



Soil organic carbon of mangrove forests (*Rhizophora* and *Avicennia*) of the Venezuelan Caribbean coast



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ABSTRACT

In order to understand the processes that control organic matter preservation in tropical wetlands, we have evaluated the mineralogy, total organic carbon (TOC wt%), soluble organic matter (SOM wt%), bulk density (g/cm^3), and carbon stock (Mg/ha), and used FTIR to identify functional groups in SOM of soil in mangrove forest dominated by *Rhizophora* or *Avicennia* with different conditions (live, deteriorated and dead). Six locations along the Cuare Inlet and Morrocoy National Park were studied. Mineralogical analysis showed the presence of minerals, such as pyrite and rhodochrosite, from anoxic environments. *Rhizophora* mangrove soils have higher TOC compared with *Avicennia*, but we did not find significant differences in SOM. TOC/SOM ratios were lower for *Avicennia* soils. The carbon content ranged from 11.30 to 59.84 Mg/ha for the first 10 cm of soil. Regardless of stand condition, the TOC/SOM ratio was lower at a depth of 20–40 cm. The results of the TOC/SOM ratio are attributable to: (a) the association of TOC with clays and non crystalline minerals; (b) the leaching processes of soluble compounds of the OM; (c) a higher proportion of recalcitrant compounds; (d) a lower decomposition rate for recalcitrant or non-recalcitrant compounds; and (e) physicochemical conditions that limit biological activity, such as high salinity, soil anoxia and hypoxia. The soils can be divided into three groups according to the presence and intensity of functional groups detected by FTIR. The functional groups identified could not be related to the sampling sites, to species composition or conditions. These differences may be due to other sources of organic matter, as well as to degree of preservation. Information of soil organic matter properties and their relationship with mangrove composition and conditions is important to understand carbon sequestration and storage potential in Venezuelan Caribbean mangrove systems.

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1. Introduction

In terrestrial ecosystems soil organic matter is the compartment with the highest organic carbon (OC) content, a key parameter in ecosystem dynamics and an indicator of soil condition and quality. Soil OC worldwide is approximately $1.2\text{--}1.5 \times 10^{15}$ kg (1220–1500 Gt) in the top one meter (Eswaran et al., 1993; Batjes, 1996; Kirschbaum, 2000). This is equivalent to almost double the amount of carbon stored in the plant biomass (Sommer et al., 2000).

Mangroves have been recognized as potential carbon sinks and are one of the most important ecosystems for long-term carbon sequestration (Alongi, 2012, 2014). Mangroves store significant amounts of carbon in both the aerial and underground biomass (Donato et al., 2011; Adame et al., 2013; DelVecchia et al., 2014),

and hence mangrove soils register relatively high concentrations of carbon (Donato et al., 2011). The carbon transformation processes and the organic matter in mangrove soils are influenced by environmental conditions, mainly weather, hydroperiod and composition of the parent material. Additionally, biotic factors such as vegetation type and stand composition contribute to the quality and quantity of organic material incorporated into the soil. Organic matter that is not transported by the tide and remains within the system is incorporated into the soil by means of other organisms, biological degradation, or chemical modification (Kristensen et al., 2008).

Furthermore, human activities such as deforestation and conversion of land ecosystems result in soil degradation and the massive loss of the soil's OC, tonnes of which are liberated into the atmosphere (Lal, 2003). Carbon dioxide emissions produced by the degradation, deforestation, and conversion of mangroves has been very little studied (Lovelock et al., 2011) due to a lack of data

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regarding the amount of carbon stored in these ecosystems (Bouillon et al., 2009).

Recalcitrant compounds are important in forest ecosystems because of the role they play in carbon sequestration, which results in the accumulation of stable organic matter in soils. The main vegetation-related compounds subject to decomposition are polysaccharides, lignin, tannins, and lipids. In the latter we find cutin, suberin, and waxes, which represent approximately 10% of plant biomass (Lützow et al., 2006). Roots, through the processes of growth and replacement of the plant biomass, provide most of the carbon contained in the soils of forest systems (Rasse et al., 2001). Roots can be more resistant to decomposition because they contain larger quantities of lignin and suberin compared to the aerial biomass (Rasse et al., 2005). However, although the molecular size and structure of biopolymers affect the decomposition process, part of the biopolymers susceptible to alteration may be preserved. This preservation can occur due to environmental factors such as: (1) climate (rainfall and temperature) and landform; (2) soils, determined by Eh (anoxic or oxic conditions), pH (acidity), and mineralogical composition (minerals belonging to the clay group and iron and aluminum oxyhydroxides); (3) the type of organic matter and its degree of preservation; and (4) communities of microorganisms that can affect the biopolymers and their alteration rates (Kristensen et al., 2008; Schmidt et al., 2011; Alongi, 2014; Lehmann and Kleber, 2015).

Other factors that can influence preservation are the protection of soil organic matter—many compounds that are labile or susceptible to alteration can be protected (encapsulated) by more resistant compounds and, therefore, preserved in the soils—and/or the role of the mineral matrix (Killips and Killips, 2005; Vandembroucke and Largeau, 2007). For example, the organic matter in soils can be physically stabilized by its association with silt and clay particles (Six et al., 2002; Lützow et al., 2006), which represent as a whole the most significant carbon sink (Jagadamma and Lal, 2010).

Lipids are a diverse group of compounds ranging from simple fatty acids to more complex molecules such as sterols, phospholipids, chlorophyll, waxes, and resins (cutins and suberins) (Chesworth, 2008). They represent a fraction of the relatively stable organic matter (Lorenz et al., 2007) and their decomposition rate depends on their chemical complexity, with waxes and resins among the substances that are most resistant to degradation (Chesworth, 2008). In the lipid fraction there is also a group of biomarkers that can be associated with plant-related compounds that contribute to soil organic matter (Lichtfouse et al., 1994, 1997; Bol et al., 1996; van Bergen et al., 1997). For example, the lipids contained in the mangrove litter can be used as biomarkers to determine the origin of the organic matter in the soils (Koch et al., 2003, 2011; Xu et al., 2006; Meziante et al., 2007; Silva and Madureira, 2012) and as paleo-indicators of mangrove dynamics during the Holocene (Koch et al., 2011).

Studies show that fatty acids identified in the organic matter (leaves) and soils of mixed stands of mangroves in Brazil represent more than 35% of total lipids. Saturated fatty acids are predominant in *Rhizophora mangle* leaves, but in *Laguncularia racemosa*, unsaturated fatty acids are more abundant (up to 33% of total lipids). On the other hand, in *Avicennia schaueriana* leaves terpenes and sterols are predominant (33% and 17%, respectively) and their proportions in the soils represent 13% and 20%, respectively. Aliphatic hydrocarbons are the least abundant at < 12% of the total lipids in leaves (Silva and Madureira, 2012).

All of these characteristics of the organic matter contained in mangrove soils describe a dynamic system of great importance for the study of environments with a high degree of preservation/accumulation of organic matter. Venezuela has several mangrove zones along its coasts, among them the Cuare Inlet and the

Morrocroy National Park, which are located in the country's central-western region (Fig. 1). As a contribution to understanding the parameters and processes that control the preservation of organic matter in tropical environments, such as organic matter input, redox condition, soil type, and organic matter alteration, we studied mangrove soils differing in floristic composition (*Rhizophora mangle* and *Avicennia germinans*) and condition (live, deteriorated, or dead mangrove) through mineralogy, total organic carbon (TOC) concentration, soluble organic matter (SOM) concentration, and bulk density (BD). Additionally, we used Fourier Transform Infrared Spectroscopy (FTIR) to evaluate SOM type.

2. Geological setting

The Cuare Inlet and Morrocroy National Park, located along Venezuela's central-western coast (Fig. 1), are one of the country's most important marine-coastal regions for its biodiversity and economic (tourism and recreational activities) potential. These two protected areas consist of muddy coastal plains with mangroves and saltflats, mudflats and lagoons, and islands of coral origin covered with mangroves and other coastal communities.

The annual rainfall measured in stations located near the study area is < 1400 mm. There are two well-defined seasons: a dry season from January to March and a rainy season from April to December. The months with the highest rainfall are April or May and November.

The mangroves studied show accelerated deterioration and massive mortality at some sites. Modifications in the hydrology and sedimentation patterns of drainage basins in the area caused by the elimination of forest cover mainly for livestock farming and agriculture, and to a lesser extent for the exploitation of timber species and road construction, have resulted in reduced freshwater flows and increased sediment loads. Other human activities contributing to the alteration of mangrove communities in the area, with the ensuing deterioration and destruction, are logging, dredging, and the filling of mangroves and its surrounding areas for the construction of roads, tourism facilities, housing complexes, and marinas (Barreto, 2008).

The study area is located at varying altitudes between 0–285 m. a.s.l., with Cerro de Chichiriviche at the highest point. The geology is represented by the Agua Linda and Ojo de Agua Formations, the Capadare limestone Formation, and Quaternary alluvial sediments. The Ojo de Agua Formation is dominated by micaceous sandstones interspersed with lutites, conglomerates and sandy and nodular limestones, with molluscs, mainly of the *Ostrea* genus (Piccoli and Stockhausen, 1991). The Capadare limestone formation consists of soft reef limestone with *Lithothamnium* sp. algae. The Agua Linda Formation consists of interspersed clays, lutites and limestones with a smaller proportion of calcareous conglomerates, calcareous sandstones and limolites (González de Juana et al., 1980).

The Quaternary alluvial sediments in the Cuare Inlet are supplied by a network of creeks that drain water from the freshwater sub-system. In the southern sector they are supplied by the runoff water from the lower slopes of the Cerro de Chichiriviche and its surrounding areas. Fluvial input produces variations in water salinity between 1–34‰ in the Cuare Inlet (Barreto, 2001). The sediments arriving at the Morrocroy National Park are supplied by drainages at the west-southwest areas of the park.

The soils of this area belong to the orders Vertisols and Gleysols, which have the poor drainage conditions and fine textures characteristic of low-lying mudflats. On the other hand, the sand bar, which is made up of recent sediments, has soils from the large groups Arenosols and Gleysols characterized by sandy soils associated with poor internal drainage conditions (Coplanarh, 1975; FAO, 2016).

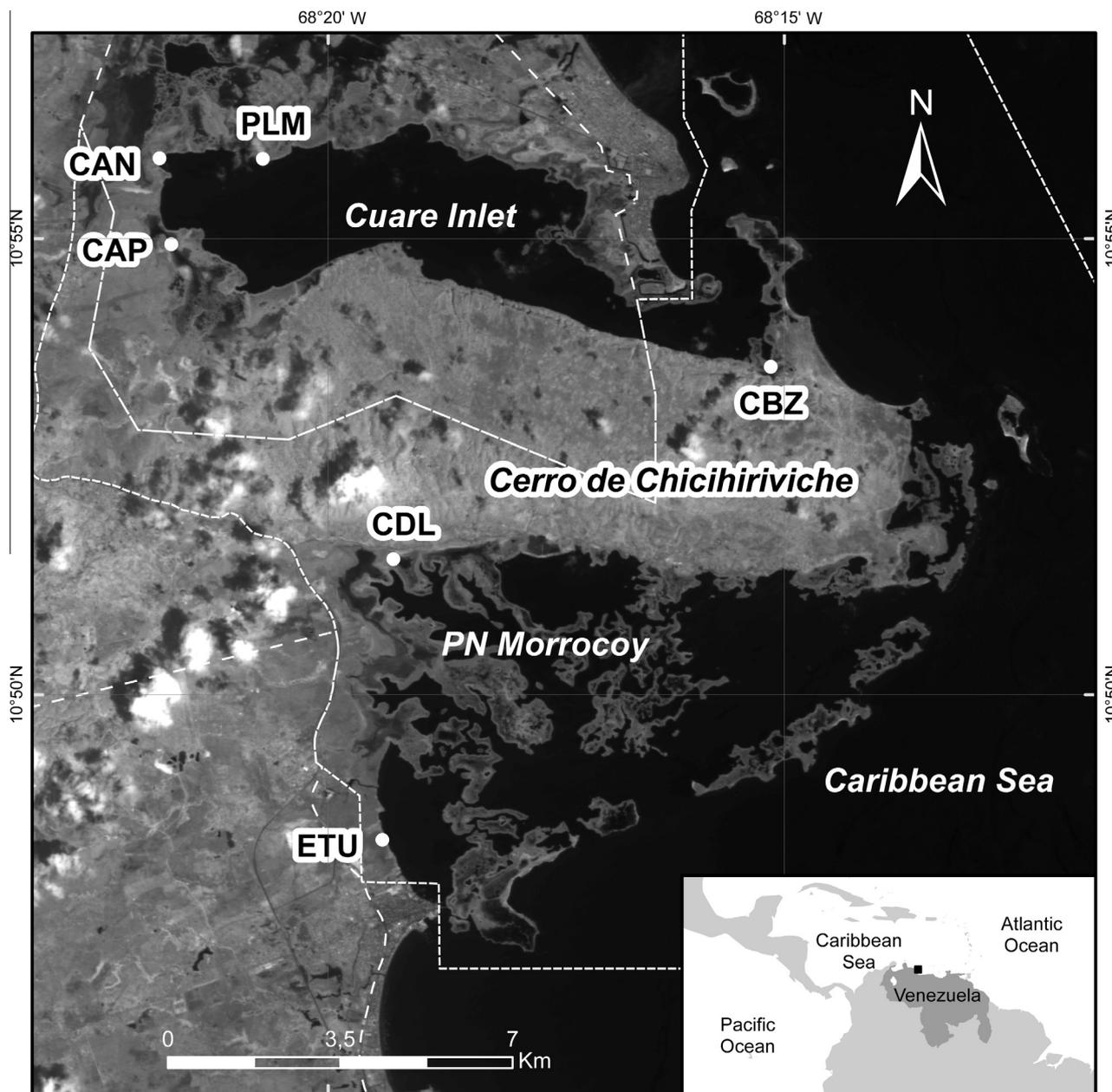


Fig. 1. Study area: Morrocoy National Park (PN Morrocoy) and Cuare Inlet, Venezuela. Image from the *Miranda* satellite, April 2012.

The general species distribution pattern for the mangrove forests where the soil samples were collected is as follows: on the outer fringe (tidal channels or inlet borders) there is mixed forest dominated by *Rhizophora mangle* L. (Rhizophoraceae) with variable densities of *Laguncularia racemosa* (L.) Gaertn. f. (Combretaceae) and some individuals of *Avicennia germinans* (L.) L. (Acanthaceae). In the inner part of the basin mangrove (lower areas with less frequent flooding), there are monospecific forests of *Avicennia* with continuous patches or zones of dead mangroves bordering the mudflat/saltflat.

3. Samples and methods

3.1. Sample collection

Soil samples were collected at six locations throughout the Cuare Inlet and the Morrocoy National Park: Punta La Matica (PLM), Ánimas Channel (CAN), Pancho Channel (CAP), Boca del

Zorro Channel (CBZ), De León Channel (CDL) and Tucácas Bay (ETU) (Fig. 1).

A total of 63 samples (54 superficial ones at depths of 0–20 cm and nine at 40–60 cm) were collected in August and November 2005 and in October 2006. The locations were georeferenced using a model GPSmap 76Cx Garmin global positioning system (GPS) receiver with ± 3 m precision. The soil samples were collected using a steel soil corer 10.2 cm in diameter. Interstitial water salinity and pH were measured in situ in each borehole once the groundwater level stabilized. In each sampling area the mangrove species and stand conditions (live, deteriorated or dead mangrove) were identified. The samples were stored in plastic bags until they were transported to the laboratory.

3.2. Sample handling

Samples were placed in plastic containers and left to dry at room temperature. The physical description of the samples was

done with the dry material and took into account Munsell's color chart (Munsell, 1973), granulometry, the presence or absence of roots, and other significant characteristics. After this description was made, the samples were crushed and sieved (2 mm mesh size) into medium sand and clay size fractions for later chemical analyses.

Prior to the mineralogical and chemical analyses, the samples were washed with distilled water to eliminate any salts (mainly NaCl) precipitated as a result of the drying process. Two techniques were used: filtration by means of long stem funnels and filter paper (Whatman No. 3) for samples with a high root content, and centrifugation and decantation of remaining water for samples with a high content of fine sand, silt, and clay size fractions. To corroborate that excess salts were removed, the chloride test was performed using silver nitrate (Skoog et al., 1996). After washing, the samples were placed in an oven at 40 °C until they were completely dry.

3.3. Mineralogical analysis

A mineralogical analysis was performed on 39 soil samples from the various collection sites. Samples were pulverized into fine grain size in an agate mortar and then placed in the sample holder of a Bruker, AXS (Siemens D-8 ADVANCE) diffractometer in order to perform the dust method (Azaroff and Buerger, 1958; Bertin, 1971).

3.4. Interstitial salinity

At each sampling site, interstitial water samples were collected using a device consisting of an aluminum pipe with multiple perforations along its length. A hose was attached to one of its ends and the samples were extracted with a syringe. The salinity of the solution was measured with an Atago Pal-06S digital refractometer.

3.5. Bulk density (BD)

To determine the BD (g/cm^3), in each of the selected mangrove stands a sample of the first 10 cm of soil was collected using PVC pipes measuring 5.1 cm in diameter and 10 cm long. The initial weight of the wet samples contained in the cylinder was determined. The dry weight was determined after the samples were placed in an oven heated to 50 °C with forced ventilation until the weight was constant. BD was calculated as the ratio between the sample's dry weight and the volume of the cylinder in which it was contained.

3.6. Total carbon (TC), total organic carbon (TOC), and inorganic carbon (IC)

TC concentration was analyzed in 63 samples using a LECO (C-144) carbon analyzer, and carbonate or inorganic carbon (IC) was determined using the Bernard calcimeter method (Hesse, 1971). Calibration curves were constructed to determine sample concentration. Certified LECO patterns were used to determine TC, and patterns with different CaCO_3 concentrations for IC. TOC concentration was obtained by the difference between TC and IC. Carbon content per volume of soil was calculated based on BD and reference depth (10 cm).

3.7. Extraction of soluble organic matter (SOM)

The extraction of SOM corresponding to the lipid fraction was performed on 61 samples. Approximately 20 g of soil was weighed in cellulose thimbles and the SOM was extracted with

dichloromethane in a Soxhlet extractor. The extracts were then vacuum evaporated and quantified.

3.8. Fourier Transform Infrared Spectroscopy (FTIR)

The main functional groups were identified by FTIR spectroscopy on 60 SOM extracts with a Thermo Nicolet (Lexus 470 FTIRESP) spectrometer. The liquid film method was used on KBr pellets, and the FTIR spectra were determined in the 4000 to 400 cm^{-1} range. The SOM corresponding to the lipid fraction was extracted with dichloromethane and analyzed using FTIR in order to identify functional groups. In the literature, FTIR spectroscopy is applied mainly to organic matter in soils and sediments. With this type of analysis we can identify the differences and similarities of the functional groups present in soil or sediment organic matter, and also identify contamination by organic compounds (Schnitzer, 1972; Ishiwatari, 1973; Kerndorff and Schnitzer, 1979; Rifaldi, 1982; Meléndez et al., 1990; García et al., 1994; Rivero et al., 1998). It has also been applied to organic matter in mangrove soils (Giovanela et al., 2004; Ferreira, 2010; Zhang et al., 2011, 2013). In this study, the SOM was analyzed using FTIR to compare the OM present in the soil samples based on their location in the intertidal zone and the species composition. To identify functional groups, we used referenced information on soil organic matter (Schnitzer and Khan, 1978; Sleighter and Hatcher, 2011) and the literature on infrared spectroscopy (Stevenson, 1994; Silverstein et al., 2005; Shriner et al., 2013).

3.9. Statistical analysis

The TOC, SOM and BD obtained at all of the collection sites throughout the various forests (*Rhizophora*, mixed, and *Avicennia*) found in various conditions (live, deteriorated, and dead) were compared using a one-way analysis of variance with a significance level of $p < 0.05$. Prior to this analysis, normality in the data distribution (Shapiro–Wilk test) and homogeneity of variance (Levene test) were evaluated. The differences in averages for TOC wt%, SOM wt%, and the TOC/SOM ratio were evaluated using Hochberg's GT2 post hoc test. The differences in averages for BD and C stock (Mg) were evaluated using the Games–Howell post hoc test. The TOC wt%, SOM wt%, and TOC/SOM ratio for two depths (0–20 cm and 20–40 cm) were compared with the paired *t*-test. The TOC, SOM, and BD ratios were analyzed using the Pearson *r* coefficient. An alpha level of 0.05 was used for all statistical tests. All statistical analyses were performed using SPSS version 20.

4. Results and discussion

4.1. Description of the sampling sites

The structural attributes of the mangroves, canopy height and basal area, showed differences according to the stand's physiographic position, species composition, and condition (Table 1).

The mangroves at PLM and CAN, located at the north and north-west end of the Cuare Inlet, have a higher degree of structural development, with the highest basal area values, along both the fringe, and basin stands. In the low intertidal zone dominated by *Rhizophora*, the trees with the largest diameter up to 50 cm are *Laguncularia*. In the mangrove's middle fringe zone the number of *Avicennia* stems increases, although there are more *Rhizophora* and *Laguncularia* individuals; stands displaying these characteristics are labeled as mixed mangrove forests. *Avicennia* monospecific stands are located in more inland sites, which borders land vegetation (bushland or halophytic grasslands). In general terms, the monospecific *Avicennia* forest had areas in which all of the

Table 1
General characteristics of sampled mangrove forests from Cuare Inlet and Morrocoy National Park.

Site	Physiographic mangrove type	Species ^a	Canopy height (m)	Basal area (m ² /ha)	Condition ^b	Descriptor
<i>Cuare inlet</i>						
Punta La Matica	Fringe	Rm/Lr	11	4.0723	l	Live <i>R. mangle</i>
	Fringe	Rm/Lr/Ag	10	1.7462	l	Live mixed
	Basin	Ag	5.5–8.5	2.0434	l	Live <i>A. germinans</i>
	Basin	Ag	–	–	d	Dead <i>A. germinans</i>
Caño Animas	Fringe	Rm/Lr	14	7.0321	l	Live <i>R. mangle</i>
	Basin	Ag	9	1.8756	l	Live <i>A. germinans</i>
	Basin	Ag	–	–	d	Dead <i>A. germinans</i>
Caño Pancho	Fringe	Rm/Lr	15.5	2.9132	l	Live <i>R. mangle</i>
	Basin	Ag	–	–	d	Dead <i>A. germinans</i>
Caño Boca del Zorro	Fringe	Rm/Lr	7	nd	l	Live <i>R. mangle</i>
	Fringe	Rm/Lr	8	0.7132	dt	Deteriorated <i>R. mangle</i>
	Fringe	Rm/Lr/Ag	6	nd	l	Live mixed
	Basin	Ag	6	0.6911	l	Live <i>A. germinans</i>
	Basin	Ag	–	–	d	Dead <i>A. germinans</i>
<i>Morrocoy NP</i>						
Caño de Leon	Fringe	Rm/Lr	15	3.1785	l	Live <i>R. mangle</i>
	Fringe	Rm/Lr/Ag	14	2.0166	l	Live mixed
	Basin	Ag	10	1.4052	l	Live <i>A. germinans</i>
	Basin	Ag	–	–	d	Dead <i>A. germinans</i>
	Basin	Ag	3	1.6467	r	<i>A. germinans</i> regeneration
	Saltflat-mudflat	Algal-microbial mats	–	–	–	Mudflat
Ensenada de Tucacas	Fringe	Rm/Lr	12.5	3.9859	l	Live <i>R. mangle</i>
	Fringe	Rm/Lr/Ag	10.75	1.8899	l	Live mixed
	Basin	Ag	10.5	1.2221	l	Live <i>A. germinans</i>

^a Mangrove species: Rm, *Rhizophora mangle*; Lr, *Laguncularia racemosa*; Ag, *Avicennia germinans*.

^b Condition: l, live; d, dead; dt, deteriorated; r, regeneration.

individuals were dead. At CAP and CBZ, the mangroves were characterized by having lower structural complexity, lower basal area values, and wider areas of dead and deteriorated trees. In the Cuare Inlet, the total coverage of live mangrove has been reduced by 55%, and a significant part of the current coverage shows signs of deterioration, i.e., an increase in the basal area of dead stems and a reduction in the canopy height (Barreto, 2008). In the transition zones or middle fringe zone of the mixed mangrove found at CP and CBZ, we observed the preferential mortality of adult *Rhizophora* and *Laguncularia* individuals and an increase in the number of *Avicennia* individuals, which are lower in diameter and height. For these reasons, the structural complexity of the mangrove is lower. Barreto (2008) reported an increase in salinity in both the transition areas and the monospecific mangrove forests, which could, in part, explain the floristic replacement in the transition zone. The annual average interstitial salinity measured in *Avicennia* dead zones exceeded 70‰, the maximum value established by various authors as the tolerance threshold for this species (Cintrón et al., 1978; Cardona and Botero, 1998; Imbert et al., 2000).

The sampling sites at Morrocoy National Park (CDL and ETU), located in muddy coastal plains, are influenced by a supply of freshwater from the continent. These watercourses have short trajectories and originate in micro-basins located near the coast. They are permanent, but their flow is highly variable and increases substantially during the wet season. These watercourses have been modified by human activities (Barreto, 2008).

The values for stand basal area and canopy height obtained at the Morrocoy National Park are similar to those observed at Cuare Inlet (Table 1). We also observed an expanse of dead mangrove in the innermost areas of the mangrove bordering the saltflat/mudflat area. In CDL, soil samples were collected from a saltflat/mudflat area and a patch of regenerating *Avicennia* adjacent to a significant expanse of dead *Avicennia* mangrove. Although canopy height in the regeneration zone is lower than that of mature *Avicennia* stands, basal area is similar.

4.2. Mineralogical composition

Of the 39 soil samples selected for the mineralogical study, 5 come from PLM, 3 from CAN, 1 from CAP, 16 from CBZ, and 8 from ETU. The mineralogical identification was complicated by the large quantities of organic matter present in the samples, which resulted in diffraction spectra with high background noise levels. In some cases, we were unable to completely identify the mineral phases present.

In general terms, all of the soils were characterized by the presence of quartz, and most contained kaolinite, which can be the result of the chemical meteorization of primary aluminosilicates. Illite or muscovite mica was also identified, but due to their structural similarities, it was difficult to differentiate them using the dust method. The presence of muscovite mica could only be inferred in the case of the ETU samples because of the intense shine observed during the visual analysis. Additional minerals detected include albite, microcline, montmorillonite, and goethite, the latter in two samples at CBZ and one at CDL.

Pyrite was detected in 10 samples: 3 in CBZ, 2 in CAN, 1 in CDL, 2 in ETU, and 2 in PLM. At these sampling sites we observed dead *Avicennia* (Agm), live *Avicennia* (Agv), live *Rhizophora* (Rmv), deteriorated *Rhizophora* (Rmd), and a mixed forest (Mx, Rm, Lr, Ag).

The presence of pyrite in mangrove soils is attributed to the anoxic conditions established in micro-reducing environments with low oxygen circulation. Furthermore, when a mangrove dies the ensuing increase in decomposing organic matter combined with the already low oxygen recirculation levels provide the necessary anoxic conditions for the formation of pyrite. We observed rhodochrosite (MnCO₃) in a sample collected in ETU (ETU-1). Its presence can be attributed to the anoxic sedimentation conditions in which Mn²⁺ can precipitate as a carbonate mineral (Otero et al., 2006). The development of anoxic conditions (identified by the presence of minerals such as pyrite and rhodochrosite) contributes to the preservation of soil organic matter since it inhibits its oxidation or alteration by aerobic organisms regardless of its

chemical structure. In other words alteration depends not only on structure, but also on environmental conditions (Schmidt et al., 2011; Lehmann and Kleber, 2015). The primary source of iron includes iron-rich siliciclastic minerals, which can form goethite and, once an anoxic environment has been established, subsequently be reduced to Fe^{2+} . An example of this can be found in the CDL sample (CL-3) in which both pyrite (Fe^{2+}) and goethite (Fe^{3+}) coexist in the soil of a dead *Avicennia* stand. This suggests that iron reduction is currently taking place due to the formation of anoxic environments that result from the decomposition of organic matter in the mangroves. The sulfur source is provided by the reduction of seawater sulfate (SO_4^{2-}) to sulfur (S^{2-}). The live forests where pyrite is present are located towards the edge of the creek or coastline (ETU case), and are therefore areas subject to frequent flooding or that remain flooded for longer periods. Nevertheless, although pyrite is mainly associated with areas in which the organic matter of *Avicennia* is in the process of alteration or decomposition (attributable to the establishment of anoxic environments), in other types of environments, and in the presence of other mangrove species, the processes that alter organic matter are controlled by the rate at which the latter is incorporated into the soil to later establish anoxic conditions. Anaerobic reactions, carried out by sulfate-reducing bacteria, consume all of the oxygen available in soils. Some mangrove species, by means of their roots, enhance the precipitation of pyrite and promote dominant anoxic conditions in soils (Sakho et al., 2015). This could explain the presence of pyrite in soils where Agm is not found.

A very small amount of calcite was detected in sample CDL-1, probably a lithological contribution from the Capadare limestone formation located at Cerro de Chichiriviche. In this sample IC values were lower than the detection threshold for the technique employed ($> 0.5\%$).

4.3. Soil TOC and SOM

Mangroves have high rates of sedimentation and production of aerial and underground biomass that promote the accumulation of organic compounds in soils (Chen and Twilley, 1999; Middleton and McKee, 2001) and generate large quantities of organic matter (Marchand et al., 2003; Donato et al., 2011; Adame et al., 2013). In the sites studied, the average TOC (wt%) for the topsoil samples (0–20 cm) collected in stands that differ in species composition and condition was 14.55 ± 0.71 wt% ($n = 60$), with variations between 0.5 and 26 wt%. Inorganic carbon was < 1.3 wt% and was only detected in eight of the 61 samples analyzed.

Regardless of the mangrove's condition, the mixed mangrove and *Rhizophora* soils had higher TOC contents than *Avicennia* soils (Table 2, $F_{4,53} = 8.125$, $p < 0.0001$). Average TOC content was significantly lower in dead *Avicennia* stands than in mixed ($p = 0.035$), live *Rhizophora* ($p = 0.006$), and deteriorated *Rhizophora* ($p < 0.0001$) stands. TOC was also lower in live *Avicennia* forests

than in live and deteriorated *Rhizophora* forests ($p = 0.061$; $p = 0.001$, respectively). These differences were significant in the case of deteriorated *Rhizophora* stands.

In general, the TOC (wt%) of topsoil samples is similar to the findings of Kauffman et al. (2014) and Adame et al. (2015) in mangroves in the Dominican Republic and the Mexican Pacific coast, respectively. Nevertheless, it is lower than the surface soil TOC (wt%) of mangroves dominated by *Rhizophora* along Mexico's Caribbean coast (Adame et al., 2013).

Average SOM was 0.75 ± 0.04 wt%, with a range between 0.01 and 1.76 wt%. There are no statistical differences for the various types of mangroves and conditions (Table 2, $F_{4,52} = 2.233$, $p = 0.078$). The TOC/SOM ratio was lower in *Avicennia* mangroves ($F_{4,53} = 5.810$, $p = 0.001$). These differences were more statistically significant for live *Rhizophora* than for live *Avicennia* ($p = 0.013$) and dead *Avicennia* ($p = 0.002$). Mixed stands also had a higher TOC/SOM ratio than dead *Avicennia* stands ($p = 0.030$).

The lower TOC content present in dead *Avicennia* stands is the result of the decomposition of the underground biomass and the lack of new root biomass production. In contrast, the higher relative content of SOM wt% could be attributable to the contribution of dead aerial biomass, such as detritus from tree trunks, a recalcitrant material with very low decomposition rates (Robertson and Daniel, 1989). This supply of organic matter may contribute to the accumulation of recalcitrant compounds in dead mangroves, which are located in visibly lower-lying areas caused by the erosion of the topsoil once the vegetation dies.

In mangrove soils with high relative concentrations of lipids, leaf detritus is the main source of organic matter, whereas soils whose main source are branches, trunks and roots have lower lipid content (Hernes et al., 2001; Kristensen et al., 2008; Vane et al., 2013). In mangroves studied in Puerto Rico, the average lipid content of *Rhizophora*, *Laguncularia*, and *Avicennia* leaf material was 26% (Vane et al., 2013). The lipid content of leaves and pneumatophores of different mangrove species was higher than the lipid content of stalks (Vane et al., 2013) and roots (Oku et al., 2003).

Soils samples were collected in CAN, CBZ, and CDL at two depths (0–20 cm and 20–40 cm). The results indicate that TOC content varies according to depth and stand condition. In live *Rhizophora*, mixed, and monospecific *Avicennia* mangroves TOC increased significantly with depth (18 ± 1 vs 20 ± 1 , paired t -test, $t = -5.454$, $p = 0.003$, $n = 6$). Conversely, in dead stands TOC content decreased with depth (14.7 ± 4 and 10 ± 2 wt%, 0–20 cm and 20–40 cm, respectively). However, these differences were not statistically significant (paired t -test, $t = 2.335$, $p = 0.145$, $n = 3$).

Regardless of stand condition, the TOC/SOM ratio was lower at a depth of 20–40 cm (paired t -test, $t = 3.044$, $p = 0.008$, $n = 9$), which suggests a preferential accumulation of organic recalcitrant compounds at higher depths.

Silts and clays are mineral particles effective in sequestering organic carbon in soils. In referring to temperate forests, Lorenz

Table 2
Total organic carbon (TOC wt%), soluble organic matter (SOM wt%) and TOC/SOM ratios in mangrove soils of *Rhizophora*, mixed, and *Avicennia* of live, deteriorated and dead stands from Cuare Inlet and Morrocoy National Park. The mean and standard error of the mean is shown.

Forest type	Condition	TOC (wt%)	SOM (wt%)	TOC/SOM	N
<i>Rhizophora</i>	Live	17 ± 1 ab	0.66 ± 0.06 a	25 ± 2 a	16
<i>Rhizophora</i>	Deteriorated	20 ± 1 a	1.0 ± 0.2 a	22 ± 2 abc	8
Mixed	Live	16 ± 2 ab	0.7 ± 0.2 a	24 ± 2 ab	9
<i>Avicennia</i>	Live	12 ± 1 bc	0.75 ± 0.07 a	17 ± 2 bc	13
<i>Avicennia</i>	Dead	10 ± 1 c	0.70 ± 0.08 a	16 ± 1 c	12
<i>Avicennia</i> regeneration	Live	0.9 ± 0.4	0.03 ± 0.08	31 ± 8	2
Muddy plain/salt flat	– ^a	0.91 ± 0.04	ND	–	2

N: number of samples; ND: not detected.

Mean values in a column within a treatment type followed by the different letters are significantly different at $p \leq 0.05$ using Hochberg's GT2.

Data from *Avicennia* regeneration and muddy plain were not included in the ANOVA test.

^a Presence of algal and microbial mats.

et al. (2011) emphasized the importance of the physical and chemical stabilization of organic carbon and the role of mineral particles. The authors reported that the amount of organic carbon associated with minerals (mostly lipids and root lignin) increased with depth. TOC had a positive linear correlation with SOM (Fig. 2), which was significant for *Rhizophora* ($n = 23$, $R^2 = 0.451$, $p < 0.0001$) and *Avicennia* ($n = 27$, $R^2 = 0.506$, $p < 0.0001$) soils, regardless of stand condition. The TOC/SOM ratio varies according to the type of vegetation studied. Martens et al. (2003) reported significant positive correlations of these two parameters in forest and meadow soils, but they observed no correlation in cultivated soils. They attributed these differences to the negative effect farming has on the quantity and composition of microbial flora present in soils, as most of the fatty acids quantified come from microorganisms.

Organic matter stabilization mechanisms can explain the higher SOM content in *Avicennia* soils, especially in dead stands (Kleber and Johnson, 2010; Schrupf et al., 2013). This is likely due by the differential decomposition of the more labile compounds, at higher rates (Koch et al., 2005), and by the preservation of recalcitrant compounds in *Avicennia* soils, in which silts and clays dominate the mineral fraction (Kleber and Johnson, 2010; Schrupf et al., 2013). In *Rhizophora* and mixed stand soils, on the other hand, textures range from clay loams to sandy loams.

4.4. Soil bulk density and stock of carbon

Determining soil BD is essential in extrapolating carbon concentration expressed in wt% to carbon storage per surface or in the soil profile (Johnston et al., 2004). BD was higher in the dead *Avicennia* stands and at the site with regenerating *Avicennia* ($F_{5,12} = 21.824$, $p < 0.0001$, Table 3), and was inversely proportional to TOC ($n = 27$, $R^2 = 0.794$, p -value < 0.0001 , Fig. 3). The BD of topsoil samples tends to increase as we move from the outer fringe bordering the coastline to the inner part where basin mangroves dominated by *Avicennia*. The BD of topsoil samples (0–20 cm) lies within the range of values reported for mangroves throughout the Caribbean region (Adame et al., 2013; Kauffman et al., 2014).

In dead *Avicennia* stands, the subsidence caused by root decomposition, the absence of radical growth, and the collapse of aerenchymatous tissue due to the consolidation of aerial spaces

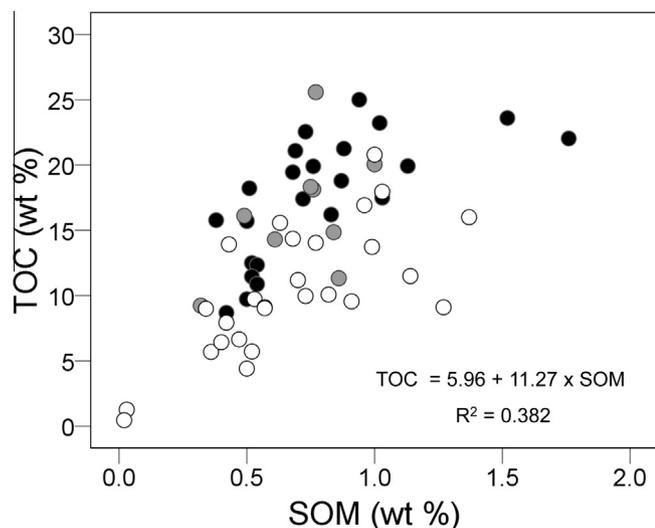


Fig. 2. Relationship between TOC and SOM with mangrove forest composition and conditions. *Rhizophora* live and deteriorated (black), mixed forest (gray) and *Avicennia* live and dead forest (open symbols). *Rhizophora* ($\text{TOC} = 11.266 \times \text{SOM} + 5.963$; $R^2 = 0.451$; $p < 0.0001$; $n = 23$). *Avicennia* ($\text{TOC} = 10.363 \times \text{SOM} + 3.404$; $R^2 = 0.506$; $p < 0.0001$; $n = 27$). Mixed ($p = 0.187$ (n.s.)).

Table 3

Stock of TOC (Mg/ha) and bulk density (g/cm^3) in surface mangrove soils of different types of mangrove vegetation from Cuare Inlet and Morrocoy National Park. The mean and standard error of the mean is shown.

Forest type	Condition	BD (g/cm^3)	N_{BD}	TOC (Mg/ha)	N_{TOC}
<i>Rhizophora</i>	Live	0.23 ± 0.01 a	22	37 ± 2 bc	14
<i>Rhizophora</i>	Deteriorated	0.22 ± 0.01 a	3	44 ± 3 ab	6
Mixed	Live	0.26 ± 0.02 a	7	34 ± 3 bc	8
<i>Avicennia</i>	Live	0.26 ± 0.01 a	21	31 ± 2 c	12
<i>Avicennia</i>	Dead	0.39 ± 0.03 b	16	38 ± 6 bc	9
<i>Avicennia</i> regeneration	Live	0.91 ± 0.07 c	3	8 ± 4 bcd	2
Muddy plain/salt flat	– ^a	$1.29 \pm$	1	15 ± 4 d	3

Mean values in a column within a treatment type followed by the different letters are significantly different at $p \leq 0.05$ using Games–Howell test.

^a Presence of algal and microbial mats.

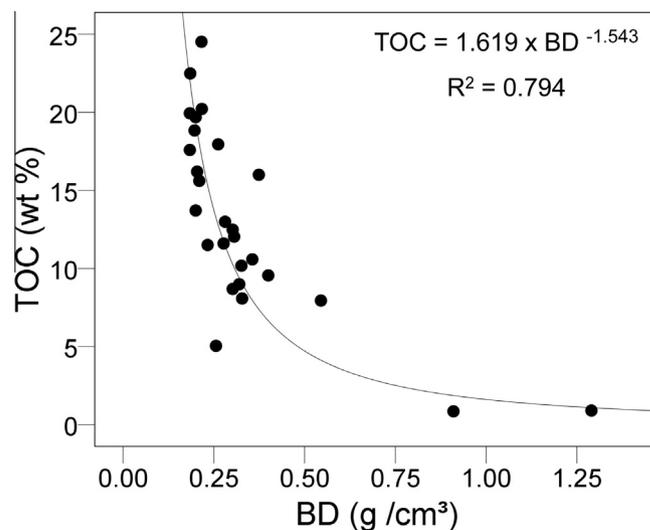


Fig. 3. Relationship between TOC and bulk density (BD) for the different mangrove forest composition and conditions.

(Lang'at et al., 2014) result in the compaction of sediments, as shown by the increase of BD in the sites with dead mangroves.

The TOC of *Rhizophora* soils collected in ETU was markedly lower than the TOC found in the rest of the *Rhizophora* stands (average TOC t 10.9 ± 0.61 vs 20.1 ± 0.70). BD in ETU was higher than in other sites (average 0.31 ± 0.02 vs 0.194 ± 0.006 g/cm^3) and similar to the BD calculated for live *Avicennia* stands (Table 3). These differences can be explained by the texture of the soil in which the sand fraction is larger than at other sites where the mineral fraction is dominated by silts and clays.

For the different types of forests and conditions, the average content of organic carbon in the first 10 cm of soil was $35 \text{ Mg} \pm 1$, and varied between 11.30 and 59.84 Mg. Statistically significant differences were observed in the groups ($F_{6,10} = 17.603$, $p < 0.0001$). The lowest carbon content was found in the regenerating *Avicennia* stand in the mud plain (Table 3).

In general terms, TOC (wt%) and TOC content (Mg) decrease from the low intertidal zone dominated by *Rhizophora*, followed by mixed stands towards the middle zone, to the inner *Avicennia* forest that has shorter individuals and higher soil salinity.

Differences in TOC could be associated with the structural complexity of the mangrove stand and the composition and location of the intertidal zone (Adame et al., 2013, 2015; Kauffman et al., 2014; Rahman et al., 2015). The mangroves studied show a differential species distribution pattern and a reduction in structural complexity from the low intertidal zone towards the land. This is associated with differences in soil conditions such as texture, BD, and salinity. Interstitial salinity measured in *Rhizophora* areas

varies from 25‰ to 59‰, and in live *Avicennia* from 47‰ to 85‰. The highest values were observed in dead *Avicennia* (70–99‰). Carbon stock values (Mg) of the topsoil samples collected for this study are comparable to those reported by Kauffman et al. (2011, 2014) in Micronesia and the Dominican Republic. However, they are lower than those estimated for mangroves dominated by *R. mangle* on the Mexican Caribbean coast (Adame et al., 2013).

Aside from vegetation characteristics, other factors such as climate and clay type and content have been associated with soil TOC (Jobbágy and Jackson, 2000). Precipitation and temperature were the best predictors for soil TOC in the first 20 cm, but in the deeper layers the best predictor was clay content (Jobbágy and Jackson, 2000). This is possibly due to the higher content of slower recycling organic carbon at greater depths (Paul et al., 1997; Trumbore, 2000), associated with clay and non-crystalline minerals, which protect and stabilize organic matter (Paul, 1984; Torn et al., 1997). Most of the soil's organic carbon was stored in the clay and fine silt fractions and was made up of partially decomposed plant matter dominated by alkanes and fatty acids (Höfle et al., 2013).

In conclusion, according to our results, as well as the findings of other authors, the higher TOC content observed at greater depths and the lower TOC/SOM ratio are attributable to: (a) the association of TOC with clays and non-crystalline minerals (Paul et al., 1997; Jobbágy and Jackson, 2000; Trumbore, 2000); (b) the leaching processes of soluble compounds of the OM; (c) a higher proportion of recalcitrant compounds (Paul et al., 1997; Trumbore, 2000); (d) a lower decomposition rate for recalcitrant compounds (Lorenz et al., 2007); and (e) physicochemical conditions that limit biological activity, like high salinity, soil anoxia, and hypoxia (Trumbore, 2000).

The differential accumulation of refractory matter and the roots growth that determine the formation of organic soils in mangroves (Chen and Twilley, 1999; Middleton and McKee, 2001) are key for the stability and survival of the system vis-à-vis rising sea levels (Cahoon and Lynch, 1997; Cahoon et al., 2003).

4.5. Fourier Transform Infrared Spectroscopy (FTIR)

The main functional groups identified in the SOM (Table 4) are the OH group of alcohols and phenols, the aliphatic CH₃ and CH₂ group, the N–H group of amines or amides, and the carbonyl (C=O) group of carboxylic acids or ketones. The OH group of alcohols and phenols (3450–3340 cm⁻¹) and the CH₂ and CH₃

(2930–2840 cm⁻¹) group were observed in all of the samples with strong, medium and weak absorption intensities. Other functional groups (observed only in some samples) were detected around 1600–1580 cm⁻¹ and can be assigned to C–C stretching vibrations of aromatics or N–H bending vibrations of primary amines. The bands occurring at 910–900 cm⁻¹, 820–760 cm⁻¹ and 670–660 cm⁻¹ can be assigned to C–H out-of-plane bending vibrations of alkenes, which occur at 1000–650 cm⁻¹. A detailed analysis of the data (Fig. 4) allows us to divide the spectra into three groups based on the presence of main functional groups and intensity:

Group I (Fig. 4A): Spectra that have bands of –OH stretching vibrations (alcohol or phenol) with strong intensities, and bands of C–H stretching vibrations of aliphatic groups (–CH₃, –CH₂–) with weak to medium intensities. Another important characteristic of these spectra is that the functional group corresponding to the N–H bending group of amides (RCONH₂) and amines is always present in the form of a narrow band with medium intensity. This intensity is stronger than the one observed in the spectra dominated by the CH₃ and CH₂ aliphatic groups. Additionally, a broad O–H out-of-plane bending band with medium intensity was identified at around 730–710 cm⁻¹.

Group II (Fig. 4B): Spectra with strong absorption frequencies for the C–H stretching vibrations of aliphatic groups (–CH₃, –CH₂–) and –OH stretching vibration bands associated with alcohols and phenols have a weak intensity. The absorption band for the carbonyl groups was not detected in the group I samples. Nevertheless, as with group I, the signals corresponding to the N–H bending of amides and amines are present, albeit in the form of weak and narrow bands. We also observed an absorption band in the 730–710 cm⁻¹ region, associated with rocking vibrations of CH₂ (ρCH₂), which in group I were associated with the O–H vibration of alcohols and phenols due to its strong and broad band. In this group we also detected bands attributed to C–C stretching vibrations of aromatics, N–H rocking vibrations of primary amines (1600–1580 cm⁻¹), C–O stretching vibrations of alcohols and phenols (1170–1150 cm⁻¹), C–O stretching vibrations of phenols (1030 cm⁻¹), and C–H out-of-plane stretching vibrations of alkenes (820–760 cm⁻¹ and 670–660 cm⁻¹).

Group III (Fig. 4C): Spectra whose absorption bands are attributed to aliphatic groups (–CH₃, –CH₂–) and have a strong to medium absorption intensity, and –OH stretching vibration bands associated with alcohols and phenols with medium intensity. Additionally, C=O stretching of carboxylic acids or ketones is

Table 4
Absorption frequencies and assignment of functional groups by FTIR for the SOM in soils of mangroves.

Frequency (cm ⁻¹)	Assignment
3450–3340	O–H stretching vibrations in alcohols, phenols. N–H stretching
2930–2840	Aliphatic C–H stretching, methyl (–CH ₃) and methylenic (–CH ₂ –) groups
1720–1700	C=O stretching vibrations of carboxylic acids and ketones
1660–1630	C=O absorption of amides: stretching vibration (amide I band). Quinone and/or C=O of H-bonded conjugated ketones
1650–1620	NH bending vibration (amide II band)
1600–1580	C–C ring stretch within the aromatic ring. N–H bending vibrations in amines
1515	N–H bending band in secondary aromatic amines. C–C ring stretch within the aromatic ring
1475–1450	C–H symmetrical bending vibrations in aliphatic CH ₃ . scissoring bending C–H in aliphatic CH ₂
1383–1377	C–H symmetrical bending vibration in aliphatic CH ₃
1280–1260	C–O stretching vibration (esters, ethers or carboxylic acids). C–N stretching in amines
1170–1150	C–O stretching vibration in esters, ethers or phenols
1030	C–O stretching vibration in alcohols or phenols
910–900	C–H bending vibrations out-of-plane in alkenes absorb between 1000 and 650 cm ⁻¹ . so these frequencies absorptions may be related to the presence of alkenes
820–760	
670–660	
730–710	C–H bending vibration (CH ₂ rocking). out-of-plane O–H bending vibration in alcohol or phenols

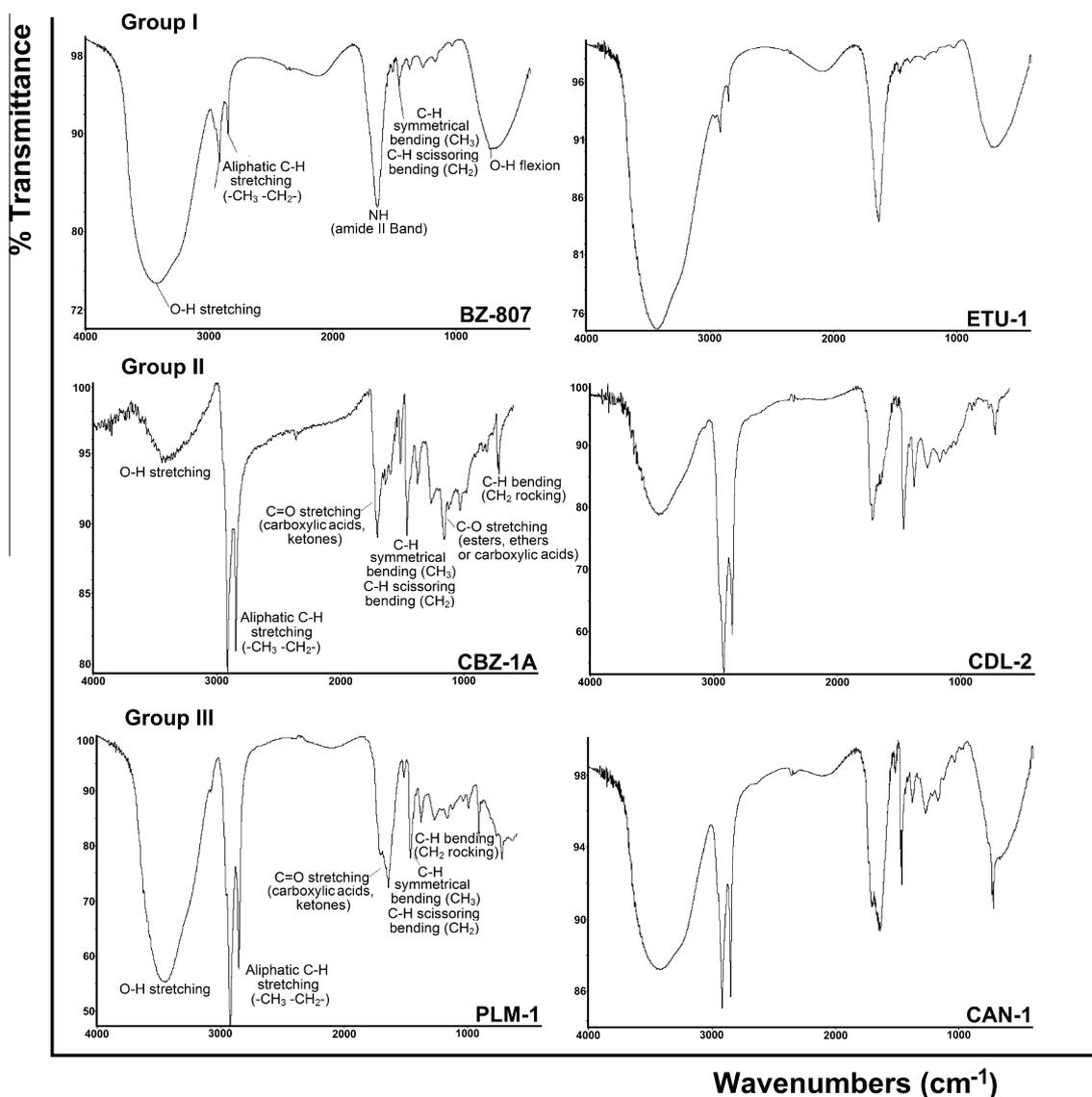


Fig. 4. FTIR spectra of selected samples from groups I, II and III based on functional groups detected.

present, as well as N–H bending signals of amides and amines, both with similar intensities.

In the three spectra groups, the functional groups detected are amides, amines, carbonyl-containing compounds, and alcohols which suggest that the SOM extracted from the soils is aliphatic in nature. Additionally, we detected aromatic functional groups and –OH from phenolic groups. These functional groups are related to compounds found in the biomass, such as proteins (amino acids), carbohydrates, *n*-alkanes, *n*-alcohols, ketones *n*-fatty acids, lignin, and tannins, among others. This suggests the presence of organic compounds differing in origin and susceptibility to the biodegradation in the soils analyzed, and whose preservation depends on the environment's physicochemical conditions (Schmidt et al., 2011; Lehmann and Kleber, 2015). The SOM contained in mangrove soils comes from sources such as leaf litter and subterranean roots, but also allochthonous sources, such as those associated with river and marine inputs (Kristensen et al., 2008). Because the organic matter found in mangrove soils has such diverse origins, its chemical composition corresponds to different functional groups. Studies on the chemical composition of leaf litter have identified compounds such as carbohydrates, amino acids, phenol-derived lignin, tannins, fatty acids, triterpenoids, and *n*-alkanes. Some of these compounds are used as potential tracers in the identification of

organic matter derived from leaf litter, as well as in its preservation during the diagenesis processes (Hernes et al., 2001; Kristensen et al., 2008; Koch et al., 2011). In addition, according to Giovanela et al. (2004), the influences of the marine environment are reflected in the FTIR, as demonstrated by the presence of functional groups with nitrogen, mainly amides. Zhang et al. (2011), report that the increased presence of phenolic groups is attributable to the autochthonous contribution of OM to the mangroves.

Despite the differences we observed, which allowed us to classify the spectra into three groups according to the presence and intensity of functional groups, we were unable to establish a direct relationship between sampling sites, as all three groups were observed in the soil samples collected throughout the six areas of study (PLM, CAN, CAP, CBZ, CDL, and ETU) mangrove species, or condition (live, deteriorated, or dead). Nevertheless, these differences reflect the dynamics of mangrove systems regarding OM input and its possible origins: the decomposition of OM characteristic of mangrove ecosystems, the terrestrial input supplied by the runoff of river systems, and the marine environment. The three groups identified by FTIR reflect differences in the degree of preservation of the organic matter, which can be due to physicochemical and biological conditions of the environment (Schmidt et al., 2011).

5. Conclusions

The presence of pyrite indicates anoxic conditions in the mangrove soils studied. Goethite was also observed in some instances, which reflects the process of Fe reduction and the development of anoxic conditions in these soils. The relationship between conditions and type of mangrove forest with TOC suggest differences in carbon transformation processes based on stand composition (*Rhizophora* vs *Avicennia*) and TOC (wt%) content. However, no significant differences were observed between carbon stock and mangrove composition or condition. Consequently, regardless of the dominant species, the different types of mangrove forests have comparable values as surface carbon sinks.

Regardless of the condition and depth of soil sample, the TOC/SOM ratio was lower for *Avicennia* forests. Future investigations could shed more light on these differences between mangrove forests. The higher TOC content observed at greater depths and the lower TOC/SOM ratio are attributable to: (a) the association of TOC with clays and non-crystalline minerals; (b) the leaching processes of soluble compounds of the OM; (c) a higher proportion of recalcitrant compounds; (d) a lower decomposition rate for recalcitrant or non-recalcitrant compounds; and (e) physicochemical conditions that limit biological activity, such as high salinity, soil anoxia and hypoxia.

With the SOM FTIR analysis we were able to identify three groups based on the presence and intensity of the signal corresponding to the functional groups. Those three groups could not be related to the sampling sites, the mangrove species present (*Rhizophora* and *Avicennia*), or its condition (live, deteriorated or dead). These differences, however, must be related to the organic matter supplied by the mangroves and other sources, as well as to its degree of preservation. A more detailed study of the saturated hydrocarbon fraction of the SOM is required in order to identify terpenoids or sterols that can be related to the mangrove or to other sources of marine or land organic matter.

In order to preserve mangrove carbon sequestration and storage potential it is important to prevent their conversion and minimize degradation rates. However, the lack of information regarding basic aspects such as their current status or conditions, soil properties (such as carbon content and organic matter composition throughout the soil profile), and threats to their environment in the context of climate change hinder efforts to manage these soils as potential carbon sinks.

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