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Biogeochemistry of mangrove sediments in the Swamp of Mallorquin, Colombia

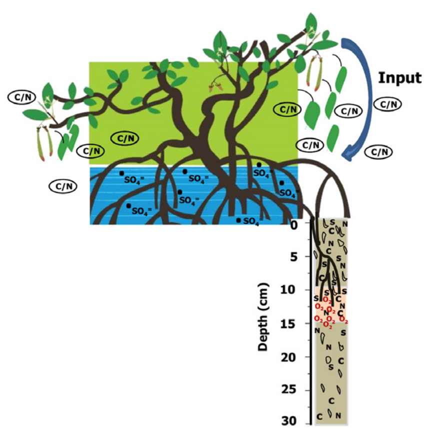
Efrén Castro - Rodríguez [a], Iván León - Luna [a,*], José Pinedo - Hernández [b,*]

[a] University of Atlántico, Faculty of Basic Sciences, Group Coastal Areas, Barranquilla, Colombia
[b] University of Córdoba, Faculty of Basic Sciences, Department of Chemistry, Water, Applied and Environmental Chemistry Group, Laboratory of Toxicology and Environmental Management, Montería, Cereté, Colombia

HIGHLIGHTS

- Mangrove sediments may decrease the availability of nitrogen for eutrophication.
- Mangrove plants may affect the sedimentary record in their surrounding sediments.
- The C/N ratio indicates that the organic matter would be derived from mixed sources.
- Mangrove sediments have been used as efficient records of environmental changes.

GRAPHICAL ABSTRACT



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ABSTRACT

Sedimentary environments of the Swamp of Mallorquin in two different settings, one under the influence of mangrove plants and another without plant covering were analyzed in order to establish the incidence that such plants may have on textural, physicochemical (salinity and pH) and geochemical (total carbon, inorganic carbon, total nitrogen and total sulfur) properties of their adjacent sediments. Textural analysis reveals a predominance of mud, especially in the mangrove zone, which at the same time showed higher contents of salts, organic carbon (total carbon is assumed to be total organic carbon due to the nearly total lack of carbonates), total nitrogen and total sulfur, and also a higher acidity. C/N and C/S ratios ranged from 10.7 to 16.6 and from 2.5 to 10.4 respectively in the analyzed mangrove sediments. The results indicate that the sedimentary organic content of the Swamp of Mallorquin would derived from mixed sources (e.g. algal, terrestrial and sewage), and that depositional processes in recent years have taken place under marine and brackish conditions. While mangrove sediments have been considered efficient records of environmental changes (e.g. sources and cycle of organic matter, depositional environments and paleosalinity), this study found that mangrove plants affect such records by modifying the chemistry and the distribution patterns of some variables such as carbon, nitrogen and sulfur in their surrounding sediments.

1. Introduction

Mangrove ecosystems are unique transitional coastal ecosystems, between marine and terrestrial environments, generally confined to the tropical and subtropical regions (Bayen, 2012). They

* Corresponding authors.
E-mail addresses: efren.castro1985@gmail.com (E. Castro), ileon1964@gmail.com (I. León), jjoaquinpinedo@correo.unicordoba.edu.co, josejph@hotmail.com (J. Pinedo).

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play an important role in the flow of energy and the cycle of nutrients in most of the tropical coastal zones (Silva et al., 1990), and are among the most productive terrestrial ecosystems due to the fact that they provide food sources to local faunal communities, and to the adjacent coastal food webs (Bouillon et al., 2008a; Kristensen et al., 2008; Zhou et al., 2010).

Mangroves act as an important sink of carbon and nutrients (Twilley et al., 1992; Ong, 1993; Rivera-Monroy et al., 1995a, 1999; Marchand et al., 2006a; Donato et al., 2011), as their vegetation requires from a high demand on essential nutrients, thus creating an efficient system of capture, uptake and recycle of nutrients (Alongi, 1992, 1994; Alongi et al., 1993; Kristensen et al., 1994, 2008). In addition, they can act through their roots as traps of sedimentary particles and organic matter, as well as giving greater stability to the sediments. (Lacerda et al., 2000).

Due to these characteristics, mangroves can be indicators of environmental changes. For that reason, they have been extensively used to reconstruct coastal (Daoust et al., 1996) and paleoenvironmental changes (Versteegh et al., 2004).

Down core variations in sediment cores may reflect the geochemical history of a given region, including any anthropogenic impact (Szefer and Skwarzec, 1988; Rubio et al., 1996, 2001). Therefore, when establishing the vertical profiles of the components that make up the sediments, it is possible to obtain relevant information about the load rate of each of them, as well as their cycle in the environment. The relationships between some of these components, have been extensively used to characterize sedimentary environments, since it is possible to use the relationship between carbon and nitrogen, to understand the sources and the cycle of organic matter (Bouillon et al., 2008b), and also to rebuild the paleoenvironment (Wilson et al., 2005), as well as the relationship between carbon and sulfur in order to discriminate the conditions of ancient and recent marine depositional environments, and as an indicator of paleosalinity (Odum and Heald, 1975; Berner and Raiswell, 1984; Raiswell and Berner, 1985).

Mangrove plants are able to induce changes in the chemistry of the sediment, since they exudate oxygen through their roots, to avoid toxic effects of the anaerobic condition of the sediments, creating in this way, an oxidized rhizosphere with completely different characteristics to those of the surrounding sediments (Nickerson and Thibodeau, 1985; Lacerda et al., 1993; Clark et al., 1998; Marchand et al., 2006b; Ferreira et al., 2007; Zhou et al., 2011). Therefore, if mangrove plants modify the conditions of their adjacent sediments, then, they can generate changes in the distribution pattern and the behavior of the components that make them up, which could result in alteration of the information that a vertical profile of sediments would provide.

The purpose of the current study is to provide a baseline for future comparisons of changes in sediment biogeochemical properties and provide a valuable benchmark from which to assess ecosystem changes following future restoration activities in the area. In order to do this, it is imperative to compare the vertical profiles of some geochemical variables (Total carbon, total nitrogen and total sulfur), physico-chemical variables (pH and salinity) and texture in sediment cores extracted in two different settings, one under the influence of black mangrove plants (*Avicennia germinans*) and another without plant covering.

2. Material and methods

2.1. Study area

The current research was carried out in the mangrove ecosystem of the Swamp of Mallorquin, located in the Colombian Caribbean coast (Fig. 1), which was recently declared "*Ramsar site*" (Decreto 3888 de 2009). The Swamp of Mallorquin (CM) is a shallow estuarine coastal lagoon with an area smaller than 650 ha. It possesses a variable volume that depends on the rainy and summer season, high temperatures, diverse salinities and muddy and sandy bottoms (Arrieta and De la Rosa, 2002; Franco and León, 2012). Salinity and temperature of surface water in the CM vary from 20 to 32 ups and from 24 to 30 C° respectively, while depth of this water body varies from 0.35 to 1.56 m (Mangones and León, 2014). The CM receives contribution of marine water from the Caribbean Sea, through a sandy barrier that has some seasonal opening periods, and fluvial waters from Arroyo León and Magdalena River (Uninorte, 1993). The weather is characterized by an annual average temperature of 28 C° and a rate of precipitation and evaporation of 835.5 and 1948.9 mm, respectively. It has two different seasons: a dry season from December to April and a rainy season from May to November (Arrieta and De la Rosa, 2002). The CM is surrounded by mangrove plants, mainly by *Avicennia germinans, Conocarpus erecta* and *Laguncularia racemosa* species, and *Rhizophora mangle* rarer (López and Sierra, 2005; Fyhr, 2007; Mangones and León, 2014). However, the latter has had a substantial increase in the last years due to sowing processes which have been carried out with the aim of restoring the mangrove ecosystem. Due to its characteristics, the CM is a highly productive ecosystem from which diverse species, with commercial interest that several families use for their support, are extracted. In spite of this, the CM is subjected to an enormous anthropic pressure, because it works as a receptor for waste waters, product of domestic and industrial activities and a variety of polluting substances carried by the Magdalena River, Arroyo León and the ancient landfill of Barranquilla (Franco and León, 2010, 2012; Mangones and León, 2014).

2.2. Sample collection and preservation

The sediment samples were taken from two previously selected zones, the first one with a wide covering of black mangrove (*Avicennia germinans*) (M) and the other one, without any plant covering (SM) with the purpose of making comparisons (Fig. 1). Those zones were equidistant from the shore of the swamp and they were separated by a relatively short distance, which allows to state that they are subject to the same sources of pollution and they show the same frequency of tidal flooding and salinity regimes. In each chosen zone, two cores of sediment were extracted using PVC tubes (9 cm i.d.). One core of each zone was used to measure in situ pH and salinity (each 5 cm depth), and the other core for textural and geochemical analyses. The pH was measured with a pH meter model HI9810-Hanna, inserting the probe directly (previously calibrated using 4 and 7 standards) in the sediment core. To exclude the resulting modifications due to contamination with atmospheric oxygen, each measurement was made after inserting the electrode 10 mm below the exposed core surface, until stable values were reached (Sundby et al., 2003; Marchand et al., 2004). Salinities were determined using an Atago refractometer after extracting a drop of interstitial water from sections of 5 cm from the core, through filter paper in a hand press (Marchand et al., 2004). For textural and geochemical analyses, the core was divided in sections of 5 cm, which were collected, hermetically sealed and transported in plastic bags, under refrigeration, to the laboratory where they were stored under temperatures below 4 C° until their analyses.

2.3. Sample analysis

In the laboratory, the samples were homogenized and oven dried at 65 C°. The remains of roots were removed from the samples using acid-cleaned plastic spatulas. Samples were divided in two, one part was used for granulometric analysis by standard sieve and pipette technique after organic matter destruction with H_2O_2 (Guitián and Carballas, 1976). The remaining sediment was

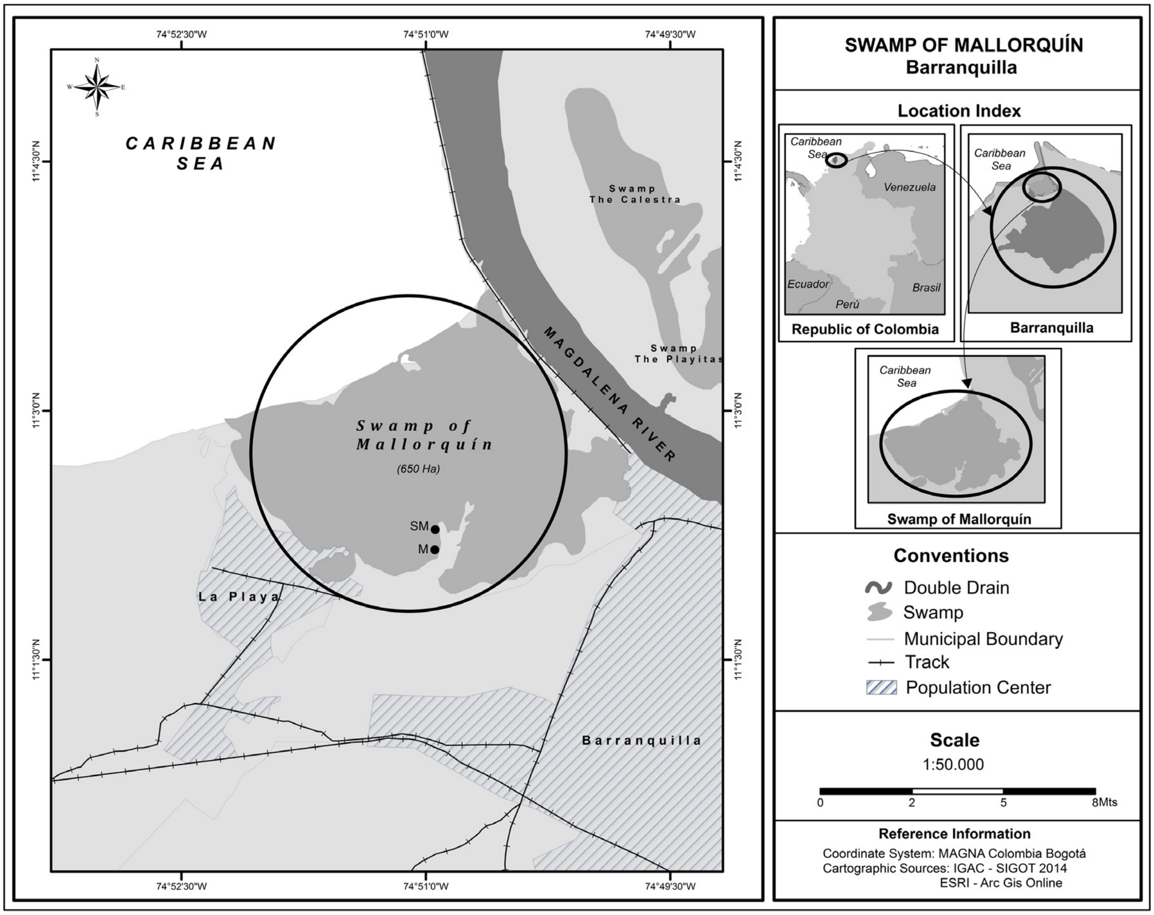

Fig. 1. Map of the study area showing the location of sampling sites at the swamp of Mallorquín (NE Colombia). Labels M and SM stand for the sediment cores taken from the zone with black mangrove and from the zone without mangrove respectively.

Table 1
Analyses of reference material PACS-2 used in the analyses of C_T, N_T and S_T.

Element	Reference value (%)	Measured value (%)	Detection limit (%)
$\mathbf{C_T}$	3.30	3.20 ± 0.08	0.01
$\mathbf{N_T}$	1.29 ± 0.13	1.33 ± 0.02	0.05
$\mathbf{S_T}$	–	0.31 ± 0.00	0.01

used to determine the total carbon (C_T), inorganic carbon (C_I), total nitrogen (N_T), and total sulfur (S_T). The C_T and C_I were determined by an elemental analyzer Carlo–Erba. Due to the nearly total lack of carbonates, total carbon is assumed to be total organic carbon. The concentrations of N_T and S_T, on the other hand, were analyzed simultaneously with an elemental microanalyzer CHNC 1108. The elemental analyses were carried out at the University of Vigo, Spain, by using a reference standard PACS-2. Table 1 shows precision and accuracy relative to reference standards and the respective detection limits.

3. Results and discussion

3.1. Physico-chemical characteristics of sediments

The vertical profiles of pH and salinity in sediment cores from the CM are shown in Fig. 2. The sediment core over the zone with black mangrove and the core from the zone without mangrove were called core M and core SM respectively. pH values measured ranged between 6.6 and 7.9 with a mean value of 6.9 ± 0.34. This parameter showed a different behavior in each sampling zone, showing in general terms more acidic conditions in the mangrove zone. In this area, a trend to the decrease of the pH was observed until 10 cm of depth, in which its lower value was reached. After that, this value increased in a progressive form to the lower layers of the core, where the maximum value to this zone was found. This is a contrasting fact because the lowest pH values were measured at the same depth where mangrove roots were abundant. In addition, the sediment showed a mottled coloration with orange, brown and gray tones, while in the rest of core M and core SM, the colorations were black and gray.

The orange and brown colorations found on the subsurface of the mangrove zone are the result of the precipitation of iron oxyhydroxides that produce this distinctive coloration, indicating partially oxidized conditions due to the release of O_2 by living mangrove roots, while the gray and black tones observed in the rest of the layers indicate reduced conditions due to the microbial sulfate reduction (Harbison, 1986; Clark et al., 1998; Zhou et al., 2011). The decrease of the pH presented in the root zone could be due to the release of oxygen from mangrove roots which may cause sulphides and other reduced compounds in the sediment to oxidize (Bloomfield and Coulter, 1973), and produce sulfuric acid (Evangelou, 1995) and the associated release of protons which acidifies the surrounding interstitial water (Otero et al., 2006).

The behavior of the pH in the SM zone was different from that observed in M, showing initially a rising trend to a depth of 15 cm where it reached the maximum value measured during the study. This was followed by a gradual decline to the bottom of the sediment profile. The minimum value measured for SM was found in the most superficial level.

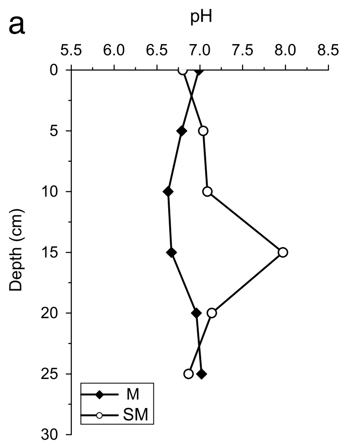

Fig. 2. Vertical distribution of physico-chemical parameters in sediment cores obtained from the Swamp Mallorquin (Black mangrove: M, without any plant covering: SM). (a) pH; (b) Salinity.

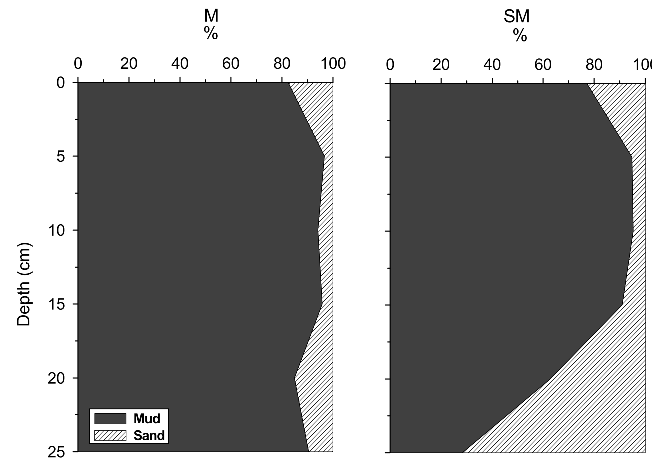

Fig. 3. Granulometric distribution in sediment cores obtained from the swamp of Mallorquin.

The vertical distribution of the salt contents in the pore water (Fig. 2b) showed a tendency to increase, regarding the increasing depth in both areas. Their values were between 44 and 70 with a general average value of 56.8 ± 11.05. These measures are clearly higher than those recorded for the water column of any water body because they correspond to the interstitial water of mangrove sediments, which are subjected to processes of evaporation and water consumption by plants and in consequence accumulate high amounts of salt. Although these values correspond to hypersaline conditions it has been demonstrated that *Avicennia* can tolerate a wide range of salinities, with values ranging from 5 to 55 at the sediment surface (Marchand et al., 2004). The salinity in M zone showed higher values than in the SM zone in the first 10 cm, later, both values reached the same level at 15 cm deep. In M the levels were maintained until they reached 20 cm deep, and then, they were followed by a slight decrease to the bottom of the core. It was not possible to determine the salinity in the last 10 cm of core SM, because the physical features of the sediment did not allowed to extract the interstitial water necessary for that purpose. The upper layers of the area covered by mangrove were more saline than the area without vegetation, probably as a result of water consumption and evapotranspiration by the mangrove plants, and also of longer residence times of water inside the mangroves, allowing a stronger evaporation and higher salt concentrations in these sediments (Ovalle et al., 1990; Lacerda et al., 1993; Barr et al., 2014). However, evapotranspiration occurs in the upper layers of sediment and do not explain the high salinities found toward the base of cores in both stations, taking into account the low permeability of these substrates. Some possible explanations for this fact are the vertical migration of water through holes created by animals such as crabs (Ridd, 1996), or by mangrove anchor roots and downward migration of salts through convectional processes (Marchand et al., 2004), which can occur as a gravitational adjustment, given the fact that the interstitial water in an upper layer has higher salinity and density than the water below it (De Vos et al., 2002).

The distribution of the granulometric fractions in the sedimentary record is shown in Fig. 3. The texture in both study areas was represented mainly by the mud fraction (<63μm) and to a lesser extent by the sand fraction (63μm – 2 mm), while the gravel fraction remained absent throughout the sedimentary record. Mud in M zone was higher (90.7 ± 5.91%) than in SM zone (74.8 ± 26.07%), showing a similar pattern of vertical distribution for both cores in the first 15 cm depth, after which, a gradual decrease toward the base of core SM was presented, while in the case of core M only slight variations occurred. The behavior of grain size along the vertical profiles reflects the hydrodynamics of the CM for a period of time, determined mainly by the sedimentation rates of the study site. Although the particle size distribution of both cores showed certain similarities, mud percentages were always higher in core M, which is due to the root system of mangroves which form a dense grid of vertical pneumatophores and aerial roots that traps floating detritus and reduces tidal flow, eventually creating conditions where suspended silt and clay particles settle (Soto-Jiménez and Páez-Osüna, 2001). On the other hand, the increasing trend which showed the sand fraction in the last 10 cm of core SM may be related to an event that increased the hydrodynamics of the swamp, at least toward the sampling point for a period of time, which could not be strongly reflected in core M due to the reasons prior exposed.

3.2. Elemental composition and ratios in sediments

The vertical profiles of the C_T, N_T and S_T, as well as C/N and C/S ratios given in sediment cores are shown in Fig. 4. C_T values varied between 0.69 and 8.16% with a mean value of 3.90 ± 2.12%, higher values appearing along the profile of the M zone. The behavior of C_T was also different between the sampling points, showing a general tendency to decrease with respect to increasing depth in mangrove sediments while the distribution in bare sediments was characterized by a tendency to increase at the top of the core (upper 10 cm), followed by a progressive abatement toward the base of the sedimentary column, where the lowest values were reached. The distribution pattern of C_T in the M zone shows an enrichment of carbon as depth decreases and differs substantially from the distribution of C_T in the SM zone. This would reflect the existence of specific conditions for each of the zones, which may favor or not the accumulation of organic carbon in those sediments. Mangroves in first instance are known to have an efficient ability to trap suspended material of organic origin from the water column, which can come from the organic material produced autochthonously, such as mangrove litter and benthic microalgae which are usually the most important autochthonous carbon sources in these environments (Kristensen et al., 2008). Also anoxic conditions in sediments is one of the major drivers allowing higher preservation of organic matter in mangrove sediments. Another factor that would contribute to create a better record of organic carbon in mangrove sediments is the richness of mangrove leaves in tannins and other phenolic compounds, which have the ability to inhibit microbial activity and growth (Alongi, 1994), and

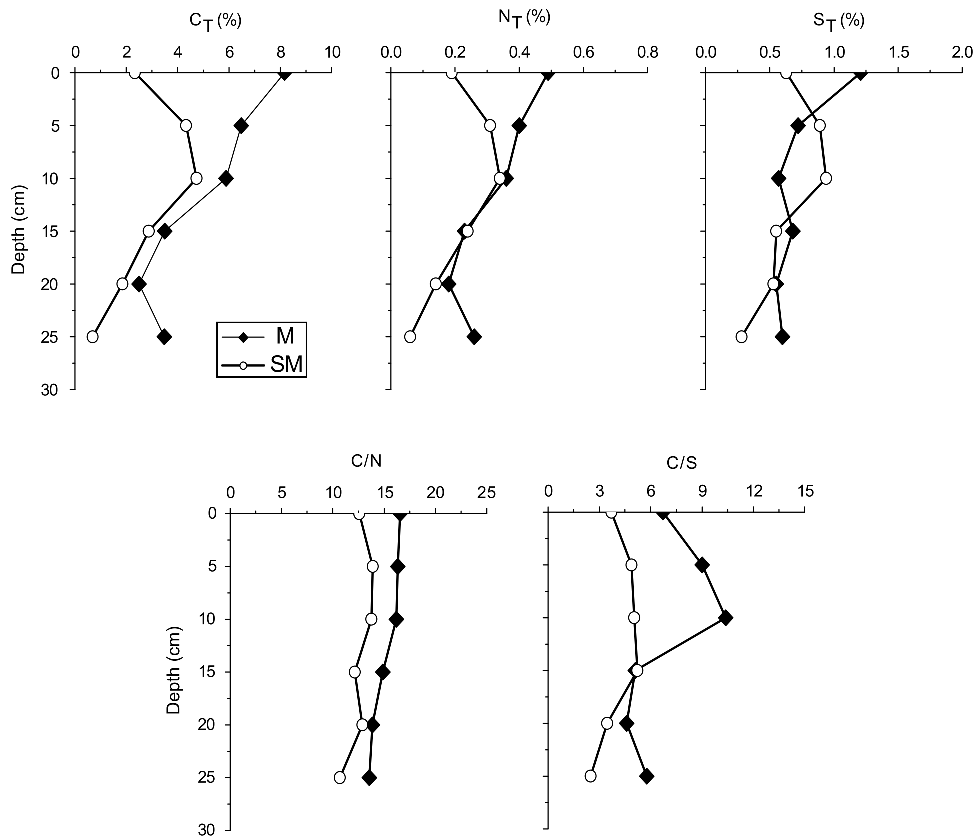

Fig. 4. Vertical profiles of C_T (total Carbon), N_T (total Nitrogen, S_T (total Sulfur) and C/N (Carbon-to-Nitrogen) and C/S (Carbon-to-sulfur) ratios in sediment cores of the swamp of Mallorquín.

thus slow down the process of organic matter decomposition and improve its conservation in the sedimentary column.

The pattern of vertical distribution of N_T in both sediment cores was similar to that presented by the C_T, with values ranging from 0.06%–0.49% and a mean value of 0.27 ± 0.11%. Overall, N_T concentrations were higher in the sediment associated with mangrove plants, which may be related to the high organic load this shown, regarding the SM zone, thus corroborating the existence of an increase in the contributions of organic matter in that sampling area. However, the nitrogen load of sediments can be increased in a significant way due to the entry of sewage with high content of nitrogenous substances to the CM (León and Mangones, 2011; Mangones and León, 2014).

Some studies (Nedwell, 1975; Rivera-Monroy et al., 1995a, 1999; Twilley and Day, 1999) concluded that mangroves can be important sinks of these inorganic forms of nitrogen entering dissolved in tidal waters. This may be due to the immobilization of nitrogen through fixation by sedimentary bacteria (Rivera-Monroy et al., 1995b), which are responsible for keeping nutrients (especially N and P) in mangrove ecosystems (Alongi et al., 1993; Ray et al., 2014), so that they can be used by mangrove plants and the same bacteria, which can even compete when there is little available nitrogen in the sediment (Holguin and Bashan, 2007). Because of this, it has been found insignificant losses of nitrogen through denitrification process (conversion of NO_3^- to N_2), which is the main mechanism of N loss in anthropogenically influenced mangrove sediments (Rivera-Monroy and Twilley, 1996; Oliveira et al., 2012) probably because the NO_3^- is converted into NH_4^+ and then are assimilated (Holguin and Bashan, 2007). Another factor that can influence the dynamics of nitrogen in the mangroves is the presence of tannins in the sediment from mangrove leaves, since these substances can form stable complexes with proteins, which are resistant to microbial degradation (Maie et al., 2008). This makes mangrove sediments a more efficient sink for nitrogen and would provide another reason for the higher contents of nitrogen in the M zone.

The S_T showed a different behavior in each sampling area with contents that varied between 0.28 and 1.21%. In the sediments associated to mangrove plants the S_T values showed a general tendency to decrease with increasing depth, occurring an irregular increase at 15 cm depth and another slight increase at the bottom of the core. In the control area, on the other hand, there was an uneven distribution of the contents of S_T, characterized by an increasing trend during the first 10 cm deep and a progressive decline from there to the base of the sedimentary column.

Sulfur accumulation in sediments is primarily controlled by the rate of sulfate reduction and the oxidation state of the sediment (Holmer et al., 1994). The greatest accumulation of S_T in the mangrove zone may be related to a higher rate of sulfate reduction by sulfate-reducing bacteria, which oxidize organic matter using SO_4^{2-} as electron acceptor (Kristensen et al., 2008). This process occurs in anoxic conditions and depends mainly on the amount of organic matter (higher in the M zone) and sulfates available in the system (Borrego et al., 1999), being sulphides its primary product (Marins et al., 1997). Although the amount of organic sulfur in the samples was not determined in this study, the higher amount of OM in the mangrove zone clearly has an effect in the accumulation of sulfur in sediments.

The decrease in the proportion of S_T presented at 10 cm deep in core M may be due to the oxidation of insoluble sulphides to sulfates and sulfuric acid by the oxygen translocated by aerenchyma and then exuded by mangrove roots (Armstrong, 1978; Evangelou, 1995; Otero et al., 2006), which may be related to the low pH registered in the same subsurface level and may result in the post-depositional migration of the substances produced to a level of the sedimentary column where they are reduced again to sulphides. This fact would explain the increased S_T content presented at 15 cm depth.

About the C/N ratio, its application has been specially used in coastal regions to obtain information about the origin of organic matter (Müller and Mathesius, 1999). The differences in the elemental composition of the sediment may lie mainly in the composition of the material that comes to it and settles. Although a relatively high C/N ratio may indicate that the sediments contain a significant mangrove detritus load, the wide range makes its interpretation difficult, so that it can reflect pure mangrove detritus in an advanced state of decomposition, or a variable contribution of other carbon sources (Kristensen et al., 2008), which are mixed together in the sediment where they have different degradation rates and experience changes in their composition through physical, chemical, and biological agents, hampering to establish the identification and the degree of contribution of each of them (León, 2005).

Typically, it is considered that algae have atomic C/N ratios between 4 and 10, whereas vascular land plants have C/N ratios higher than 20 (Meyers, 1994) therefore, terrigenous addition to marine sediment can be identified based on an observed enrichment of C over N atoms in marine sediments (C/N$<$10, Parsons, 1975) as compared to terrestrial sediments (C/N$>$12, Kukal, 1971). The values of the C/N ratio in the sediment cores studied ranged between 10.7 and 16.57 with mean values of 15.23 $\pm$ 1.32 and 12.67 $\pm$ 1.18 for the M and SM zones respectively. Considering that the CM is surrounded by large extensions of mangroves, and that the C/N ratios found along the sediment cores are not within the C/N ranges of 24–78 reported by Rao et al., (1994) and 31–66 by Alongi and Christoffersen (1992) for mangrove detritus, it is very likely that C/N values found in the CM do not indicate that mangrove debris has been the main source of organic matter to the sampling site. Rather, these values are typical of organic matter derived from mixed sources and are more close to phytoplankton C/N values than typical C/N values from decomposed mangrove tissues.

The CM has a clear problem of pollution due to several factors such as human settlements on its shores, which have no sewage system and/or management of domestic wastewater, the freshwater inputs coming into the CM which carry high sediment loads from the industrial activity and the leachates from the old dumping of Barranquilla which is located in the surroundings of the Swamp (Franco and León, 2010, 2012). Nonetheless, potential effects in the waterbody have not been observed in the sediment cores in function of C/N ratio, possibly due to mangroves are recognized to act as a natural barrier to shoreline erosion since they have the ability to stabilize fine sediments, thereby helping coasts to accrete. Mangroves also maintain the water quality by extracting nutrients from potentially eutrophic waters (Yusoff et al., 2006).

In general, the behavior of the C/N ratio in the sedimentary record associated with mangroves is different from that observed in the bare sediments (Fig. 4). Along the mangrove sediment profile there were higher C/N ratios than those recorded in the other area, which showed a tendency to decrease with respect to increase in depth, slightly for the first 10 cm and more pronounced toward the bottom, while the C/N values of the unvegetated area had an irregular fluctuation along the sedimentary column. Marchand et al. (2003) obtained in an area which called senescent mangrove forest (due to its advanced stage of development), C/N ratios with values similar to those found in this study to examine the contents of sedimentary organic matter in relation to the development of a forest dominated by *A. germinans*. In this zone, the C/N ratios were recorded relatively higher (between 9 and 19) and by petrographic studies it was found a predominance of lignocellulosic waste, which are factors that characterize the organic matter derived from higher plants. Lallier-Verges et al. (1998) concluded from similar results and taking into account complementary analyses, that sedimentary OM of developed mangroves is predominantly derived from the microbial decomposition of tissues of higher plants.

This allows to affirm that the differences that occur between the C/N ratios of both sampling areas of the current study are due more to different degrees of contribution from the sources cited at the study site than differences in the sources of OM, as well as different conditions of preservation of the OM in each area, since diversified sources of OM are possible in impacted mangrove sediments (Sanders et al., 2016). Four hypotheses could explain these differences: (i) a greater influence of mangrove wastes on the M zone, which besides having higher C/N ratios, they are less reactive to decomposition than the OM derived from algae; (ii) the root system of mangroves catches and retains more efficiently the organic wastes that come to it, also the fact that underground organic matter supply by root decay also occurs and can affect the whole carbon input to the sediments; (iii) the mangrove-derived tannins that can suppress microbial activity, accordingly improving the conservation of OM and (iv) sewage input that appears to be an additional organic matter source, which can affect the source signature of organic matter (Carreira et al., 2002).

Although the C/N values recorded in the current study may indicate a mixture of organic matter from different sources and in different proportions, it is also partly due to variations because of transformations of organic matter by diagenetic processes, which will vary between sampling areas depending on their conditions of preservation of the vertical evolution of OM (e.g. bioturbation and rhizosphere processes can promote OM degradation enhancement at variable depths and stead state diagenesis may not occur, associated to an unknown degree of sediment mixing, borrowing, etc.).

The values of the C/S ratios ranged between 2.49 and 10.39, with mean values of 6.93 $\pm$ 2.3 and 4.13 $\pm$ 1.08 for mangrove and bare sediments, respectively. These levels are characteristic of environments with high primary productivity and varied income of organic material to the system (León, 2005), since there is a tendency to increase the values of C/S ratio beyond the normal range in sediments with high content of C_{org} such as vegetated sediments (Berner and Raiswell, 1983). The C/S method is based on the positive correlation between the content of pyritic sulfur and organic carbon in sediments (Berner and Raiswell, 1983; Leventhal, 1983). This is because the total amount of metabolizable organic matter available to support the sulfate reducing bacteria increases with the total proportion of organic matter reaching the sediment, which has the consequence that the content of sedimentary pyrite is positively correlated with the unmetabolized amount (refractory or unused) of organic matter (Rullkötter, 2006). However, it should be noted that the production of pyrite may be limited by the supply of traces of C_{org}, sulfate and reactive iron (Berner, 1984; Huerta-Díaz and Reimer, 2010), which leads to variations in the C/S ratios and allows differentiating between the characteristics of depositional environments.

In Woolfe et al. (1995), the applicability of the C/S ratio as an indicator of paleosalinity is shown, based on C/S ratios that are created depending on the supply of the independent factors limiting the formation of FeS or FeS_2 in one depositional environment. In this respect, it has been established that low C/S ratios (1–4) are characteristic of marine conditions and intermediate ratios (4–11) are related to brackish with saline influence waters.

The C/S variations obtained in this study appear to record depositional conditions as those described above, which may be associated with the features found in the CM, receiving contributions from marine and freshwater sources in a variable way throughout the year. However, there are marked differences between the C/S profiles in both zones, despite being subjected to the same patterns of tidal flooding and salinity regime. This may be due primarily to higher proportions of C_{org} that occurred along the sediment core from the M zone, reflecting the OM derived from mangrove plants observed there, which is often resistant to decomposition and has the capacity to substantially modify C/S interpretations (Woolfe et al., 1995), since the presence of a refractory carbon phase in the sediment may decreases the action of sulfate reducing bacteria and in consequence the positive correlation between organic carbon and pyritic sulfur. Although organic sulfur phases from sewage input would also modify such interpretations in the study area, it has been found that in sediments organic sulfur from sewage is bacterially oxidized and fixed as $SO^{2-}4$ rapidly (Drzewicki et al., 2015). Additionally it was found a high-degree of positive correlation between carbon and sulfur in both zones, but significantly higher in the SM zone which would corroborate the relation between organic carbon and the rate of sulfate reduction by bacteria in that zone and the presence of a refractory phase of OM and in consequence organic sulfur in the M zone.

Moreover, there was an irregular increase in the C/S at 10 cm deep in the same zone which can be taken as an alteration of the profile by mangrove roots, which induce post-depositional migration of sedimentary sulfur as was explained before. Deborde et al. (2015) recorded a similar increase in the C/S ratio of a stand dominated by *Avicennia marina*. Despite this, the SM zone continued recording C/S ratios that indicate depositions under marine and brackish conditions, which is corroborated by the salinity ranges that have been obtained in several previous studies in the CM (Uninorte, 1993; Arrieta and De la Rosa, 2002; Fyhr, 2007; Garcia and Luque, 2008; Corrales and Redondo, 2008; Franco and León, 2010; León and Mangones, 2011; Franco and León, 2012; Mangones and León, 2014). The decrease of C/S values at the bottom of both profiles (last 10 cm), can also be due to variations in the supply of the limiting factors, such as losses of C_{org} (as CO_2) and increases in the levels of reduced sulfur, since there is a close connection between OM remineralization during early diagenesis and microbial sulfate reduction (Rullkötter, 2006).

4. Conclusions

The results suggest that mangrove plants create conditions on their surrounding sediments that favor the deposit of both fine particles and organic material and allow them to act as more efficient sinks of organic carbon, sulfur and nitrogen than unvegetated sediments. This is particularly important in the case of nitrogen, since it is fixed at higher rates in mangrove sediments reducing the possibility that the CM undergo a process of eutrophication. On the other hand, it was possible to notice that mangroves roots have the ability to modify the characteristics of the sediments under their influence, disrupting the distribution patterns of certain variables such as salinity, pH and sedimentary sulfur. Through C/N and C/S ratios was possible to characterize the sedimentary environments of the study area, which yielded a record of the conditions that have been established in the CM during a given period. C/N values recorded in this study were relatively high (>10), suggesting that the sedimentary organic content would derived from mixed sources (e.g. algal, terrestrial and sewage), where mangrove plants would have relevance due to their high development in the CM. However, higher C/N ratios were recorded in the mangrove zone, thus reflecting a higher proportion of mangrove detritus. C/S ratios meanwhile registered depositional processes under two different conditions, marine and brackish with saline influence, in contrast with the conditions that the CM has undergone at least the past 20 years as is ratified by previous studies. In spite of this, the C/S scheme obtained from the sediments associated to mangrove plants seems to be altered by factors inherent in them, such as higher proportions of refractory OM from mangroves and the oxidation of the rhizosphere that leads to mobilization of sedimentary sulfur. The results indicate that although mangroves have been considered efficient records of environmental changes by retaining and stabilizing sediments more efficiently than bare sediments, certain factors can cause changes in the distribution of certain variables, which would prevent their use as monitors of environmental changes, as these can alter to some extent the information that would provide a sediment core.

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