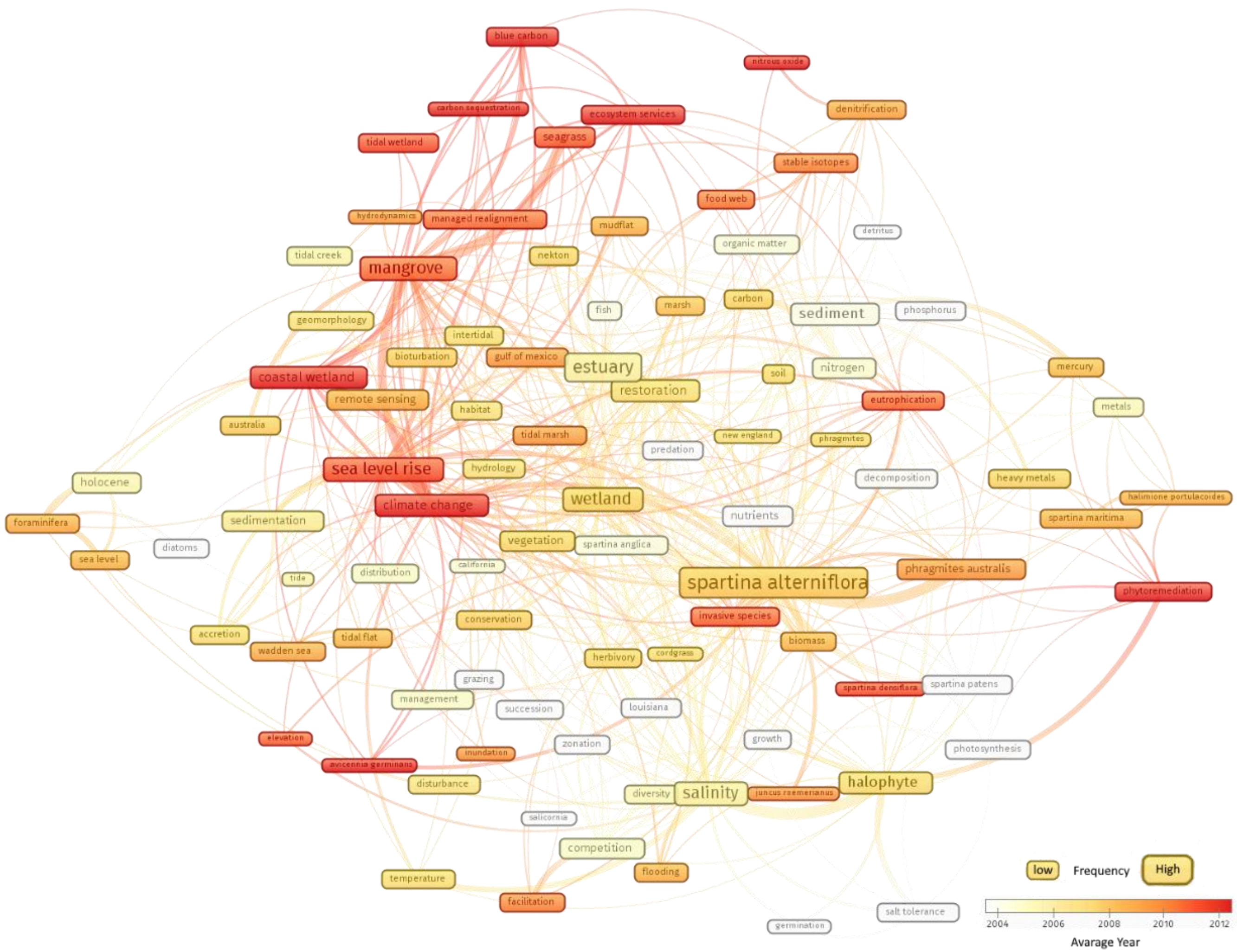

Figure 2.4. Occurrence, co-occurrence and average year of publication of keywords on saltmarshes studies. (links lower than 5 co-occurrence were not showed).

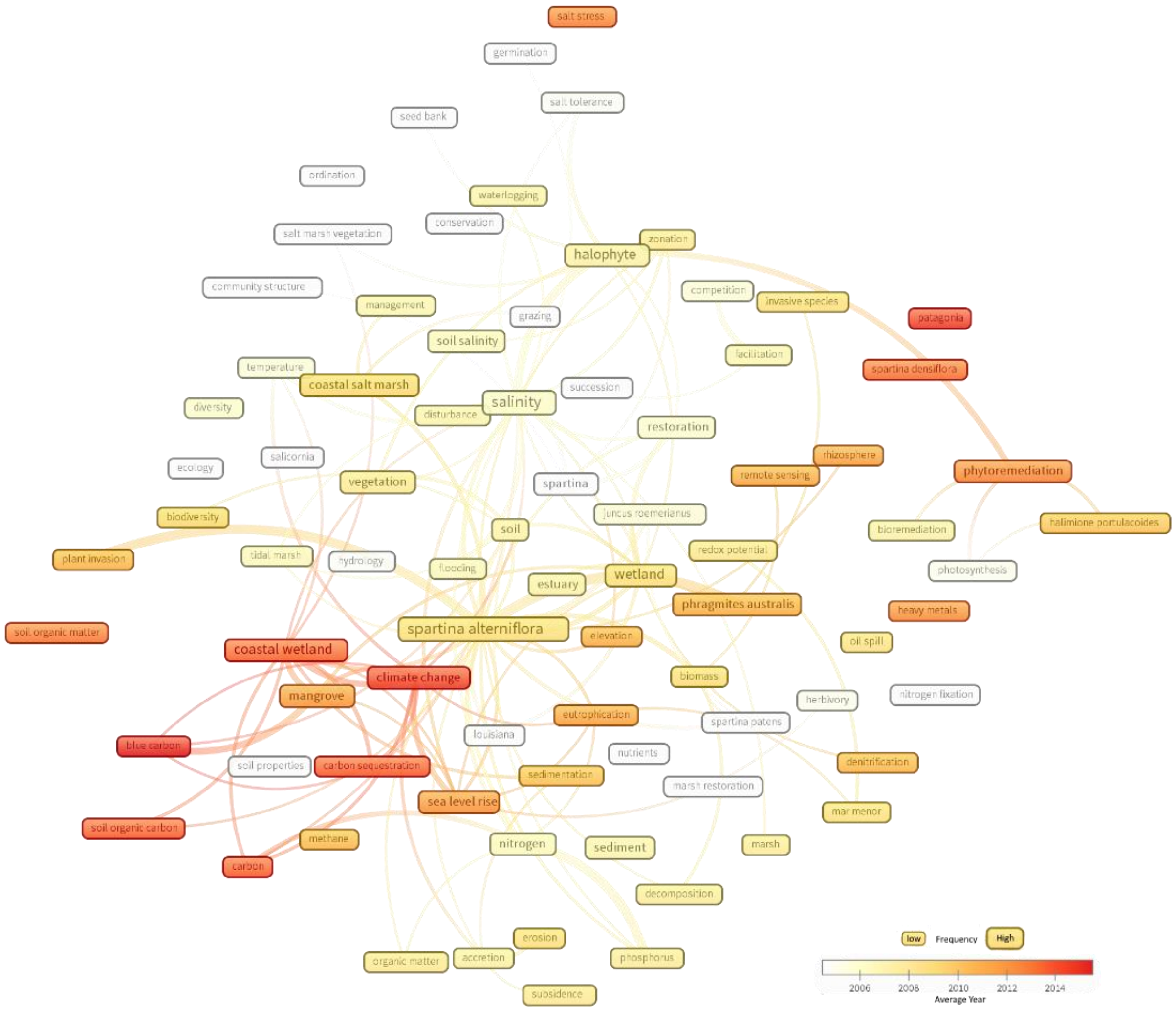

Figure 2.5. Keywords occurrence, co-occurrence and average year of publication from saltmarsh and soils studies (links lower than 3 co-occurrence were not showed).

Nitrogen (N) appeared with the highest frequency as a keyword on saltmarsh soil studies, but it is not directly related to any pedogenetic process. For this reason, iron (Fe), carbon (C) and sulphur (S) were chosen to be analysed on this study.

There is a clear difference between the number of publications' keyword related with at least one of the four selected chemical elements on "Saltmarsh" (620 publications), "saltmarsh and soils" (403 publications) and "saltmarsh and pedology" (10 publications).

The frequency of these keywords is lower than expected, mainly on the research topic "saltmarsh and pedology", once pedological processes are related to these chemical elements. However, it was observed that some works have not used these keywords, instead, they used correlated words, e.g. "pyrite" to "iron" and/or "sulphate", or "organic matter" instead "carbon" or "blue carbon".

Among these four chemical elements, nearly 50% of the publications regarded "carbon", and almost 30% "nitrogen", while "sulphur" reached less than 20% but was not used as a keyword on pedological studies, where "iron" appeared in 20% of the studies (Figure 2.6). It is important to highlight that this does not mean that sulphur has not been studied on saltmarshes but means that it was not used as a keyword (as for example pyrite –FeS2) or it was not related with the principal objective of the studies.

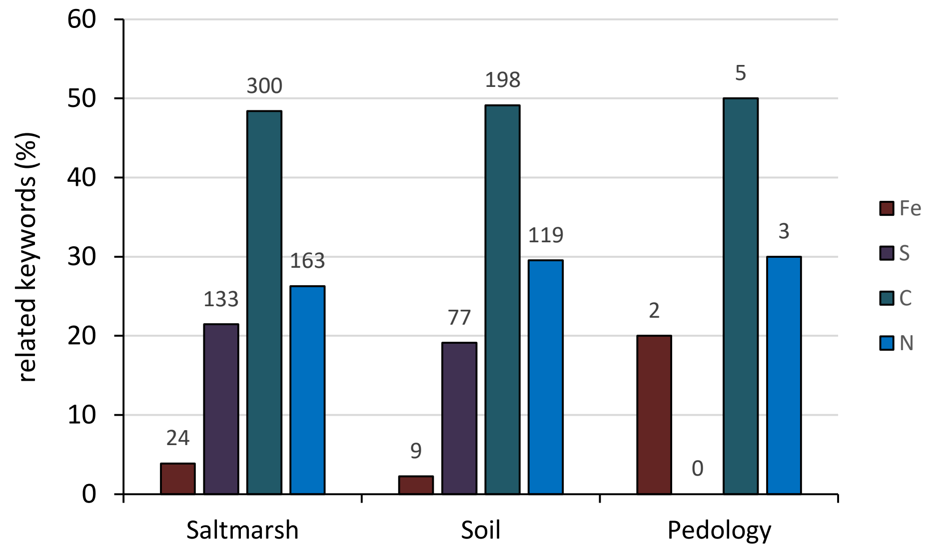

Figure 2.6. Per cent of works that used the words Iron, Sulphur, Carbon and Nitrogen as keywords (number of related keywords is indicated above the bar) for each search (Saltmarsh, Saltmarsh and Soil; Saltmarsh and Pedology).

Soil classification is a useful tool to improve changes of information about soil between scientist and users (e.g. politics of land use and management, farms, engineers, ecologists and others). In this way, to have soil classes that include coastal wetland soils is important to protect these areas and to improve the sharing of specialized knowledge.

The main soil classification term found as a keyword was "subaqueous soil" and "paleosol", which are not the official orders in Soil Taxonomy or WRB (IUSS, 2014) systems. All soils could be related to hydromorphic conditions or coastal wetlands, as Arenosols and Gleysols (Figure 2.7).

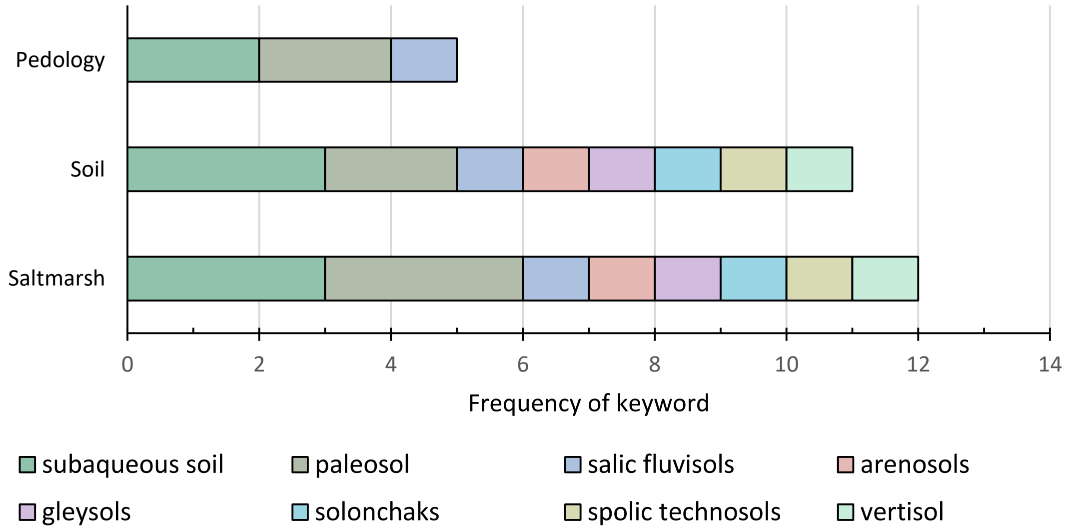

Figure 2.7. Frequency of keywords about soil classes on each search (Saltmarsh and Pedology; Saltmarsh and Soil; and only Saltmarsh)

2.4. Final Considerations

Studies about coastal wetlands as saltmarshes are increasing worldwide, it is important not only to understand these ecosystems but also to protect, and recovery them. Thus, it was observed the increment of soil studies and climate change keywords.

Despite pedology has not a clear increment of studies, could be associated with the scientific area that studies it. Concentrated in marine scientists, biologists and ecologist, and a lack of earth and soil scientists (more term "sediment" than "soil"). However, it shows that there is a gap of information about pedology in this ecosystem, which should be filled and integrated into mangroves, seagrasses meadows and hypersaline tidal flats.

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3. MORPHOLOGICAL CHARACTERIZATION AND CLASSIFICATION OF SALTMARSHES SOILS ALONG THE BRAZILIAN COAST

ABSTRACT

Saltmarshes not only cover a large area over the globe but also contribute with a wide range of ecosystem services, providing faunal habitat, restoring point to migratory birds, sink of CO_2 and contaminants. The characterization and classification are essential tools to improve the knowledge and the management of these soils but also to mitigate and avoid land degradation. Saltmarshes soils are formed under different vegetation and by different parent materials, for this reason, it has different morphological and chemical characteristics. Once there is no description of saltmarsh soils in Brazil, this was done to characterize chemical and morphologically different saltmarshes soils on the Brazilian coast. Also, to classify its soils the on international classification and in a national system. A Tropical (Bragança – Pará) and subtropical (Laguna– Santa Catarina) saltmarsh soils were sampled for this study Macro and micromorphology was done, such as chemical and mineralogical (DRX) analyses. The soils have different morphology and mineralogy, which reflects on a difference in chemical behaviour. The most important difference was related to soil depth and particle size distribution, such as soil mineralogy, where there is the presence of jarosite on Bragança soil. Also, Bragança soil has a very low pH while Laguna has a neutral pH, however, it is potential acidy by oxidation of pyrite. Tropical saltmarsh soil was classified as Gleissolo Tiomórfico órtico sódico (Hyperthionic Tidalic Eutric Gleysol (Clayic, Sodic)), and subtropical soils were Gleissolo Tiomórfico órtico sódico (Tidalic Eutric Gleysol (Arenic hypersulfidic sodic)) and Gleissolo Tiomórfico órtico típico (Tidalic Eutric Gleysol (Arenic hypersulfidic)).

Keywords: Soil classification, Pedology, Coastal wetland soils

3.1. Introduction

Coastal wetlands cover approximately 6% of globe surface, of wich $140x10^6$ ha are covered by saltmarshes, $15x10^6$ by mangrove forests and $18x10^6$ ha by seagrass meadows (Duarte et al., 2008; Reddy and Delaune, 2008).

Brazil is one of the countries that hold the largest coastline in the globe (16^{th}), with a coastline of 7,491 km (CIA, 2019). Along its widely diverse coastline, a series of distinct coastal wetland ecosystems coexist with its distribution controlled by factors such as climate and coastal geomorphology (Perillo et al., 2009). Among these ecosystems are the mangrove forests, the seagrass meadows, the hyper-saline tidal-flats and the saltmarshes (Duarte et al., 2008, Perillo et al., 2009).

Saltmarshes are mainly composed of grasses, herbaceous plants and small shrubs, which are adapted to the saline or brackish water action. It is an ecosystem found worldwide mainly on mid to high latitudes, also appearing scattered with mangroves in the subtropical and tropical regions (Adam, 1990).

Saltmarshes not only cover large areas around the globe but also contribute with a wide range of ecosystem services, such as faunal habitat, restoring point to migratory birds, sink for CO_2 and contaminants, and land protection against storms (Barbier et al., 2011; Boorman, 1999).

These ecosystem services are, to a certain extent, directly warranted by the functioning of the saltmarsh soils (Barbier et al., 2011). However, despite the well-established recognition of coastal wetland soils as key components for providing many of the ecosystem services in coastal wetland environments (Boorman, 1999) the scientific research from a pedological standpoint remain scarce. In Brazil, mangroves (Ferreira et al., 2007), seagrass (Nóbrega et al., 2018) and hyper-saline tidal-flat soils (Sartor et al, 2018) have been studied from a pedological approach. However, saltmarshes soils remain poorly studied despite their spatial and ecological importance (Griffin and Rabenhorst, 1989, Otero and Macias, 2003).

Saltmarshes are mostly recognized as typical subtropical ecosystems (Adam, 1990) contrasting with the tropical domain of the mangrove forests (Perillo et al., 2009). Despite these general assumptions, some studies have registered the occurrence of saltmarsh ecosystems within the tropical regions (Shin et al., 2001, Gonzales and Dupont, 2009, Ruiz-Fernández et al., 2018). Both subtropical and tropical saltmarsh ecosystems are formed under contrasting conditions (e.g. climate, vegetation cover and sedimentary environment), for this reason, it is expected that its soils would differ considerably.

With the goal to contribute to the knowledge of the diversity of saltmarsh soils in the Brazilian coast, spanning from the subtropical to the tropical region, this work provides the first soil description and classification of saltmarsh soils from Brazil.

3.2. Material and Methods

A tropical and a subtropical saltmarshes were sampled for this study. The first one is located in Bragança city, Pará State (PA), and the subtropical saltmarsh is located in Laguna city, Santa Catarina State (SC).

In Pará, the saltmarsh covers an area slightly more elevated than the surrounding mangrove forest. At this site, the saltmarsh is dominated by the vegetation of *Eleocharis geniculate* and *Spartina alterniflora*.

In the subtropical saltmarsh at Santa Catarina state, two saltmarshes were sampled, one vegetated by *Spartina densiflora* and other by *Spartina alterniflora*.

Bragança is under the influence of an Am2 climate type (tropical monsoon climate by Köppen-Geiger classification), with the rainy season occurring from January to July, the dry season extending from September to November (with the presence of a hydric deficit), with a total of 2597mm a year and an average temperature of 25 °C. The sampled site is formed by a mix of fluvial deposits of fine material; and fine and very fine quartz from marine deposition (Kjerfve et al., 2002, Souza-Filho et al., 2009).

Laguna, on the other hand, has the rain well distributed over the year, without a clear dry season, and thus present a Cfa climate type (Humid subtropical climate by Köppen-Geiger classification), with total precipitation of 1339mm and an average temperature of 20°C (Figure 3.1). Sampled site is located in the coastal plain, composed by marine fluviodeltic sediments from Holocene, and it is influenced by Tubarão river which is the main source of clastic sediments (Silva and Leites, 2000).

In the present study, only the data corresponding to three representative soil profiles of each study site are provided. In Laguna, cores were drilled during low tide with stainless-steel auger for flooded soils; samples were analysed in the field up to 60 cm depth (presence of water table below 60 cm).

In Bragança (PA), a soil pit (175 cm) was opened for the soil description and sampling of soil horizons (Santos et al., 2015). In Santa Catarina, two representative soil profiles were sampled and studied; on vegetated by the species *Spartina alterniflora* and the second one by the species *S. densiflora*. In both sites, soils were sampled with an adapted auger, which made possible the soil description. After soil description, subsamples of each soil horizon were collected, washed with ethanol (60 %) to remove soluble salts, until the absence of reaction with silver nitrate; subsequently, soil samples were dried, ground, and sieved to determine exchangeable cations capacity (CEC) based on Sumner and Miller, (1996) and Teixeira et al., (2017) methodologies.

Particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986), after the organic matter oxidation using hydrogen peroxide (30% vol), by a combination of overnight shaking and chemical dispersal method (1 M NaOH + 0.015 M

$(NaPO_3)_6$). All analyses were performed by methods proposed by the Brazilian Soil Classification System (Santos et al., 2018).

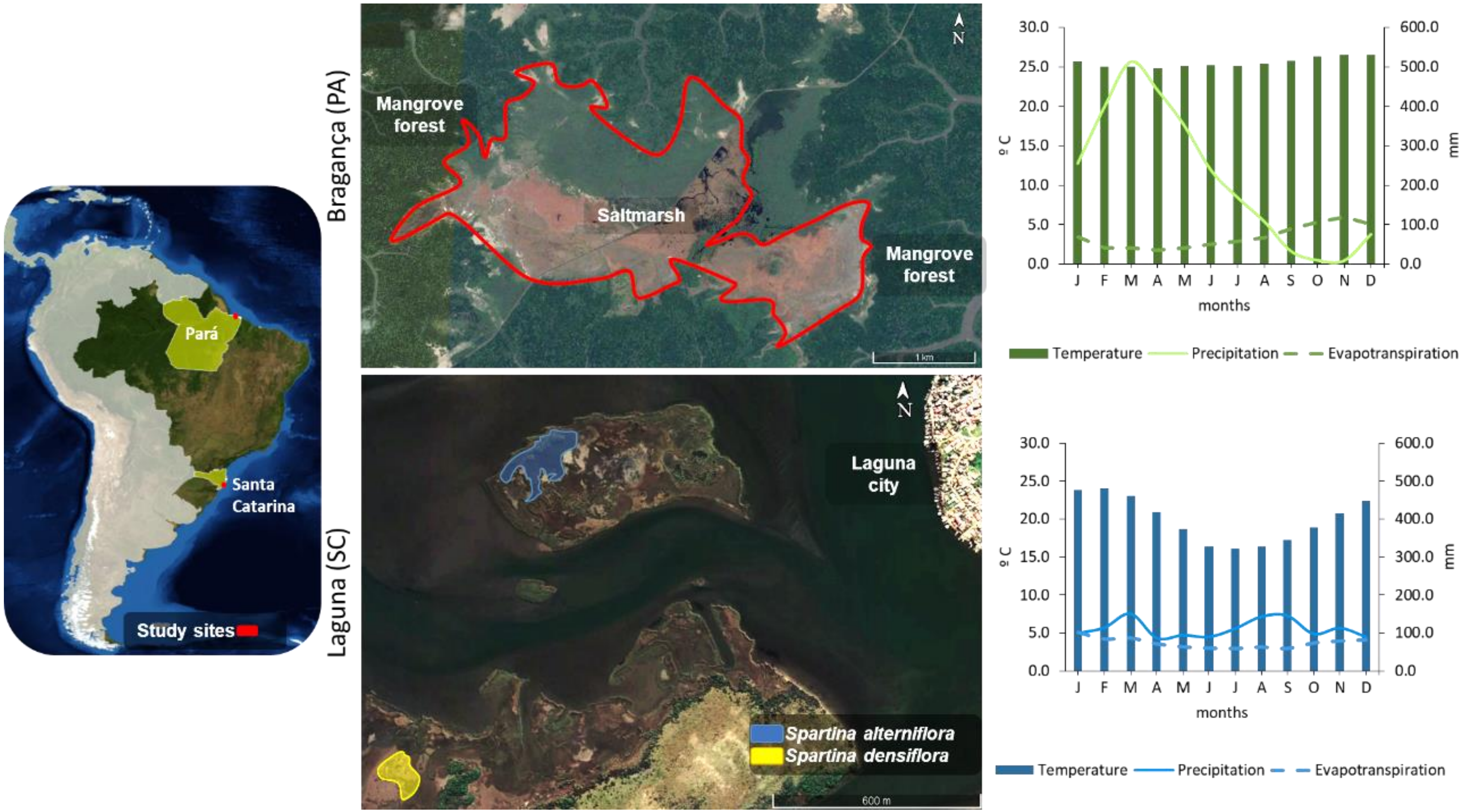

Figure 3.1. Study sites and climate information about Bragança (PA) and Laguna (SC) regions.

Electrical conductivity (E.C.) was determined using the methodology for subaqueous soils, where refrigerated moist soil subsamples were mixed with 5 parts (by volume) with distilled water before E.C. determination (Soil Survey Staff, 2014).

Potential redox (Eh) and pH were measured with a field electrode to avoid oxidation of samples. The total potential acidity (pHoxidation) was determined to measure the pH after sample oxidation with H2O2 (Konsten et al., 1986). The X-ray diffraction analyses were performed on powder samples after they were treated with H_2O_2 (20%) to remove organic matter, dried, ground and sieved to 2mm. The diffractograms were obtained using a miniflex II desktop X-ray diffractometer Rigaku with CuKα radiation.

An undisturbed sampled was kept under refrigeration until the impregnation for micromorphology analyses. In this study was used a mixture of Epoxy resin (epoxiglass 1204) diluted by acetone and fluorescent powder, also a solidifier (epoxiglass 1604). The solution was done with the viscosity of 14.5 to 15.0 cP (centipoise) and a ratio of 1:10 of resin/solidifier.

The solidifier was diluted in acetone with the fluorescent dust (0.21 g). After that, 300ml of the solution was added to the sample under vacuum for 25 minutes, this step was repeated until the saturation of the sample and kept under vacuum for 24 hours. After that, the block was kept in a fume hood until total hardened (5 days until the appearance of glass) under 35-37°C (Nascimento, 2019). The impregnated and hardened blocks were cut into 0.5 cm thick slices for preparation of thin sections with dimensions of 4.5 × 7 cm for posterior micromorphological description

The thin sections were analysed in a polarizing Zeiss optical microscope and a Zeiss binocular stereoscope under both plane-polarized light (PPL) and cross-polarized light (XPL). The descriptions followed the criteria and terminology proposed by Bullock et al. (1985) and Stoops (2003)

All soils were classified on the World Reference Base for Soil Resource (IUSS, 2014) and Brazilian Soil Classification Systems (Santos et al., 2018).

3.3. Results and Discussion

3.3.1. Bragança (PA)

Bragança soil showed a very distinct variety of colours. Upper horizons showed reddish-dark (5R 2/1) colours, contrasting with the greyish-brown (10YR 5/2) and dark-grey (4N) colours on the bottom of the soil profile. Mottles of different colours were found in all soil depths along with some iron nodules from 40 to 130 cm, mainly (horizons Cjcf1 and Cjcf2 - Figure 3.2 II).

Low values and chroma colours at the bottom of the PA soil profile (> 130cm) indicates the constant presence of water table and reduction of iron oxides, while Low values and chroma colours at the top (30 to 40cm) could be influenced by rains forming a temporarily suspended water table. Yellowish colours may be associated with iron oxides (goethite), though, in coastal areas, it could indicate the presence of jarosite formed from the oxidation of iron sulphites in response to the sulfuricization process (see Fanning et al., 1993; 2017). Yellow mottles appeared mainly on vertical channels, associated with fine roots pores or fissures (Figure 3.2). Small to coarse reddish iron nodules were found on Cjcf1 and Cjcf2 horizons, the smaller ones could be broke with fingers or with the knife, while the largest ones (Figure 3.2 II) neither broke with the knife nor after submersion in water.

Many fine roots were present from the top to 22cm, fewer roots until 30cm, and rare below 40cm, beside roots, reddish and yellowish mottles were also found (Figure 3.2 I).

Soil aggregation was observed only at the superficial horizons (A, A2, A3), with subangular blocks (Figure 3.2 I), some prisms and granular structure (Table 3.1). Below A3, all horizons showed a massive structure, with some plans of weakness. By the absence of structure, these horizons were called C's. As this soil kept wet or moist for a long time, aggregation was limited to superficial layers, once soil aggregation is formed by shrinking and swelling in drying and wetting cycles.

Surface horizons showed less stickiness and plasticity, due to the presence of organic matter, contrasting with the sticky and plastic to very sticky and very plastic on subsurface horizons. These characteristics agree with grain size distribution since the Bragança soils present >60% clay content (Figure .3).

Morphological characteristics also are observed in micro-morphology of this soil, the CA horizon (Figure 3.3) with a homogeneous thin section with massive microstructure and redoximorphic features, presence of Fe nodules and concretions (30%) with diffuse and not diffuse boundaries. Redoximorphic features are iron lens and nodules, and also matrix grey colour (iron depletion). There is lower content of coarse material (5-10%) and it is located inside the aggregates and nodules, and more than 90% of fine material (open porphyric related distribution) and relation C/F $_{2\mu m}$ ratio of 1:6. B-fabric is striated and specked. Soil structure is angular blocky very fine, with pores interaggregate. There are Fe coatings and hypocoatings (Figure 3. V and VI), and was observed minerals of pyrite within a clay aggregate (Figure 3.I and II).

Iron nodules are mainly hematite (reddish colour) and are surrounded by goethite, with the predominance of hematite indicating that nodules are being undone. Also, there are broken features (Figure 3.III and IV). As the parent material of the region is clay-rich and there are iron concretions, the breaking shows that actual pedo-conditions are unstable for plintitite/petroplintite. Moreover, this material is a Fe source for the estuary.

The lower organization of clay in the aggregates and indicates that this environment has lower dry periods, once the cycles of dry-humid season favour the clay organization. Furthermore, the angular blocky indicate low activity clay, such as kaolinite.

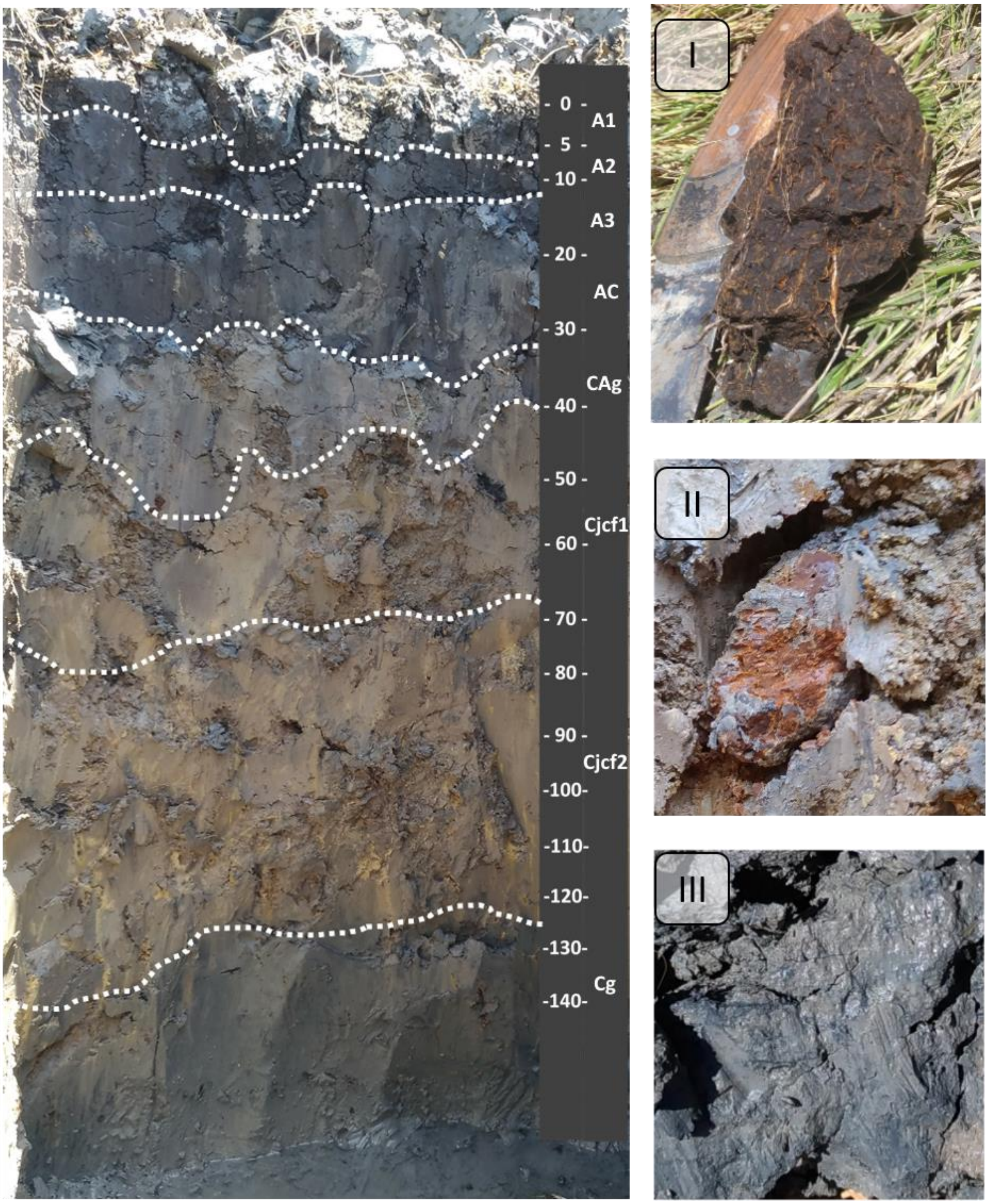

Figure 3.2. Soil profile from Bragança (PA) saltmarsh. I) The blocky structure on the surface horizon (A1); II) Iron nodule on Cjcf2 horizon; III) Dark-grey colour on a wet sample of Cg horizon.

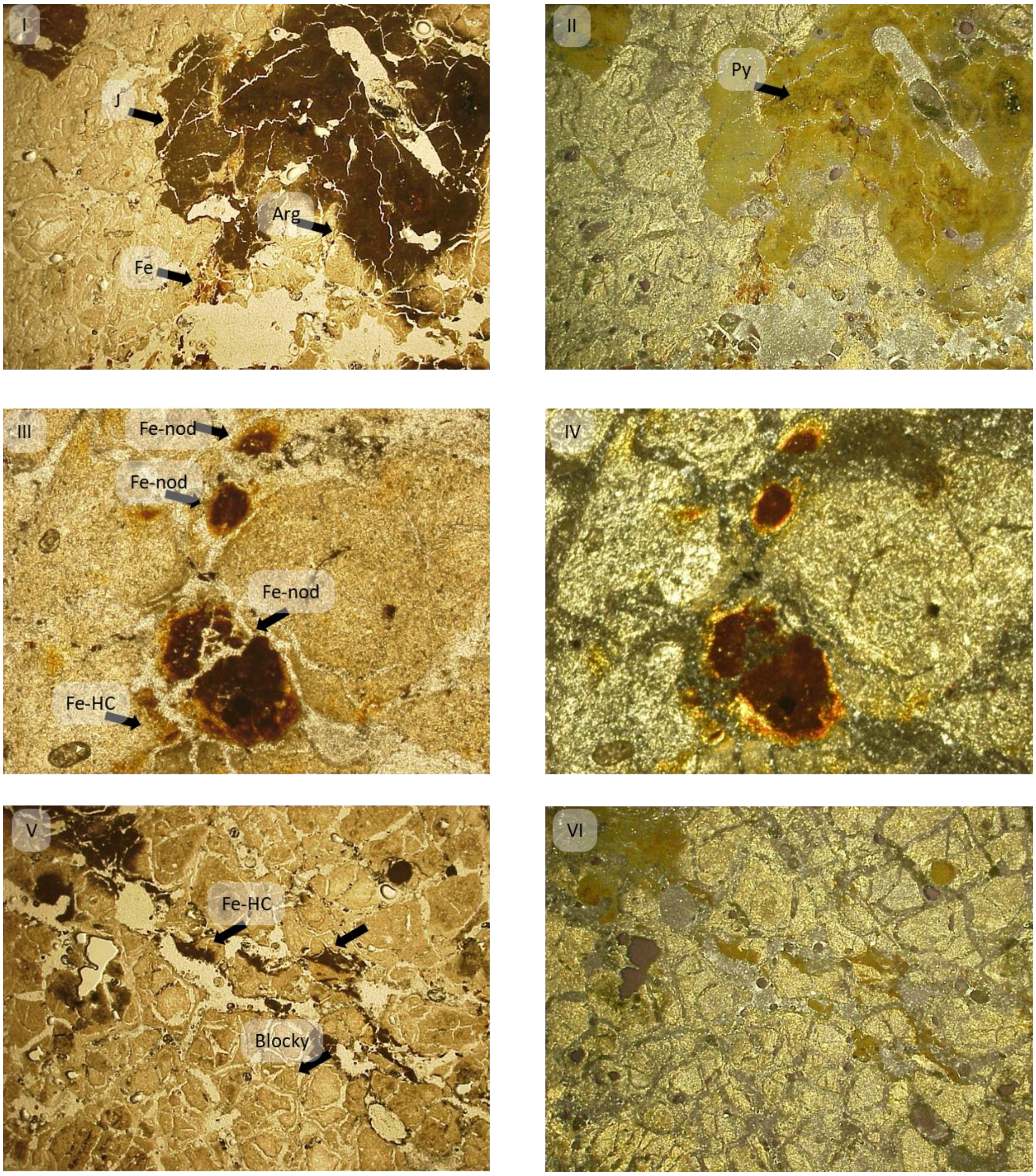

Figure 3.3. Thin section from AC horizon with microstructure massive and redoximorphic features (I- ppl) jarosite (J) formation close to (II - xpl) pyrite (Py) within clay aggregate (I-Arg); (III-ppl) Fe nodules (Fe-nod), fragmented nodule and (IV-xpl) more goethite surround hematite shows the decomposition of the nodule. (V-ppl and VI-xpl) Iron hypocoatings (Fe-HC) and angular blocky structure.

Table 3.1. Morphological properties of Bragança saltmarsh soil.

Soil Horizon	Depth (cm)	Bound[1]	Colour Moist	Redoximorphic Features %	Redoximorphic Features Colour	Redoximorphic Features Size[2]	Structure Type[3]	Structure Size[4]	Structure Grade[5]	Consistence Dry[6]	Consistence Moist[7]	Consistence Stick[8]	Consistence Plast[9]
A1	0-6	AS	5R 2/1	5	5YR 4/6	FP	SB	M	W	VH	-	SST	SPL
							P	C	W	H	-		
							G	FM	S	H	-		
A2	6-12	AS	5R 2/1	3	5YR 4/6	FP	P	C	W	H	FI	SST	SPL
							SB	M	M	VH			
A3	12-22	AS	2.5YR 2/1	< 1	2.5YR 4/8	VP	P	M	W	-	VFI	SST	SPL
				< 1	2.5YR 3/6	FMP							
AC	22-30	CS	2.5YR 3/1	1-2	5YR 4-6	FD	M	-	-	-	-	ST	PL
CA g	30-44 (40-50)	CW	5Y 4/1	< 1	10R 3/6	V	M	-	-	-	-	ST	PL
				< 1	5Y 8/6	V							
				1	5YR 4/6	F							
Cjcf 1	44-67	CS	10YR 5/2	15	10YR 5/6	D	M	-	-	-	-	VST	VPL
				5	5YR 4/6	D							
				3	5YR 5/8	P							
Cjcf 2	67-135 (119-150)	CI	10YR 5/2	20	7.5YR 5/8	MC	M	-	-	-	-	VST	VPL
				3	2.5YR 6/8	P							
				< 1	5Y 8/6	VP							
				< 1	5YR 5/8	VP							
				< 1	5YR 4/6	VP							
C g	135 - 175+		4/N	< 1		CD	M	-	-	-	-	VST	VPL

[(1)]**Boundary** (AS: Abrupt Smooth, CS: Clear Smooth, CW: Clear Wavy, CI: Clear Irregular). [(2)]**Size** (FP: Fine Prominent, VP: Very Fine Prominent, FMP: Fine to Medium Prominent, FD: Fine Distinct, V: Very Fine, F: Fine, D: Distinct, P: Prominent, MC: Medium Coarse, CD: Coarse Distinct). [(3)]**Structure Type** (SB: Subangular Blocky, P: Prismatic, G: Granular, M: Massive). [(4)] **Structure Size** (M: Medium, C: Coarse, FM; Fine to Medium). [(5)]**Structure Grade** (W: Weak, S: Strong, M: Moderate). [(6)] **Dry** (VH: Very Hard, H: Hard), [(7)]**Moist** (FI: Firm, VFI: Very Firm), [(8)]**Stickiness** (SST: Slightly Sticky, ST: Sticky, VST: Very Sticky) [(9)]**Plasticity** (SPL: Slightly Plastic, PL: Plastic, VPL: Very Plastic)

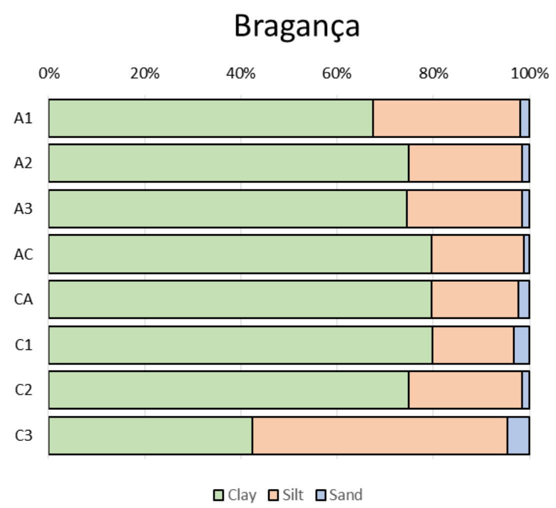

Figure 3.4. The particle size distribution of Bragança saltmarsh soil

PA soil showed low pH on the field (Table 3.2), where some soil horizons presented pH values below 3.5 (CA, Cjcf2 and Cg) evidencing the presence of a thionic horizon (pH < 4.0 – WRB - IUSS, 2014). Contrarily, the soil horizons which showed higher pH values (≥ 3.5) suffered sharp pH decreases after the hydrogen peroxide (H_2O_2)

oxidation test, which evidenced the presence of hypersulfidic material (pH ≥4.0 that undergoes ta drop in pH <4.0 and the pH drop ≥ 0.5 units – WRB - IUSS, 2014).

The presence of sulfidic material associated to the sulfuric horizons clearly indicates that the sulfidization process is no longer active in these soils and that the sulfidic material is a paleo-feature from a previous pedogenetic pulse where conditions were more prone to sulphate reduction. In fact, this soil clearly shows morphological characteristics that are indicative of an active sulfurization process (yellowish colour) and extremely low pH below 50 cm.

In fact, in this site, Souza-Filho et al., (2009) described a buried mangrove, which was dated by ^{14}C with 724 years. In this case, the studied saltmarsh could correspond to a previous mangrove ecosystem which was replaced by a saltmarsh ecosystem in response to the low salinity and acidic conditions which are known to limit mangrove species development (Waycott et al., 2011, Lovelock et al., 2017).

Table 3.2. Chemical analyses of soil under saltmarsh in Bragança (Pará).

	Soil Horizon	Depth (cm)	pH		EC[1]	P	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SB[2]	H^{+}	Al^{3+}	CEC[3]	V%[4]	ESP[5]	m%[6]
			field	H_2O_2	dS m^{-1}	mg kg^{-1}	cmolc kg^{-1}										
Bragança - Pará	A	0-6		3.50	4.05	8.20	5.09	17.96	17.48	1.16	41.69	6.12	0.20	48.01	86.8	36.4	0.48
	A2	6-12	4.41	3.15	1.85	7.02	0.05	21.49	17.04	1.21	39.80	5.35	0.21	45.36	87.7	37.6	0.52
	A3	12-22	4.42	3.15	2.14	10.91	4.16	16.24	19.22	1.16	40.78	6.40	0.34	47.52	85.8	40.4	0.83
	AC	22-30	4.54	3.67	2.21	5.42	3.28	16.96	16.87	1.16	38.27	4.89	0.53	43.69	87.6	38.6	1.37
	CA	36-44	3.40	3.06	3.69	9.45	3.09	13.79	15.22	1.16	33.26	4.39	0.73	38.38	86.7	39.6	2.15
	Cjcf1	44-67	3.66	2.38	1.84	13.96	3.14	15.42	16.70	1.21	36.47	4.07	1.09	41.63	87.6	40.1	2.90
	iron nodule	70	3.38	3.05	2.93	17.02	4.43	17.87	17.22	1.26	40.78	4.41	1.01	46.20	88.3	37.3	2.42
	Cjcf2	67-135	3.40	2.95	2.8	4.66	3.20	15.51	14.26	1.01	33.98	3.58	0.88	38.44	88.4	37.1	2.52
	Cg	135-175	2.88	1.25	2.97	14.59	3.34	12.43	11.83	0.64	28.24	2.53	19.48	50.24	56.2	23.5	40.82
		175+	2.27	0.83	3.49	13.69	4.73	7.64	13.65	0.40	26.42	9.83	21.25	57.50	45.9	23.7	44.58

[1]E.C. – Electrical Conductivity; [2]SB – Sum of bases (Ca+Mg+Na+K); [3]CEC - Cation Exchangeable Capacity; [4]V – Bases saturation; [5]ESP – Exchangeable Sodium Percent; [6]m – Exchangeable Aluminium Percent

Electrical conductivity (EC) varied considerably in this soil; the most superficial horizon showed EC values higher than 4 dS cm^{-1} what is enough to characterize a protosalic horizon (WRB - IUSS, 2014) or a *caráter salino* (according to SiBCS – Santos et al., 2018). When compared to other coastal wetland ecosystem soils the EC registered in the PA saltmarshes are considerably low (Fernández et al., 2010; Otero and Macias, 2002; Vittori Antisari et al., 2017). These relatively low EC values corroborate the allegedly inoperative sulfidization process in these saltmarsh soils since sulphate would be a limiting factor.

On the other hand, the exchangeable sodium content was high; with ESP values higher than 15% in A3, CA and Cjcf1. These results indicate that Na occupies a great portion of exchangeable sites. In this case, the base saturation, which is higher than 50% (eutric), has much sodium influence.

The PA saltmarsh soil profile is composed mainly of clay (Figure 3.3), and the X-ray diffraction patterns (Figure 3.4) showed the presence of kaolinite, quartz and jarosite. Based on the XRD results (Figure 3.4) the yellowish colours and mottles could be actually caused by jarosite, especially at the deepest soil horizons (100 and 175 cm) were the lowest pH values where recorded Jarosite is a product of pyrite oxidation, and upon its formation, sulfuric acid is produced causing sharp pH decrease (see reactions 1 and 2 after Kawano and Tomika, 2001), which would explain the extreme acidity evidenced in this soil profile (Table 3.2).

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (1)$$

$$K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow KFe_3(SO_4)2(OH)_6 + 6H^+ \quad (2)$$

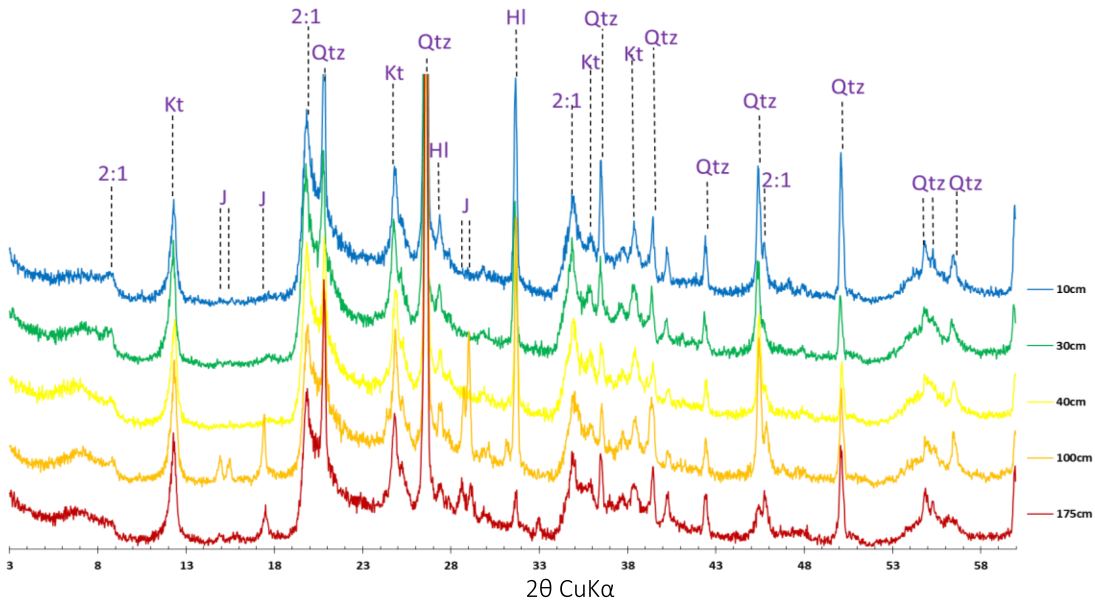

Figure 3.4. X-ray diffraction of Bragança soil profile (Kt: Kaolinite, Qtz: Quartz, J: Jarosite; Hl: Halite).

3.3.2. Laguna (SC)

Both saltmarsh soils from Laguna were morphologically similar. The soil under *Spartina alterniflora* showed a deeper superficial horizon (33 cm) when compared to the *S. densiflora* soil profile, with 19cm. On the other hand, soil colour was darker on *S. densiflora* than *S. alterniflora* (Figure 3.5). The main change between the soils under these species was related the soil colour patterns and the depth of soil horizons.

Spartina alterniflora soil showed a yellowish colour (from 5Y 3/2 to 10Y 2.5/1) while *S. densiflora* presented a dominance of yellow soil colours (2.5Y 3/2), both with low values and chromas (≤ 3) evidencing the intense waterlogged soil conditions. Roots were found mainly on superficial horizons (A and AC), and it could be the reason for the slightly higher chroma colours, by the increased oxygenation by root activity favouring the precipitation of iron oxides (goethite and hematite). In fact, several studies have evidence great efficiency of saltmarsh species in promoting the O_2 diffusion to the anoxic soils (see Gribsholt et al., 2003; Luther et al., 1982). The dominance of sandy texture and a mineral composition mainly composed by quartz (Figure 3.6 and 3.7) make the soil matrix easily coloured by colloidal material. Mottles were evident in soils although on the sub-superficial horizons of *S. densiflora* (Cg1 and Cg2) it was more evident and presented higher chromas.

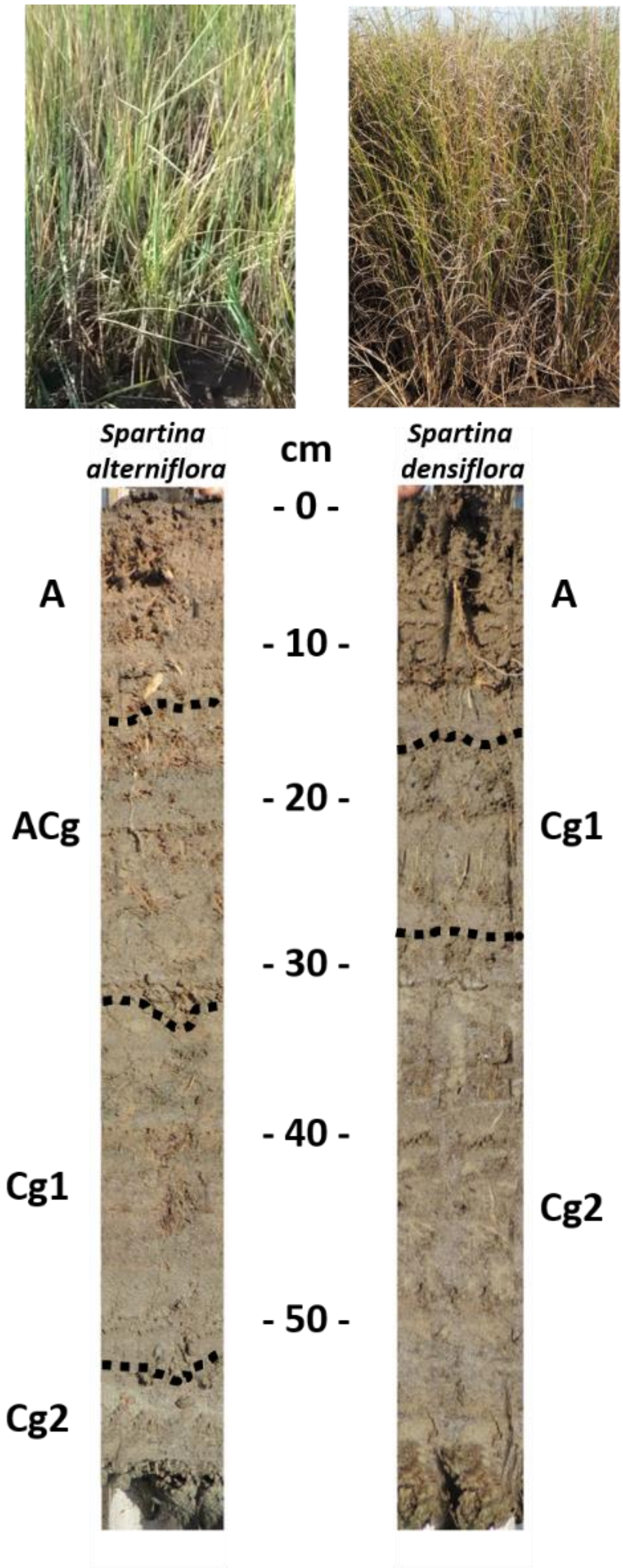

Figure 3.5. Soil profiles from Laguna (SC) under two saltmarshes vegetation (*Spartina alterniflora* and *S. densiflora*)

In addition to the high sand contents found in both soil profiles (Figure 3.6), soil colours evidence a constantly water-saturation, which favoured the absence of soil aggregation and the massive aspect of all soil horizons (Table 3.3). Sandy texture also was responsible for the slightly to non- sticky and slight to non-plastic characteristics in both soils (Table 3.3). In both soils, the low content of clay prevents the aggregate formation.

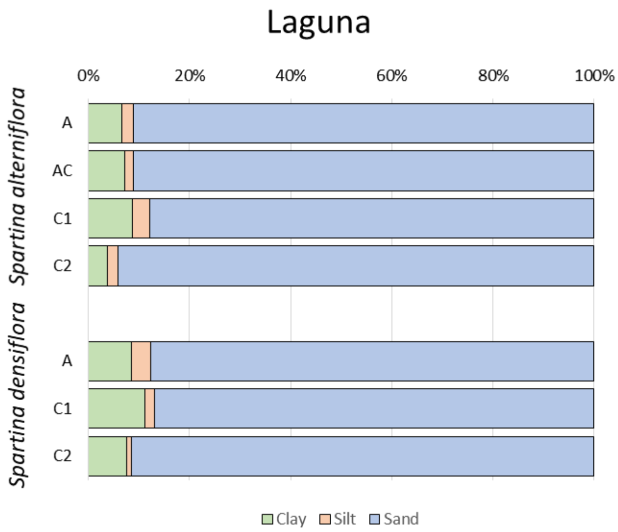

Figure 3.6. Particle size distribution on Laguna field

Table 3.3. Morphological properties of Laguna (SC) soils.

Soil Horizon	Depth (cm)	Bound[1]	Colour	Redoximorphic Features			Structure	Consistence	
			Moist	%	Colour	Size[2]	Type[3]	Stickiness[4]	Plasticity[5]
					Spartina alterniflora				
A	0-14	CS	5Y 3/2	-	-	-	M	SST	SPL
AC g	14-33	CS	5Y 3/2 2.5Y 5/3	50%	-	-	M	SST	SPL
Cg1	33-52	CS	5Y 3/2 5Y 4/2	50%	-	-	M	NST	NPL
Cg2	52-62	-	10Y 2.5/1	-	-	-	M	NST	NPL
					Spartina densiflora				
A	0-19	CS	2.5Y 3/2	-	-	-	M	NST	NPL
Cg1	19-28	GS	2.5Y 3/2	1	2.5Y 4/2	FP	M	NST	NPL
Cg2	28-60	-	5Y 2.5/2 5Y 4/1	1	5Y 5/1	FMP	M	NST	NPL

[(1)]**Boundary** (CS: Clear Smooth, GS: Gradual Smooth). [(2)]**Size (FP:** Fine Prominent**; FMP:** Fine to Medium Prominent). [(3)]**Structure Type** (M: Massive). [(4)]**Stickiness** (SST: Slightly Sticky, NST: Non-Sticky) [(5)] **Plasticity** (SPL: Slightly Plastic, NPL: Non-Plastic).

Both SC soils showed low E.C. values (4 dS cm^{-1}), the lagoons that make up the Lagunar Complex are shallow (average of 2 m). In these sites, salinity values are strongly influenced by wind-driven circulation and rainfall. This chocked estuary is a microtidal system (< 0.5-m tidal range) which exhibits a seasonal variation controlled by the high water levels associated to the low salinities especially in the rainy season (Costa et al., 2019).

Soil pH values remained higher than 6.0 and dropped below 3.5 after the oxidation test with hydrogen peroxide (Table 3.4). In this case, despite not being under an acidic soil reaction the SC soils are Potentially Acid Sulphate Soils (Madsen and Jensen, 1988). In his case, upon drainage (natural or anthropic) the sulfurization process would be installed with the release of sulphuric acid as a by-product of the oxidation mainly of iron sulphides (e.g. pyrite). Once there is the low content of clay to hold the H^+ formed, the effect of oxidation of pyrite would be more drastic.

Table 3.4. Laguna soil chemical analyses under both saltmarshes vegetation

	Horizon	Depth (cm)	pH		E.C.[1]	P	Ca^{2+}	Mg^{2+}	Na^+	K^+	SB[2]	H^+	Al^{3+}	CEC[3]	V%[4]	ESP %[5]	m%[6]	SAR
			field	H_2O_2	dS m^{-1}	mg kg^{-1}	cmolc kg^{-1}											sodium adsorption ratio
								Spartina alterniflora										
Laguna - Santa Catarina	A	0-14	6.4	1.57	2.12	24.91	1.57	1.80	0.96	0.40	4.73	1.10	0.20	6.03	78.4	15.9	4.06	0.7
	AC	14-33	7.0	1.01	2.16	14.96	1.41	2.93	1.30	0.55	6.19	1.00	0.10	7.29	84.9	17.9	1.59	0.9
	C1	33-52	7.1	1.04	2.25	14.66	0.78	1.23	0.61	0.47	3.09	1.24	0.12	4.45	69.5	13.7	3.74	0.6
	C2	52-60	7.1	1.03	1.728	18.47	0.74	1.23	0.43	0.25	2.65	1.71	0.69	5.05	52.5	8.6	20.66	0.4
								Spartina densiflora										
	A	0-19	6.4	1.00	1.85	30.87	2.13	4.38	0.87	0.54	7.92	1.79	0.05	9.76	81.1	8.9	0.63	0.5
	C1	19-28	6.5	0.96	2.46	26.46	1.47	1.95	0.96	0.41	4.79	1.92	0.06	6.77	70.8	14.1	1.24	0.7
	C2	28-60	6.7	1.11	1.98	26.64	1.60	2.66	0.96	0.41	5.63	1.44	0.10	7.17	78.5	13.3	1.75	0.7

[1]E.C. – Electrical Conductivity; [2]SB – Sum of bases (Ca+Mg+Na+K); [3]CEC - Cation Exchangeable Capacity; [4]V – Bases saturation; [5]ESP – Exchangeable Sodium Percent; [6]m – Exchangeable Aluminium Percent

The X-ray diffraction patterns from the Laguna saltmarsh soils evidence the presence of quartz, feldspars (including potassium feldspars) and plagioclases (Figure). Feldspar and plagioclase are primary minerals, thus, are in the sand and silt fractions. Minor amounts of both 2:1 and 1:1 (kaolinite) minerals were identified. Indeed, climate (lower temperature and precipitation) is an important soil formation factor, and it could be involved in the lower weathering of soils on this region, for this reason, the higher content of primary minerals.

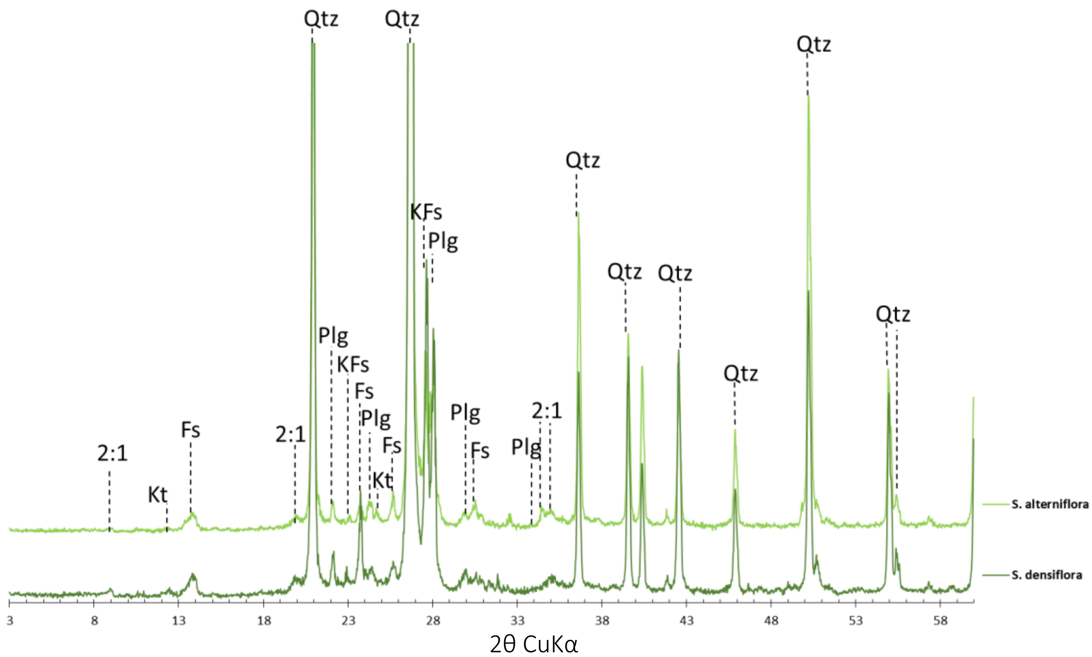

Figure 3.7. X-ray diffraction from soils in Laguna (Qtz: Quartz, Plg: Plagioclase, KFs: K-Feldspars; Fs: Feldspars, Kt: Kaolinite)

It is important for a classification system to keep updated and address all soil from the territory, for this reason, the Brazilian System of Soil Classification (SiBCS) is in constant improvement. In this system, the Bragança saltmarsh soil was classified as "**Gleissolo Tiomórfico órtico sódico**", in response to its gley horizon conjugated with a sulfuric horizon and the presence of sulfidic material and the high exchangeable sodium percentage (ESP ≥ 15% – *sódico* name) of. *Órtico* means that there is not a remarkable characteristic at 3rd level. In the WRB classification system, this soil is a "**Hyperthionic Tidalic Eutric Gleysol (Clayic, Sodic)**". Both classifications with similar information; though, WRB includes tidal influence and the textural class information.

Coastal wetland soils have been poorly studied in Brazil. Despite that, few soils on coastal wetland areas are classified or even mapped. Laguna soils are "**Gleissolo Tiomórfico órtico sódico**" under *Spartina alterniflora* and "**Gleissolos Tiomórficos órticos típicos**" under *Spartina densiflora*, where the difference is on the sodium percentage. Like Bragança's soil, these are characterized by a gley soil horizon conjugated with sulfidic material. Furthermore, the 3rd and 4th classes are "*órtico sódico*" and "órtico *típico*" because these soils do not have any remarkable feature by the SiBCS. However, there is a remarkable characteristic on these soils, there are sandy from top to bottom. Once coastal wetlands are formed mainly by sediments from Holocene, the textural class is indicative of parent material. In this way, we suggest "*psamítico*[1]" as the 3rd level for this soil, indicating his formation by the deposition of sandy material; contrasting with the Bragança's soils (clayic). Thus, Laguna's soils should be "***Gleissolos Tiomórficos psamíticos sódicos***" and "***Gleissolos Tiomórficos psamíticos típicos***".

In the WRB classification system, Laguna soils are classified as "**Tidalic Eutric Gleysol (Arenic hypersulfidic sodic)**" and "**Tidalic Eutric Gleysol (Arenic hypersulfidic)**", highlighting the tidal influence and the absence of a thionic horizon, but the presence of hypersulfidic material, which is potentially acid.

Indeed, Bragança and *S. densiflora* (SC) soils already have a thionic horizon and morphological characteristics of pyrite oxidation while *S. alterniflora* soil has a sulfidic material, which is a potential hazard. For management purposes, this is a piece of important information and it should appear on their classification. However, WRB has a thionic horizon and sulfidic (hyper and hyposulfidic) materials to indicate this pH difference. It could be a suggestion for SiBCS to separate "*horizonte sulfúrico*" from "*material sulfídrico*" or include the prefix (hyper and hypo) in sulfidic material definition.

Some saltmarshes are classified as Solonchak despite the presence of a *salic horizon* or absence of *thionic horizon* on the first 50 cm from the soil surface. Thus 16 from 23 soils analysed by Álvarez Rogel et al. (2001) were classified as Solonchaks, and there were only a few Fluvisols, Regosols and Calcisols on SE Spain (semiarid Mediterranean climate). Since in Bragança and Laguna soils, there is no presence of *salic horizon* and there is the *thionic horizon* and also a *gleyic horizon*, these are Gleysols, instead of Solonchaks. In Italy, Ferronato et al. (2016) studied Tidalic Gleysols (arenic) (Sodic Psammaquents on Soil Taxonomy), their soil was not classified as thionic due to the relatively high contents of carbonates, which act as a powerful buffering agent avoiding the pH decreases.

Such as others saltmarsh soils (e.g. Álvarez Rogel et al., 2001; Ferronato et al., 2016; Vittori Antisari et al., 2017), Brazilian saltmarshes are limited developed, mainly with A-AC-C horizons sequence.

[1] Soils with clay content lower than 200 g kg^{-1} on most part of first 150cm from soil surface (Santos et al., 2018)

3.4. Conclusions

Differences in colour, structure and other morphological features on Bragança's soil reflect the complexity of soil processes that are occurring.

Bragança saltmarsh soil is formed from very clayic sediments above a buried mangrove. The accretion process leads it to the oxidation of sulfidic material. In Laguna, the Fe-poor parent material leads to a low iron-content in its soil, manly in the pyritic form.

These differences in the soil-forming process are summarized in the soil classification, where the tropical saltmarsh soil was classified as Gleissolo Tiomórfico órtico sódico (Hyperthionic Tidalic Eutric Gleysol (Clayic, Sodic)) and subtropical soils were Gleissolo Tiomórfico órtico típico (Tidalic Eutric Gleysol (Arenic hypersulfidic)).

The Brazilian Soils Classification System is always in improvement, in this work was suggested the inclusion of "psamítico" as a Gleissolo Tiomórfico 3rd level and better discrimination of the sulfidic material (hyper and hyposulfidic) and thiomorfic horizon.

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4. IRON GEOCHEMISTRY IN BRAZILIAN SALTMARSHES SOILS

ABSTRACT

Saltmarshes are a transition ecosystem between drylands and the marine environment, it has characteristics from both the ecosystem but also unique features. Grassland. Under anaerobic condition, the organic matter produced is stocked in the soil at high rates by changes on microbial activity. Once saltmarshes are a heterogeneous ecosystem, they vary on the type and intensity of active pedogenetic processes. It is possible to use iron (Fe) dynamics as a proxy to understand the oxi and reducing process. In this way, it is important to understand and identify the iron-related processes and intensity they occur in the soil. This knowledge is pivotal to allow the creating of plans for preserving, managing and also recovering this ecosystem to provide its ecological functions, such as carbon and metal sink. In the present study, we analysed the iron geochemistry from saltmarshes soils on the Brazilian coast to increase the knowledge about this coastal wetland soils. For that, three saltmarshes were sampled, one under the tropical environment (Pará state) and two under sub-tropical climate (at Santa Catarina state). It was studied the iron forms by sequential analyse, pH and Eh. The difference between regions was done by discriminant analyse. The iron content is higher on Pará than Santa Cataria, and it could be related to iron forms, wherein Para it is more oxide forms (low and high crystallinity) from the oxidation of pyrite (pH < 5,0), and in Santa Catarina is in sulphate form (pyrite, pH > 6,0). The iron-related processes of sulfuricization and sulfidization were observed in Pará and Santa Catarina respectively.

Keywords: Pedogenetic processes, Coastal wetland soils, Sufidization

4.1. Introduction

Saltmarshes are transitional ecosystems located between the drylands and the oceanic environment; it has characteristics from both the ecosystems but also unique features. Saltmarshes are marked by the presence organisms adapted to the oscillation of the water table and salinity, with the dominance of herbaceous vegetation and shrubs (Adam, 1990; Perillo et al., 2009). The combination between the ecotonal condition and the adapted biota triggers a great variety of chemical and biological processes, which results in a wide range of characteristics for these soils.

Its physiographic position controls frequent tidal flooding promoting a series of redox related processes. Waterlogging removes air from soil pores and decreases sharply oxygen diffusion. Under the dominant anaerobic condition, organic matter decomposition rates decrease in response to the consumption of less efficient electrons acceptors for the process. The major electron acceptors that are available in anaerobic soils are nitrate

(NO^{3-}), manganese oxides (MnO_2) and iron ($Fe(OH)_3$), sulphate (SO_4^{2-}), and carbon dioxide (CO_2) (Kristensen et al., 2008; Nóbrega et al., 2016; Ponnamperuma, 1972).

Being a sensitive element to redox oscillation, iron has its dynamic intensively altered in saltmarsh soils. Iron oxides are usually found in high contents on dryland soils and are responsible by several morphological, physical and chemical properties. The process of iron reduction is called gleyzation and may lead to several different destinies to the reduced iron Fe^{2+} (Vepraskas and Craft, 2016), which ultimately may be coupled to other processes (e.g. sulfidization).

The sulfidization regards the formation of sulphites and the synthesis of different minerals such as pyrite (FeS_2). While sulphide minerals are being formed, not only iron but also by other metals (e.g. potentially toxic) may co-precipitate along with these reduced Fe-S forms (Burton et al., 2006; Machado et al., 2014; Roychoudhury et al., 2003).

Alternatively, tides may promote oscillation of the water table, and create zones of alternating oxic /anoxic conditions. These variations promote the cyclic oxidation and reduction of iron and increase iron segregation within the soil profile favouring mottling and variable degrees of cementation. As a result, plinthite may be formed. On the other hand, under highly oxic conditions sulphite minerals may be oxidized and the sulfuricization process can occur favouring the production of acidity and the synthesis of different Fe-bearing minerals; e.g jarosite.

Therefore, many are the processes in saltmarsh soils and they are quite variable in each soil. Identifying which processes and to which intensity they occur in saltmarsh soils holds the key in understanding the core functioning of these important environments. It allows creating plans for the preserving, managing and also recovering of these ecosystems. The present study aimed to assess the iron geochemistry in saltmarsh soils from two different Brazilian regions.

4.2. Materials and Methods

Three saltmarshes were sampled for this study. One located in northern Brazil, under a tropical climate vegetated by *Eleocharis geniculate* and *Spartina alterniflora* saltmarsh. It is located in the Marine Extractive Reserve Caeté-Taperaçu (Reserva Extrativista Marinha Caeté-Taperaçu - 0°54'42.16"S e 46°40'55.04"W), and it is formed by fluvial deposits of fine material and fine and very fine quartz from marine deposition (

Kjerfve et al., 2002, Souza-Filho et al., 2006). The climate is Am2 type (Köppen-Geiger climate classification) with a marked seasonality, with a rainy season from January to July and the dry season from September to November. The mean annual temperature is 25°C and while annual precipitation reaches 2600 mm (Figure 4.1) (INMET, 2017).

The second saltmarsh is located at the Laguna city, more than 3.000 km southern, at Santa Catarina State, composed by marine fluviodeltic sediments from Holocene, and it is influenced by Tubarão river which is the main source of clastic sediments (Silva and Leites, 2000). The climate is subtropical, Cfa type (Köppen-Geiger climate classification) with mean temperatures of 20°C and precipitation of 1340 mm well distributed during the year (Figure 4.1). There, two saltmarsh sites were sampled: one vegetated by *Spartina alterniflora* and the other by *S. densiflora*.

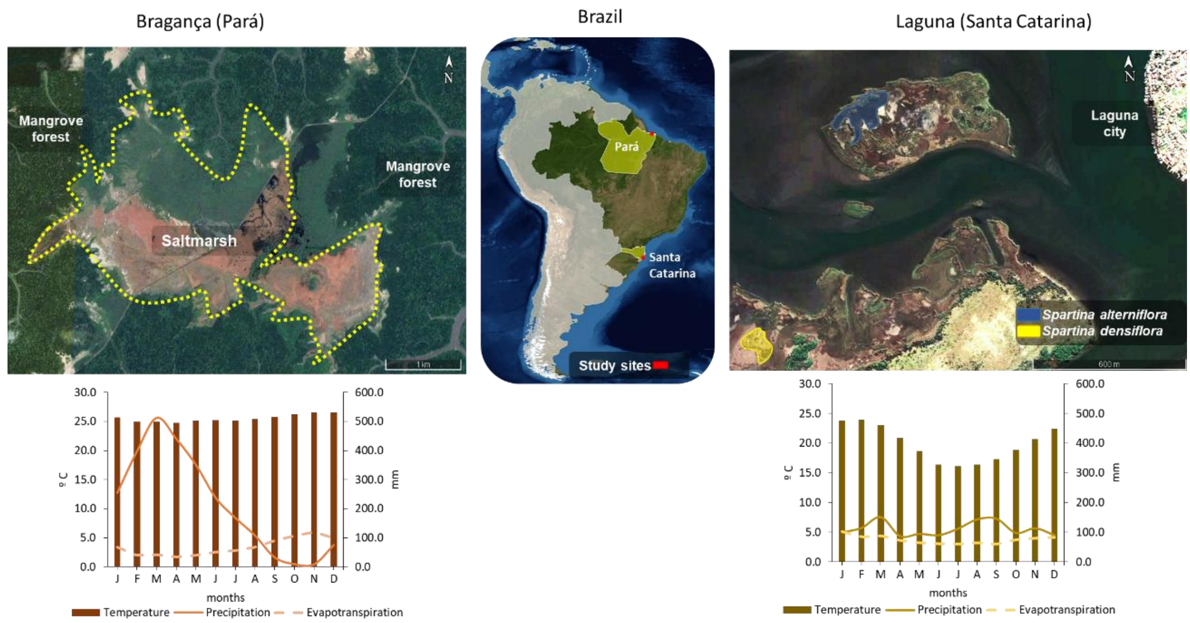

Figure 4.1. Sampled saltmarshes in Bragança (Pará State) and Laguna (Santa Catarina State), and respectively climate data.

Soil sampling was carried out during low tide, with PVC tubes of 60cm depth, which were maintained at approximately 4°C during transportation to the laboratory, where the samples were subdivided into intervals of 5 cm from 0 to 20 cm and after that, it was subdivided into intervals of 10cm from 20 until the end. Portion of each sample was air-dried and another part was stored wet at low temperatures.

Redox potential (Eh) and pH were measured with the field electrodes. The total potential acidity (pHoxidation) was determined to measure the pH after sample oxidation incubation with H_2O_2 (Konsten et al., 1986). These soils are frequently wet and a few horizons are with the water table, for this reason, electrical conductivity (EC) was determined using the methodology for subaqueous soils. In this case, the refrigerated moist soil samples were mixed with 5 parts of volume with distilled water (Soil Survey Staff, 2014).

Chemical analyses were performed after pre-treatment with ethanol (60 %) to remove soluble salts. Subsequently, soil samples were dried, ground, and sieved to determine the exchangeable cations. Calcium (Ca^{2+}), Magnesium (Mg^{2+}) and Aluminium (Al^{3+}) were extracted with KCL solution (1 mol L^{-1}) and determined by atomic absorption spectroscopy. Sodium (Na^{+}) and Potassium (K^{+}) were extracted by Mehlich 1. Potential acidity (H+Al) was determined by extraction with calcium acetate (1 mol L^{-1}, pH 7.0) and titration, H^{+} was calculated by potential acidy less aluminium (Teixeira et al., 2017).

A sample from each horizon or layer was treated with HCl (X%) to remove inorganic carbon, after that, it was dried, sieved to 2mm and analysed in LECO to determine organic carbon (C-org %).

The partitioning of Fe was performed by means of a sequential extraction from the combination of methods (Fortín et al. (1993), Huerta Diaz and Morse (1990) and Tessier et al. (1979) used in other coastal wetland soils (Otero et al., 2009, Nóbrega et al., 2018, Sartor et al., 2018) which obtains six operationally distinct fractions:

Exc - Exchangeable Fe extracted with 30 mL of 1M $MgCl_2$ (pH = 7) solution after agitating for 30 minutes;

Car - Fe associated with carbonates: extracted with 30 mL of a 1M sodium acetate solution (pH = 5, adjusted with acetic acid) after agitating for 5 hours;

Low crystallinity iron forms:

Fer - Fe-ferrihydrite: extracted with 0.04 M hydroxylamine hydrochloride + 25% (vol/vol) acetic acid during 6 hours at 30 °C

Lep - Fe-lepidocrocite: extracted with 0.04 M hydroxylamine hydrochloride + 25% (vol/vol) acetic acid during 6 hours at 96 °C

High crystallinity iron form:

Cry - Fe-oxyhydroxides: extracted with a 0.25 M sodium citrate + 0.11 sodium bicarbonate and 3 g of sodium dithionite after agitating for 30 minutes at 75 °C;

Py - Fe associated with pyrite fraction: extracted using concentrated nitric acid during 2 hours, followed by the addition of 15 mL of ultra-pure water to wash the residue. Before the extraction of Fe associated to pyrite fraction, the samples were pre-treated with HF (10 M, during 16 hours) to remove sheet silicates and with concentrated sulfuric acid (during 2 hours) to eliminate Fe associated with organic matter (Huerta -Diaz and Morse, 1992; 1990).

In each fraction, the extracts were collected after the centrifugation at 6,000 RPM during 30 minutes and, between each step, the samples were washed with 20 mL of ultrapure water followed by centrifugation. The concentration of Fe in each extract was quantified by flame atomic absorption spectrophotometry.

The degree of iron pyritization (DOP), which determines the percentage of reactive iron incorporated into the pyrite fraction (Huerta-Diaz and Morse, 1992) was calculated as DOP (%) = Py * 100 / (Fe-reactive + Py). The reactive fraction was considered the sum ΣExc → Cry and is the fraction that is able to form pyrite, whereas the pseudo-total Fe was determined by the sum of the six extracted fractions (ΣExc → Py)

A discriminant analysis was used to understand the properties of each ecosystem based on their variables and also to verify if these variables were able to separate saltmarsh soils from the south and northern regions. The statistical significance of the discriminant analyses was checked with Wilk's lambda test.

4.3. Results and Discussion

Eh and pH diagrams could be used to indicates how the environment influences the chemical element forms. These models are statics when the soil in nature is an open system and continuously changing. Bragança soils presented a more acid reaction than Laguna's soils. Additionally, the redox conditions in the first were dominantly oxic (higher Eh), while Laguna showed lower Eh values (Figure 4.2). These physicochemical conditions clearly illustrate two geochemical environments drastically contrasting between the studied regions.

In these ecosystems, the combination of organic matter, low temperatures and high humidity do not favour the high crystallinity iron forms and instead, poorly ordered compounds may precipitate (e.g. ferrihydrite and lepidocrocite).

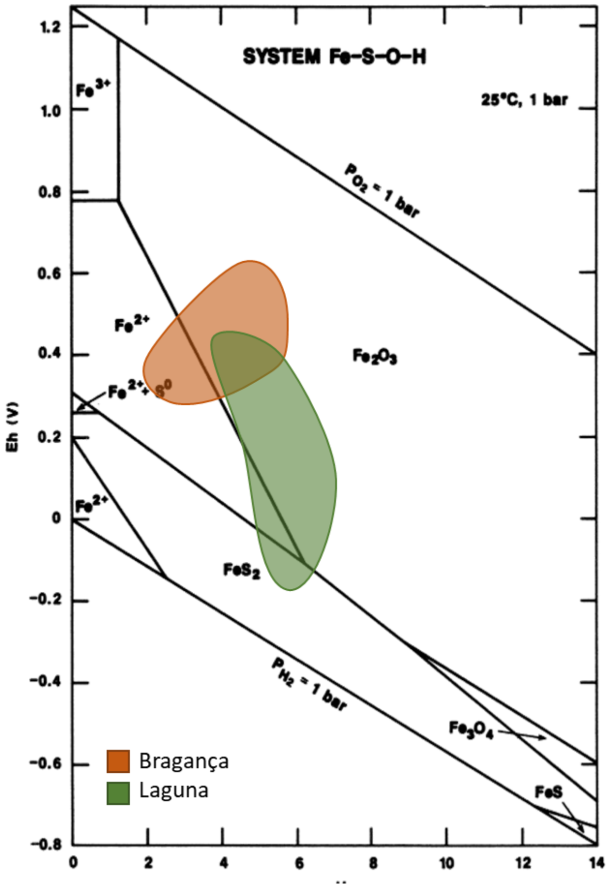

Figure 4.2. Samples plotted on Eh-pH diagram for Fe and S, adapt from Brookins (1988)

The presence of sulfidic material could be easily identified by the odour of H_2S in the field, or by the measure of pH before and after the oxidation of the material (with water for 8 weeks - Soil Survey Staff, 2014) or with peroxide of hydrogen (H_2O_2 - Konsten et al., 1986). Both methodologies are based on the oxidation of sulfidic material.

The oxidation of sulfidic material caused decreases in pH values that reached figures < 2.0 (usually bellow 3.5). A small quantity of pyrite is enough to cause this decreases, as occurs in these soils. Laguna soil showed pH values above 4.5, but, after oxidation with H_2O_2, all soil depths had pH values below 3.5, evidencing the presence of the sulfidic material. Some coastal wetlands that present carbonate-rich material may have its oxidation pH buffered (e.g. hypersaline tidal flats see Sartor et al., 2018).

Bragança soil was naturally quite more acid than Laguna's soils and had pHs below 4.0 before the oxidation test (Figure 4.3). In this case, portion of the sulfidic material was already oxidized and thus, have produced sulfuric acid. In the most part of this soil profile, the pH dropped a few units, with sharper decrease where the pyrite was not yet naturally oxidized.

The electrical conductivity (E.C.) was higher in the Laguna saltmarsh soils probably due to close contact with the tidal influence. Bragança saltmarsh is located at a higher elevation position when compared to the surrounding mangroves; in this case, the saltmarsh has a less frequent influence from saline water and showed low E.C. (Figure 4.3). Both sites have low E.C. and it is also influenced by precipitation, once the rain could reduce the salt influence on water, mainly on Bragança, where the rainy season is in few months and with high volume (2500mm).

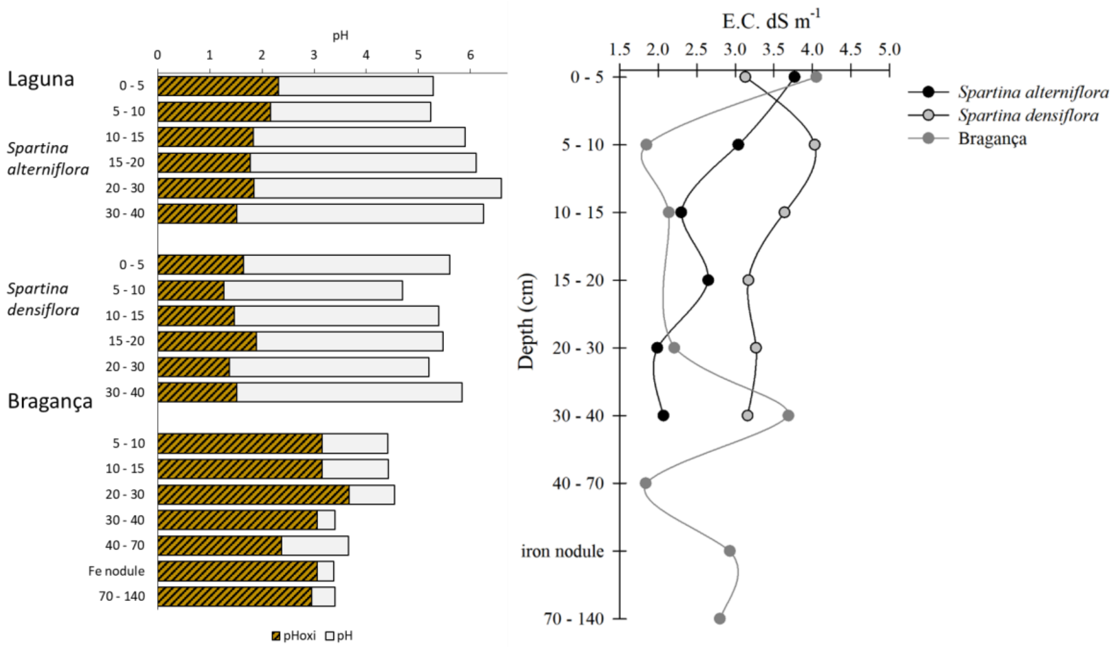

Figure 4.3. Field pH and pH after oxidation with H2O2 (pHoxi) (Konsten et al., 1986) and Electrical Conductivity (E.C.) of Laguna and Bragança saltmarshes soil

The pseudo-total Fe contents (sum of all fractions – Table 4.1) were significantly lower in the Laguna soils when compared to the Bragança's (Figure 4.4). These differences are probably related to the different parent materials in each region. Bragança is located at the Amazonian rainforest environment and surrounded by very weathered soils such as Ferralsols, which usually have with high iron contents, which can be carried to the river basin and consequently reach the estuary. In Laguna sediments that reach the estuary are mainly composed of sand from the surrounding granites which have lower iron contents.

Table 4.1. Average of chemical analyses from saltmarshes soils and iron forms

	n	CEC	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	H^{+}+AL^{3+}	P
				cmolc kg^{-1}				mg kg^{-1}
Laguna	19	7.50	1.64	2.28	1.24	0.48	1.85	18.36
Bragança	35	33.20	3.28	13.69	10.15	1.47	4.60	21.85
		Exc + Car	**Fer+Lep+Cry**	**Fe-reactive**	**Py**	$\sum Fe$	**DOP**	**C-org**
				mmol kg^{-1}			%	**%**
Laguna	19	0.3	9.2	9.5	17.8	27.4	52.3	1.7
Bragança	35	0.2	234.8	235.1	0.9	236.0	1.3	1.3

Regarding the iron forms, in Laguna soils under *Spartina alterniflora*, the iron is mainly associated with pyrite > high crystallinity iron oxides (goethite and hematite) > low crystallinity iron oxides (lepidocrocite). Pseudo-total iron contents were lower up to 20-30 cm contrasting to an increasing form of pyrite-Fe with depth (Figure 4.2).

Pyrite formation occurs by (1) oxidation of organic matter by anaerobic organism releasing Fe^{2+} and H_2S; followed by (2) formation of iron disulphate (FeS_2) (Breemen and Buurman, 2002). One approach to measuring the formation or dissolution of pyrite is calculating the degree of pyritization (DOP), where is a relation between iron content in pyrite and the reactive iron. This relation indicates how much iron is in pyrite form, if the DOP is higher than 0.9, indicate a tendency of Fe be incorporate to S forming pyrite and the environment is favourable to sulfidization (Griffin and Rabenhorst, 1989).

The low degree of Fe pyritization (DOP – Figure 4.4) indicates the absence of available iron (Ex and Car-Fe), which lead to low pyrite formation on surface, caused by oxidation of iron (presence of (Lep and Cry-Fe) and low content of Py-iron, or even the leaching of Fe to subsurface or loses by water flows. In deepest horizons, Ex and Car-Fe are available, with the sulphide, forming pyrite (high DOP) and high Pyrite-Fe.

The soil under *Spartina densiflora* had the lowest content of iron, with peaks of pyrite-Fe at 5 cm and 30 cm depths. The DOP is higher when there is ferrihydrite in the soil. It is possible that pyrite formation is limited by the lack of reactive iron. The coarse texture of Laguna's soils corroborates this hypothesis.

Bragança saltmarsh soil has high contents of iron, mainly as high crystallinity iron (goethite and hematite) and low crystallinity iron (lepidocrocite), which may hide other iron forms. Higher Crystallinity of iron oxides is harder to react, in this way, it said that is not available, so the DOP is 0%. It was observed that Brazilian coastal wetlands have a variable iron content also variable DOP (Table 4.2), not related to the ecosystem or region.

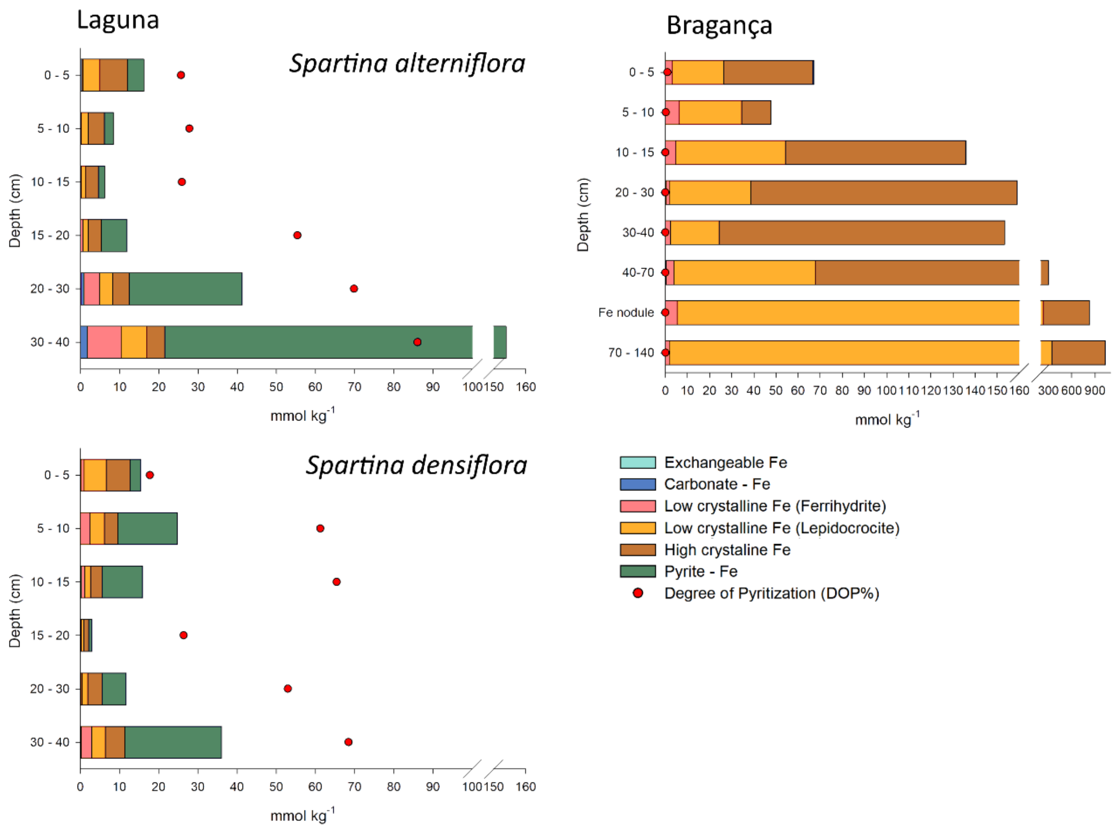

Figure 4.4. Iron sequential extraction and degree of pyritization (DOP) on sampled saltmarshes soils

Table 4.2. Iron content and Degree of Pyritization (DOP) of Brazilian coastal wetlands

Ecosystem	Brazilian region	Fe-reactive[1]	$\sum Fe$	DOP (%)[2]	Reference
Saltmarsh	**North**	**235.06**	**236.0**	**1.33**	**this study**
Saltmarsh	**South**	**9.53**	**27.4**	**52.28**	**this study**
Seagrass meadow	Northeast	26.20	78.1	62.80	Nóbrega et al. (2018)
Seagrass meadow	South	18.70	63.7	58.80	Nóbrega et al. (2018)
Hypersaline tidal flat	Northeast	46.33	53.4	7.29	Sartor et al. (2018)
Hypersaline tidal flat	Southeast	87.68	88.6	1.28	Sartor et al. (2018)
Mangrove	Northeast	89.55	117.1	22.22	Nóbrega et al. (2013)
Mangrove	Southeast	178.00	258.9	38.2	Ferreira et al. (2007)
Mangrove	Southeast	37.5	51.1	42.55	Ferreira et al. (2007)

[1] Reactive Iron $=\sum_{Exc}^{Cry} Fe$; [2]DOP$=\frac{Py}{Fe{-}reactive+Py} * 100$

Summarizing, Brazil has distinct saltmarsh soils and their forming process are different. Laguna saltmarsh soil had higher DOP, pH and pyrite-iron; while Bragança saltmarsh soils bad higher CEC, Eh, oxidation pH and iron oxides contents (both of low and high crystallinity) (Figure 4.5).

In this way, in Bragança the saltmarsh soil is characterized by an oscillation of both iron oxidation and reduction (oxic and suboxic Eh zone), with portion of the iron coming from the oxidation of pyrite. Later, the iron oxides are reduced to Fe^{2+}, which could stay in the system or removed with water to river and ocean. For this reason, the pH of Bragança is low (sulfurization process by oxidation of pyrite) and there are more iron oxides.

On the other hand, Laguna's saltmarshes soils are marked by the formation of pyrite in the deeper horizons (i.e.sulfidization) corroborated by the accumulation of sulfidic material, observed by the low pH after the oxidation test. In addition, the high DOP further evidences the formation of pyrite.

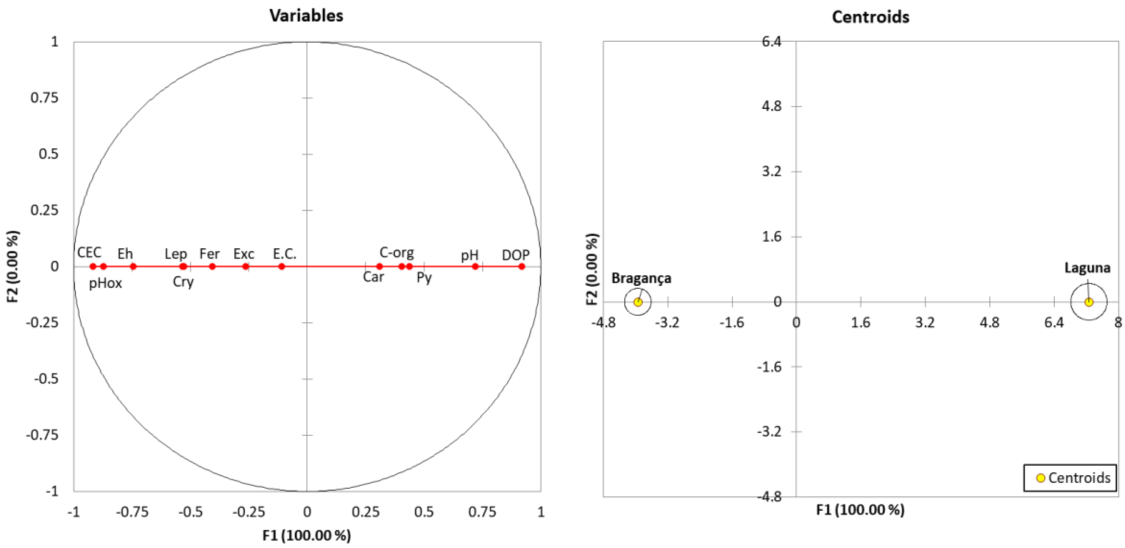

Figure 4.5 Discriminant analyses on studied soils using Iron forms from sequential analyses as variables (Wilks' lambda test p<0.0001, centroids significance level 5%).

4.4. Conclusions

Bragança saltmarsh soil is under sulfuricization process and has low pH, it could be called an active/pos-active acid sulphate soil. Also, there are no favourable conditions for pyrite formation. Laguna soils have neutral pH and environmental conditions favourable to pyrite formation (sulfidization) as corroborated by the pH after oxidation, which characterizes Laguna soils as potential acid sulphate soils.

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5. PEDOGENESIS IN A MANGROVE-SALTMARSH SOIL SEQUENCE

ABSTRACT

Coastal wetlands are among the most ecologically important ecosystems in the globe. At the temperate, to subtropical coastal regions, the spatio-temporal changes between mangroves and saltmarshes have been reported. As mangroves, saltmarshes are transitional ecosystems from upland to marine ecosystems, and has some features of both environments, with biota adapted to water saturation periods, anaerobiosis, and also to changes in salinity. These ecosystems are ideal for pyrite formation once they are frequently water-saturated and consequently anoxic, with a high content of organic matter also soluble iron. There is sulphate maintenance from seawater, which allows microorganisms to reduce it to sulphite, forming mono and disulphates of iron. The objective of the present work was to determine the variation on the iron geochemistry in a soil transect from a *Spartina alterniflora* vegetated saltmarsh through a transition site to an *Avicennia schauerianna* mangrove forest soil, in a tropical region (Pará – Brazil). Due to the elevation of saltmarsh, reduced inundation occurs and has favoured to pyrite oxidation (sulfuricization process) and in mangrove soil portion of iron is retained as pyrite, once organic matter and sulphates are available.

Keywords: Iron geochemistry, Sulfidization, Sulfuricization, Pedogenesis

5.1. Introduction

Coastal wetlands are among the most ecologically important ecosystems in the globe (Barbier et al., 2011; Beaumont et al., 2014). Although very diverse in their main components (adapted plant species, adapted fauna, hydromorphic soils) these ecosystems may sometimes occur in very intricate mosaics, which ultimately evidence a great spatio-temporal dynamic between them (Barreto et al., 2018; Ferronato et al., 2016; Yando et al., 2016). At the temperate to subtropical coastal regions the spatio-temporal changes between mangroves and saltmarshes have been reported to respond to temperature changes; e.g. freezes, mild winters (see Stevens et al., 2006).

In fact, recent studies have demonstrated that extreme weather events (e.g. hailstorms), which are expected to be more frequent in a climate change scenario (IPCC 2001), may cause fast mangrove dieback (Severino et al., 2018). Climate change is in fact expected to severely impact the distribution and extension of the different coastal wetlands by altering several factors o key importance to its development and distribution.

As mangroves, saltmarshes are transition ecosystem from dryland to ocean, and has some features of both environments, with biota adapted for water saturation periods, in anaerobiosis, also to changes in salinity (Adam, 1990). Both, mangroves forest and saltmarshes grasslands can occur on the same landscapes however, each vegetation has a preference, with regards to temperate; sub-tropical climate being more favourable to saltmarshes and sub-tropical to tropical for mangroves (Perillo et al. 2009). Despite these general concepts, it is not uncommon to both ecosystems share large stretches of coastlines (Saintilan and Wilton, 2001; Stevens et al., 2006; Geldenhuys et al., 2016).

Given the predicted scenarios in response to global climate changes and its impacts on the distribution dynamics of different coastal wetlands ecosystems studies that enlighten the mechanisms involved in these relationships are very important to predict the future fate of these ecosystems. Thus the purpose of this study is to assess the role of soil processes in controlling the distribution of both mangrove and saltmarsh ecosystems in a tropical environment.

The specific objective was to determine the variation of soil chemical parameters and iron geochemistry in a sequence from a *Spartina alterniflora* saltmarsh through a transition site to an Avicennia schauerianna mangrove forest.

5.2. Materials and Methods

The study site is located in the Marine Extractive Reserve Caeté-Taperaçu (Reserva Extrativista Marinha Caeté-Taperaçu - 0°54'42.16"S e 46°40'55.04"W). Saltmarsh and mangrove soils were sampled for this study), in the Bragança region of Pará state.

Surrounded by mangroves in all directions, the tropical saltmarsh sampled in this study is under an Am2 climate (tropical monsoon by Köppen-Geiger climate classification). The rainy season covers the months from January to July and the dry period from September to November (Figure 5.1), with a water deficit in this period and total precipitation of 2597mm a year and an average temperature of 25.°C (INMET, 2017).

A transect was set from the saltmarsh ecosystem (vegetated by *Eleocharis geniculate* and *Spartina alterniflora*) to a transition site with saltmarsh vegetation (*S. alterniflora*) to a mangrove forest (*Avicennia schaueriana*). Soil sampling was carried out during low tide. In each ecosystem, a PVC tube of 60cm depth used for was sampling. After the core removal, they were maintained at approximately 4°C during transportation to the laboratory, where the samples were subdivided into intervals of 5 cm from 0 to 20 cm and after that, it was subdivided into intervals of 10cm from 20 until the end. Part of each sample was air-dried and another portion was stored wet at low temperatures.

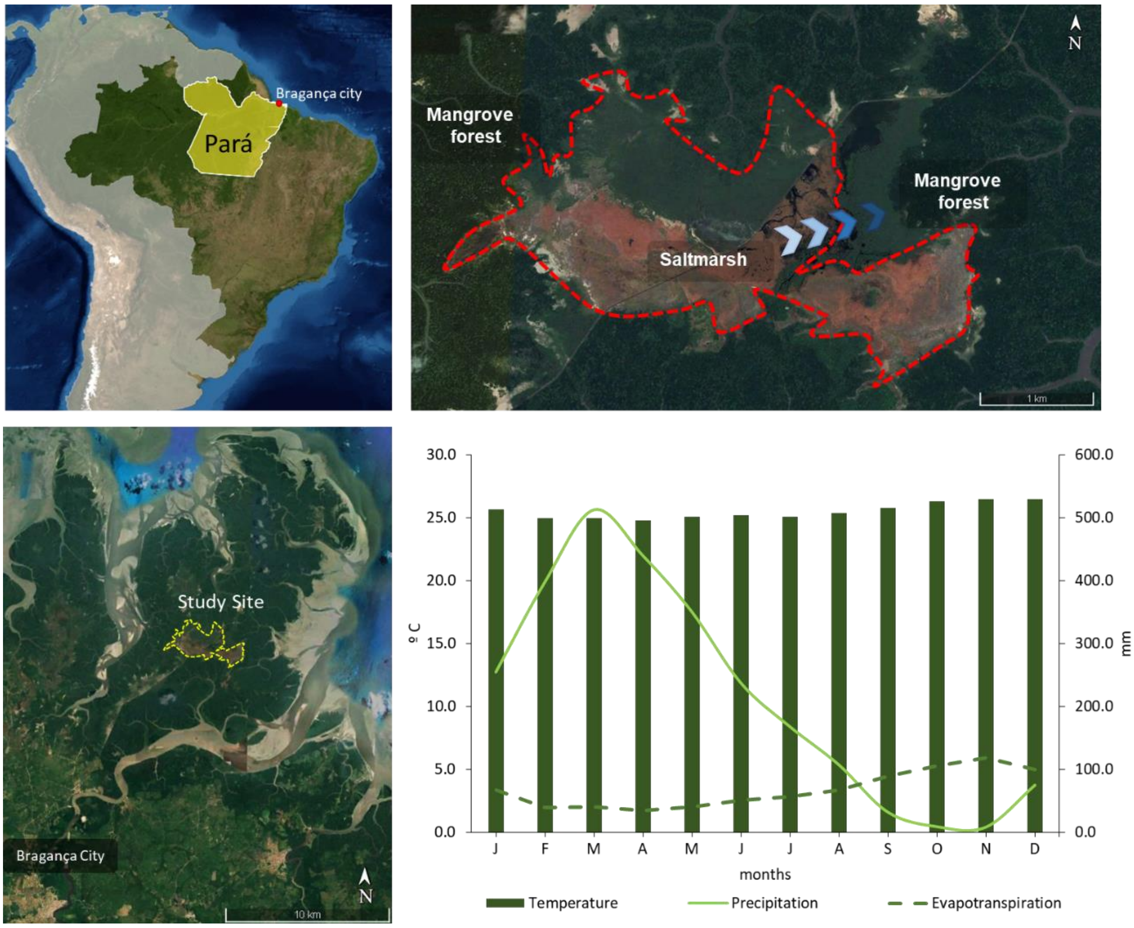

Figure 5.1. Study sites sampled in the Bragança region, in Pará State (Brazil). A transect from saltmarsh to mangrove. Climate parameters from the region.

Chemical analyses to characterize these soils were performed after the pre-treatment with ethanol (60 %) to remove soluble salts. After that, soil samples were dried, ground, and sieved to determine the exchangeable cations. Calcium (Ca^{2+}), Magnesium (Mg^{2+}) and Aluminium (Al^{3+}) were extracted by KCL solution (1 mol L^{-1}) and determined by atomic absorption spectroscopy. Sodium (Na^{+}) and Potassium (K^{+}) were extracted by Mehlich 1. Potential acidy (H+Al) was determined by extraction with calcium acetate (1 mol L^{-1}, pH 7.0) and titration, the hydrogen was calculated by potential acidy less aluminium (Teixeira et al., 2017).

Particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986), after the organic matter elimination using hydrogen peroxide (30% vol), by a combination of overnight shaking and chemical dispersal method (1 M NaOH + 0.015 M $(NaPO_3)_6$).

The partitioning of the solid phase Fe was performed via a sequential extraction designed by the combination of methods using frozen samples obtaining six operationally distinct fractions: (Fortin et al., 1993; Huerta-Diaz and Morse, 1990; Nóbrega et al., 2018; Otero et al., 2009; Tessier et al., 1979)

1) Exchangeable and soluble Fe (**Exc**) extracted using 30 mL of 1M $MgCl_2$ (pH = 7) solution agitating during 30 minutes;

2) Fe associated with carbonates (**Car**): extracted using 30 mL of a 1M sodium acetate solution (pH = 5, adjusted with acetic acid) during 5 hours;

3) Fe-ferrihydrite (**Fer**): extracted using 0.04 M hydroxylamine hydrochloride + 25% (vol/vol) acetic acid during 6 hours at 30 °C

4) Fe-lepidocrocite (**Lep**): extracted using 0.04 M hydroxylamine hydrochloride + 25% (vol/vol) acetic acid during 6 hours at 96 °C

5) Fe-oxyhydroxides (High crystallinity iron - **Cry**): extracted using a 0.25 M sodium citrate + 0.11 sodium bicarbonate and 3 g of sodium dithionite agitating 30 minutes at 75 °C;

6) Fe associated with pyrite fraction (**Py**): extracted using concentrated nitric acid during 2 hours, followed by the addition of 15 mL of ultra-pure water to wash the residue. Before the extraction of Py, the samples were pre-treated with HF (10 M, during 16 hours) to remove sheet silicates and with concentrated sulfuric acid (during 2 hours) to eliminate Fe associated with organic matter (Huerta -Diaz and Morse, 1990).

For each fraction, the extracts were collected after the centrifugation at 6,000 RPM during 30 minutes and, the samples were washed with 20 mL of ultrapure water followed by centrifugation between each step. The concentration of iron in each extracted were quantified by flame atomic absorption spectrophotometry.

The degree of Fe pyritization (DOP), which determines the percentage of reactive iron incorporated into the pyrite fraction (Huerta-Diaz and Morse, 1992) were calculated as DOP (%) = Py * 100 /(FeREACTIVE + Py). The reactive fraction was considered to the sum of the fractions exchangeable to high crystallinity (ΣExc → Cry) and is the fraction that is able to form pyrite. The sum of the six fractions (ΣExc → Py) was considered as the pseudo-total content, once there are not include iron associated to silicates (removed by HF) and associated to organic matter (removed by sulfuric acid).

Potential redox (Eh) and pH were measured with a field electrode. The total potential acidity ($pH_{oxidation}$) was determined to measure the pH after sample oxidation incubation by H_2O_2 (Konsten et al., 1986). These soils are frequently wet and a few horizons are with the water table, for this reason, electrical conductivity (E.C.) was determined using the methodology for subaqueous soils, whereas refrigerated moist soil sample is mixed with 5 parts of volume with distilled water (Soil Survey Staff, 2014).

The X-ray diffraction analyses were performed on powder samples after they were pre-treated with H_2O_2 to remove organic matter, dried, ground and sieved to 2mm. The diffractograms were obtained using a miniflex II desktop X-ray diffractometer Rigaku with CuKα radiation.

Differences between soil variables were analysed by one-way ANOVA followed by a Tukey test (5%). Furthermore, discriminant analysis was used to verify how the variables separate groups and understand the group properties based on their variables. The statistical significance of the discriminant analyses was checked with Wilk's lambda test

5.3. Results and Discussion

Ferralsols are the dominant soil order in the surroundings of the study region, which, are probably one of the main sources of sediments that are carried by the river for the estuary (Radam, 1973). In this way, fine particles that reach both the mangrove and saltmarsh soil, are probably related to the very clayey from inland soils. In the transition site, there is an increased influence of sand particles, however, in the mangrove soils, this soil particle size appears in higher amounts, mainly in deepest horizons (Figure 5.2).

Despite the lower clay content, mangrove soils showed higher cation exchangeable capacity (CEC) than saltmarsh (Figure 5.3). The main cation was sodium (Na). The sodium content decreases from mangrove to saltmarsh, which could be associated to a lower tidal influence ate the saltmarsh, once it is further from estuary creek has and at a higher elevation than the mangrove forest.

There is also an increase in acidity (H+Al) from mangrove to saltmarsh, which is probably related to lower water saturation, leading to accumulation of H^+ and Al^{3+} from organic matter decomposition, roots exudates, and also from pyrite oxidation.

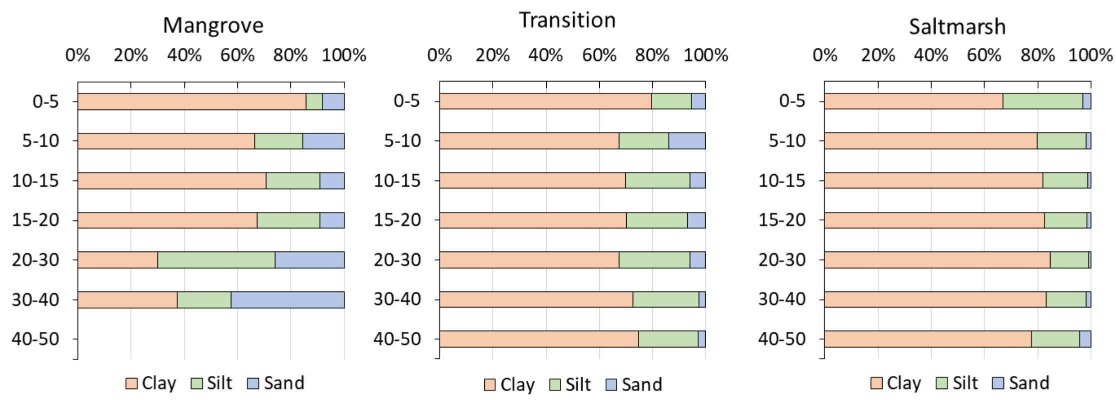

Figure 5.2. Particle size distribution by depth on each sampled ecosystem.

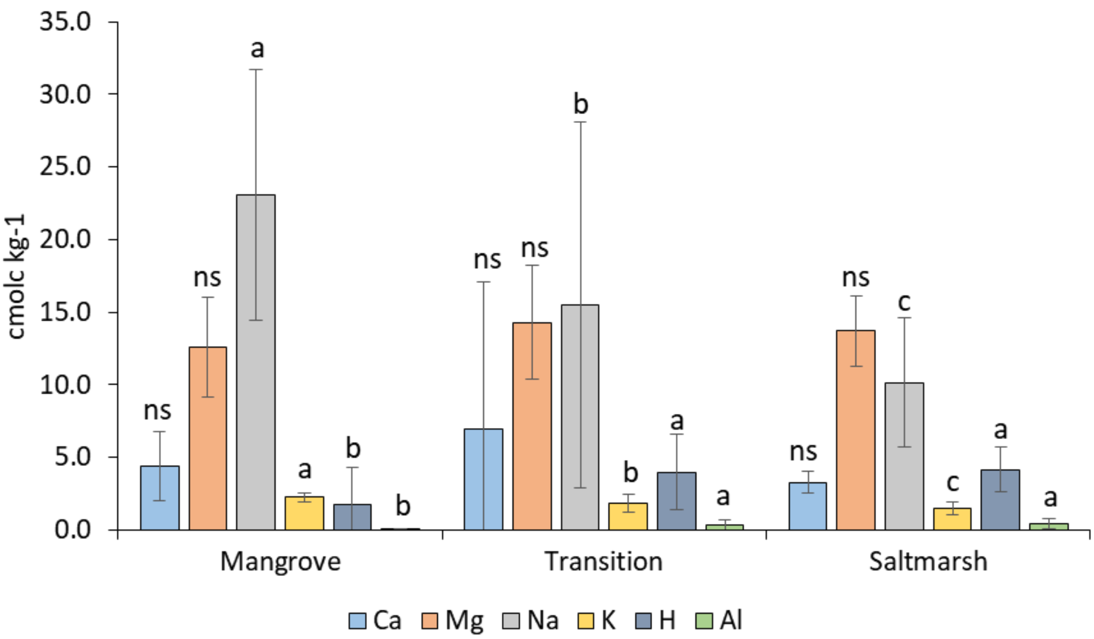

Figure 5.3 Chemical analyses of bases (Ca, Mg, N, and K) and acidy (H and Al). For each variable, the average bars followed by the same letter did not present statistically significant difference (Tukey 5%), n=35 saltmarsh and 19 for mangrove and transition; ns = not significant.

The saltmarsh is located on a higher elevation than the other ecosystems in this study. For this reason, it has a lower frequency of brackish water saturation. Also, the rain creates a suspense water table and removes salts, decreasing both, cations (as Na^+) and the electrical conductivity (Figure 5.3 and 5.4). The action of the water table is noticed by the presence of a gley horizon (CA g) at 30cm, above a yellowish horizon (C cf). The transition site seems to have a higher influence of brackish groundwater and could also receive the salts from surrounding saltmarsh, which could lead to the higher electrical conductivity values.

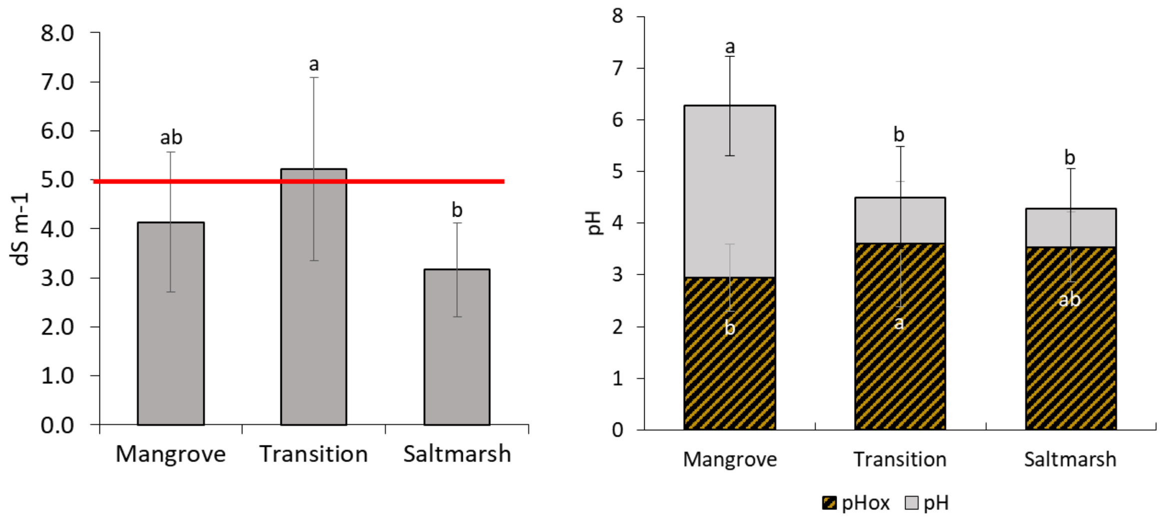

Figure 5.4. Electrical conductivity, field pH and pH after oxidation with H2O2 (pHoxi). For each variable, the average bars followed by the same letter did not present a statistically significant difference (Tukey 5%), ns = not significant.

Usually, coastal wetland soils have circumneutral pH in response to the prevailing reducing conditions which consumes H^+ from soils solution (Ponnamperuma, 1972). In the studied mangrove soils, the pH was 6.2 (± 1.0), as expected for this soils (Figure 5.4). On the other hand, at the transitional saltmarsh and saltmarsh soils field pHs varied from 4.5 (± 1.0) to 4.3 (± 0.8), respectively. Under natural conditions, some of the soil samples have reached a pH of 3.5. These values are lower than expected if these soils were under hydric conditions.

The X-ray diffraction (XRD – Figure 5.5) analyses of the Bragança soils showed patterns of 2:1 clay minerals, kaolinite, quartz and jarosite. Halite is also a possible mineral or an artefact produced during the analyses due to the high content of sodium in these soils.

An Eh-pH diagram is a useful tool to indicate the general conditions or tendencies of the soil system with respect to the main chemical elements. The mangrove samples are laying on predominance field of iron oxides (goethite) with a slight tendency on iron sulphides (pyrite – Figure 5.6), like the tropical mangroves from the Brazilian semiarid coast (Ceará, Brazil) (Araújo Jr et al., 2016; Nóbrega et al., 2013)

Not only Brazilian the mangroves but also the seagrass meadows soils showed field conditions that favour the prevalence on iron oxides, although the submerged soils are closer to the iron sulphide domain (Nóbrega et al., 2018).

As others coastal wetland soils, Brazilian hypersaline tidal flats also showed a geochemical environment more prone to the predominance of iron oxides, under field conditions, with high values of pH (between 6.0 and 8.0) and high redox potentials (Eh >400 mV). However, after oxidation, the deepest horizons showed pH < 2,0 (Sartor et al., 2018) evidencing the presence of sulfidic materials (main pyrite).

On the other hand, contrasting with these coastal soils, the northern saltmarsh studied showed geochemical conditions ranging from both the iron oxides and jarosite fields, due to the lower pH and higher Eh values.

Contrarily, mangrove soils showed geochemical conditions from iron oxides to iron sulphides (pyrite fields); Which could to suggest two distinct sections of iron forms, the first section from the surface to 20cm with 53.4 and 91.2 mmol kg^{-1} of iron content (depth 5-10 cm and 0-5 cm, respectively); The second section is below 20cm, the main iron form is pyritic (Py). The iron content raises almost to 400 mmol kg^{-1} (230.2 mmol kg^{-1} at 20-30cm and 398.8 mmol kg^{-1} at 30-40cm) (Figure 5.7).

In the transition site, pseudo total iron (∑Fe) showed an oscillation in iron contents with depth, with higher iron contents followed by a layer of lower iron contents. Whereas the high contents are at 0-5 cm (538.3 mmol kg^{-1}) and the lower at 15-20cm (213.0 mmol kg^{-1}). There were lower contents of pyrite in the transitional site than in the mangrove soil, 6.4 mmol kg^{-1} (1.2%) at 0-5cm. This layer also has 90% of high crystallinity iron (Cry), contrasting with deeper layers, which had 77% of lepidocrocite-iron (Lep).

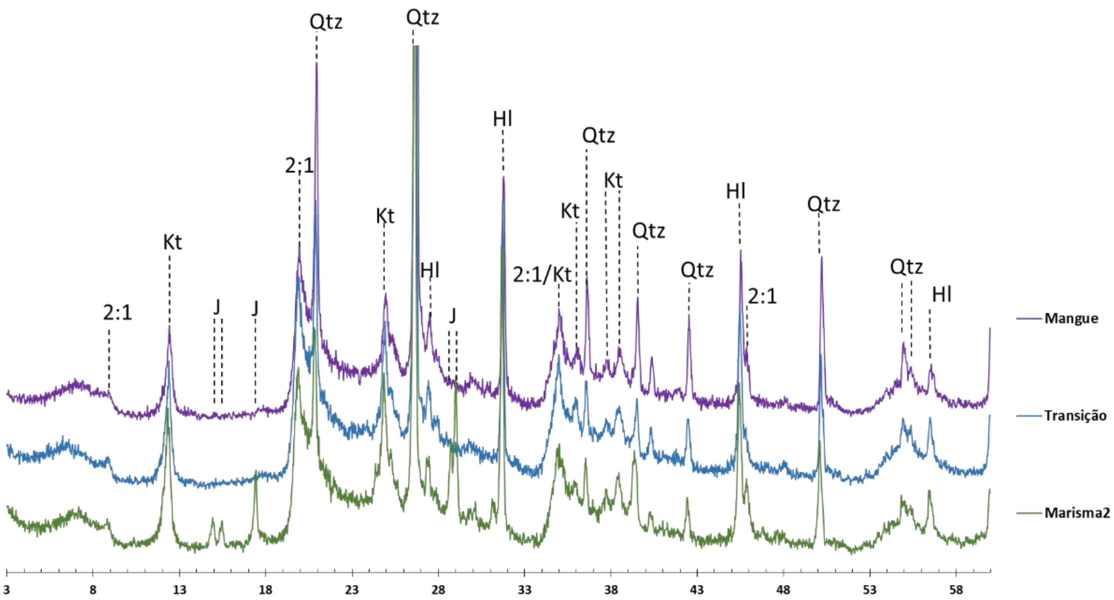

Figure 5.5. X-ray diffractogram for mangrove, transition and saltmarsh samples. Kt - Kaolinite; J-Jarosite; Qtz-Quartz; Hl-Halite; 2:1- 2:1 minerals

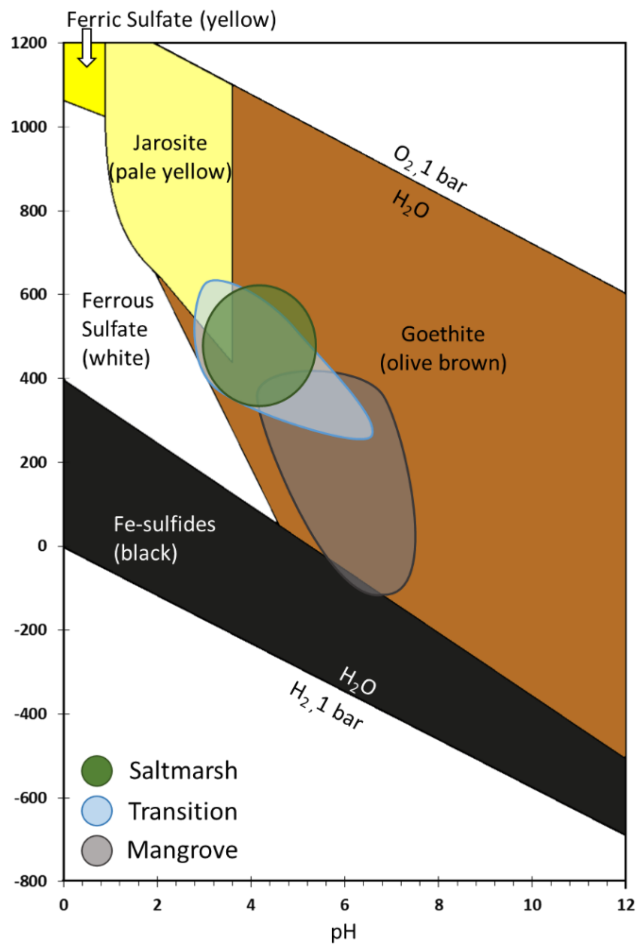

Figure 5.6. Eh-pH stability diagram for Sulphur and Iron minerals applicate to acid sulphate soils (Fanning et al., 1993) with samples of each sampled ecosystem.

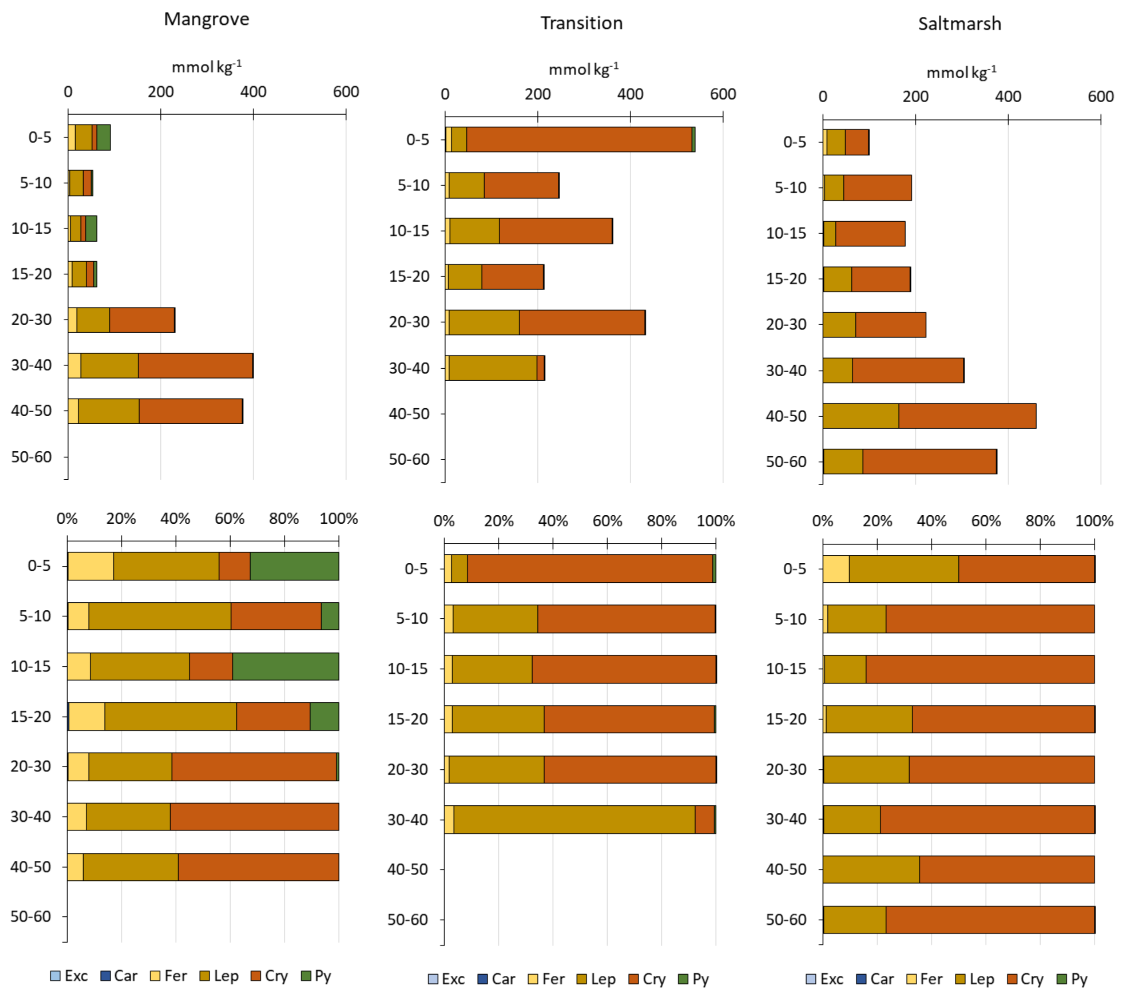

Figure 5.7. Iron forms at each ecosystem by depth in mmol kg^{-1} and percentage. Exc – Exchangeable; Car – Carbonate-Fe; Fer – Ferrihydrite; Lep – Lepidocrocite; Cry – High Crystallinity-Fe; Py – Pyrite-Fe.

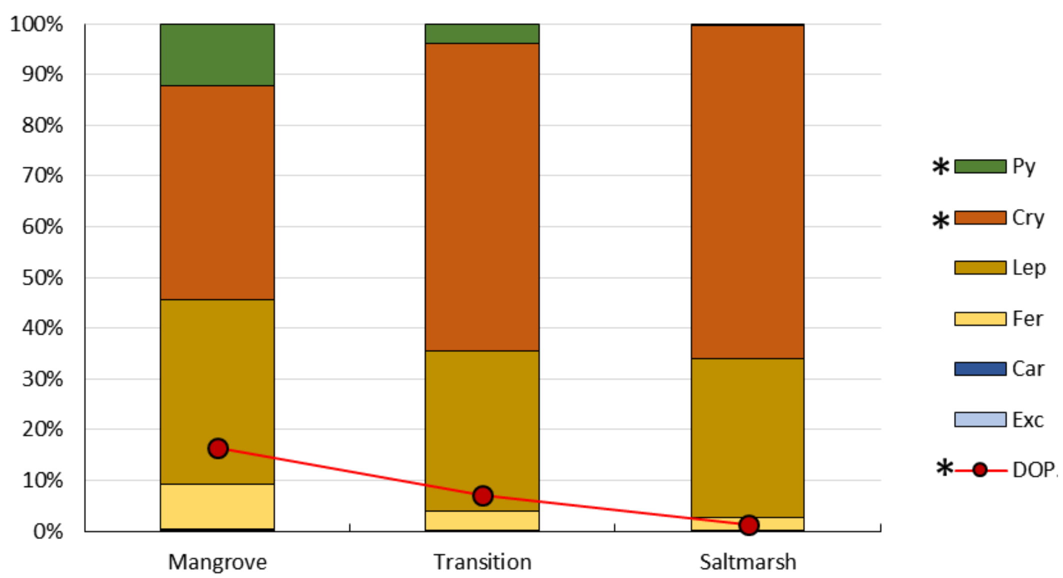

Figure 5.8. Percentage of each iron form in the ecosystem and degree of pyritization (DOP). Iron fraction marked with * is significantly different by Tukey 5%. Exc – Exchangeable; Car – Carbonate-Fe; Fer – Ferrihydrite; Lep – Lepidocrocite; Cry – High Crystallinity-Fe; Py – Pyrite-Fe.

Alternatively, saltmarsh soil showed an increase in iron contents with depth, from 98.7 mmol kg^{-1} ate 0-5cm to 461.3 mmol kg^{-1} at 40-50 cm; composed of highly crystallinity iron forms (goethite and hematite).

These results evidence there is an iron gradient from the mangrove soil to the saltmarsh, whereas mangrove has more variable iron forms but also lower iron contents overall; while the saltmarsh soils showed a dominance mainly of low and high crystallinity iron forms but with high pseudo-total iron contents (Figure 5.8).

It is important to observe that these three ecosystems are not only different from the vegetation aspect, but also from the soil characteristics, especially with regards to pH and the iron geochemistry (Figure 5.9). In this way, mangrove soils have higher pH values than both transitional and saltmarsh soils, which could be associated with a higher tide inundation frequency or higher water table, once the Eh is markedly lower in mangrove soils. In addition, mangrove showed higher values pyrite iron and DOP, meaning that soil conditions are favourable to pyrite formation (probably due to a combination of reactive iron, organic matter content and sulphate availability).

The transitional site soil showed more influence on the EC. Thus, the oscillation of the brackish water table and the evapotranspiration could favour a salt-accumulation and consequently, higher electrical conductivity. There is more influence of higher values of Eh on the saltmarsh and transition soils, indicating a dominant oxic environment, which favours the oxidation of pyrite (FeS_2).

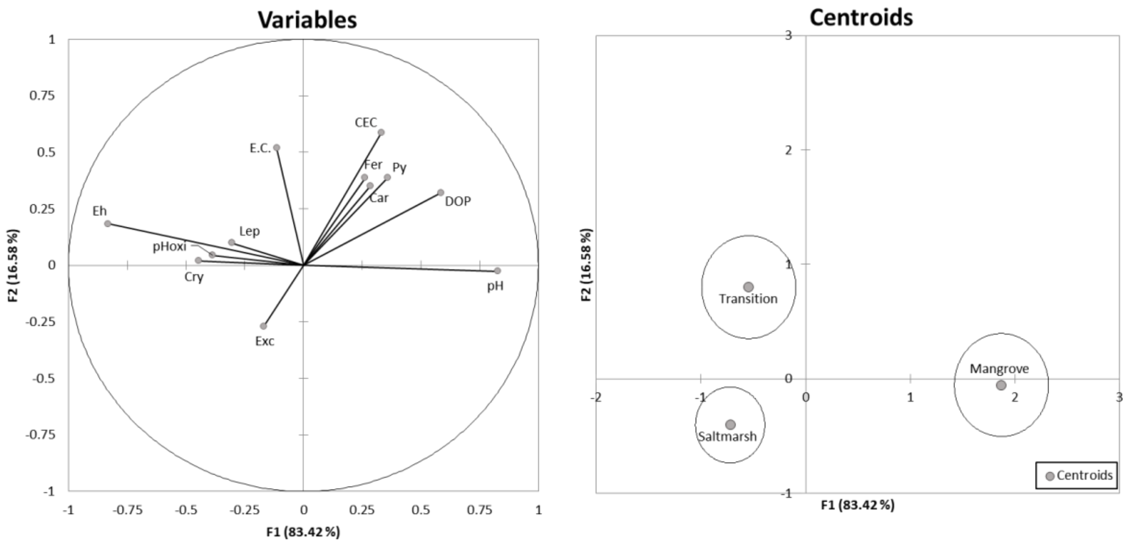

Figure 5.9. Discriminant analysis for mangrove, transition and saltmarsh environments, with iron sequential, electrical conductivity and chemical analyses as variables (Wilks' lambda test p<0.0001, centroids significance level 5%).

In the mangrove, soil sulfidization is the main process, with a dominance of pyrite iron. The transition between mangrove and saltmarsh showed both ecosystem characteristics, with pyrite and iron oxides, however, is different by higher electrical conductivity (E.C.). Saltmarsh soil is under sulfuricization process, caused by oxidation of pyrite, producing jarosite and iron oxides and lowering pH.

5.4. Conclusions

Due to the accretion of fine material, an elevation of the site occurred and consequently a reduction of the inundation period by tides. Consequently, a change in salinity levels occurred, which probably lead to the substitution of the mangrove vegetation by the saltmarsh plants. Moreover, the reduction of waterlogged periods has favoured to oxidation pyrite and soluble iron. After the establishment of the oxic environment, pyrite was oxidized triggering the formation of both jarosite and iron oxides. Additionally, the upbuilding has promoted a lower water flux from tides and promoted a superficial water table mainly from freshwater from rain, causing the removal of both soluble iron and salts from saltmarsh.

In this way, cations and iron are found at higher levels ate the transition site. Where the elevation is intermediary between the sites and the inundation still occurs partially. There is the oxidation of pyrite and a pH reduction, but an accumulation of salts also occurs.

On the other hand, in the mangrove soils, the iron oxides come probably from the parental material, and they are been destructed releasing iron to the estuary. However, portion of iron is retained as pyrite, once organic matter and sulphates are available. Moreover, seawater inundation is more frequent (daily), promoting anoxic conditions.

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6. FINAL CONSIDERATIONS

Saltmarsh publications are more related to the use of the terminology of "sediment" than "soil", with 794 (65%) and 437 (35%) publications respectively. However, it has given attention to the soil as a key factor in providing different kinds of ecosystem services . In this way, it is expected more studies using the term soil to refer to coastal wetland substrates in the next years.

Morphologically, Bragança saltmarsh soil and Laguna saltmarshes soils are distinct, mainly by depth, particle size distribution, soil mineralogy, pH and iron contents. In addition, these soils were classified as Gleissolo Tiomórfico órtico sódico in Bragança, and Laguna soils were Gleissolo Tiomórfico órtico sódico and Gleissolo Tiomórfico órtico típico.

Furthermore, the differences between tropical and subtropical soils were related to the higher iron contents at Pará than Santa Catarina, and to the iron forms, with iron oxides prevailing in Pará (poorly crystalline iron oxides), and Fe – S forms in Santa Catarina, evidencing the iron-related processes of sulfuricization and sulfidization.

Contrasting tropical saltmarsh soils with mangroves in Pará, saltmarshes occupied a slightly more elevated terrain, which reduced the inundation and has favoured to pyrite oxidation (sulfuricization process), while mangrove soils were mainly marked by the sulfidization process.