

# Wetlands Ecology and Management

## Stabilization of carbon in mineral soils from mangroves of the Sinú river delta, Colombia --Manuscript Draft--

<b>Manuscript Number:</b>	WETL-D-17-00119R2	
<b>Full Title:</b>	Stabilization of carbon in mineral soils from mangroves of the Sinú river delta, Colombia	
<b>Article Type:</b>	Original Research	
<b>Section/Category:</b>	Biogeochemistry	
<b>Keywords:</b>	soil organic carbon; stable isotopes; iron and aluminum oxides; soil mineralogy; estuarine ecosystems	
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<b>Funding Information:</b>	Alexander von Humboldt-Stiftung (KOL 1157857 IKS-2)	Ms. Jhoanata Bolivar
<b>Abstract:</b>	<p>Mangrove forests of the Sinú river delta in Cispatá bay, Colombia, show large differences in soil carbon storage between fringe (oceanic) and basin (estuarine) mangroves. We were interested in testing whether these differences in soil carbon are associated with sediment transport processes or whether most of the carbon is produced in situ within the mangrove system. Given past sedimentation dynamics of the Sinú river, we hypothesized that a large portion of soil carbon in basin mangroves is due to sedimentation.</p> <p>We determined total organic carbon content (TOC) as <math>660.93 \pm 259.18 \text{ MgC ha}^{-1}</math> for basin soils up to a sampling depth of 1 m, and as <math>259 \pm 42.61 \text{ MgC ha}^{-1}</math> for fringe soils up to 80 cm depth (maximum soil depth for fringe soils). Using analyses of mineralogy (Al- and Fe-oxides, clay minerals) as well as isotopic analyses of carbon (<math>\delta^{13}\text{C}</math>), the origin of the sediments and their carbon was determined. We found that basin soils in Cispatá bay show similar mineralogical composition than those of fluvial sediments, but the carbon concentration of river sediments was close to zero.</p> <p>Given the large capacity of the Fe and Al oxides in clay minerals to store dissolved carbon, and that the isotopic composition of the carbon is mostly of plant origin, we concluded contrary to our initial hypothesis that the carbon stored in basin mangrove soils are produced in situ. The deposited fluvial sediments do play an important role for carbon storage, but mostly in providing binding surfaces for the stabilization of organic carbon.</p>	
<b>Response to Reviewers:</b>	Answers to reviewer comments are provided in a separate file attached with this submission.	

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<b>Wetlands Ecology and Management manuscript No.</b> (will be inserted by the editor)
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# Stabilization of carbon in mineral soils from mangroves of the Sinú river delta, Colombia

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Received: date / Accepted: date

**Abstract** Mangrove forests of the Sinú river delta in Cispatá bay, Colombia, show large differences in soil carbon storage between fringe (oceanic) and basin (estuarine) mangroves. We were interested in testing whether these differences in soil carbon are associated with sediment transport processes or whether most of the carbon is produced in situ within the mangrove system. Given past sedimentation dynamics of the Sinú river, we hypothesized that a large portion of soil carbon in basin mangroves is due to sedimentation. We determined total organic carbon content (TOC) as  $660.93 \pm 259.18 \text{ MgC ha}^{-1}$  for basin soils up to a sampling depth of 1 m, and as  $259 \pm 42.61 \text{ MgC ha}^{-1}$  for

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fringe soils up to 80 cm depth (maximum soil depth for fringe soils). Using analyses of mineralogy (Al- and Fe-oxides, clay minerals) as well as isotopic analyses of carbon ( $\delta^{13}\text{C}$ ), the origin of the sediments and their carbon was determined. We found that basin soils in Cispatá bay show similar mineralogical composition than those of fluvial sediments, but the carbon concentration of river sediments was close to zero. Given the large capacity of the Fe and Al oxides in clay minerals to store dissolved carbon, and that the isotopic composition of the carbon is mostly of plant origin, we concluded contrary to our initial hypothesis that the carbon stored in basin mangrove soils are produced in situ. The deposited fluvial sediments do play an important role for carbon storage, but mostly in providing binding surfaces for the stabilization of organic carbon.

**Keywords** soil organic carbon · stable isotopes · iron and aluminum oxides · soil mineralogy · estuarine ecosystems

## 1 Introduction

Although mangroves are ecosystems with some of the largest levels of carbon storage on earth (Donato et al, 2011; Alongi, 2012), there are large variations on the amount of C stored in various systems, particularly soils. For instance, mangrove ecosystems dominated by *Rhizophora* spp. in Peninsular Malaysia store between 479 to 2205 Mg C ha<sup>-1</sup> in the belowground and soil pool (Alongi, 2012), and similar levels of variability have been observed at other sites (Jardine and Siikamäki, 2014). It is unclear however, what are the

main determinants of observed differences in soil C storage across diverse mangrove systems. It is possible that differences in soil carbon storage are due to differences in the level of productivity of different mangrove systems, or due to other external sources such as sediment transport.

This large degree of spatial variability in soil carbon storage is also well expressed in the mangrove forests of Cispatá bay, Colombia. These mangroves consist of two main forest types: basin and fringe systems, which show large differences in terms of soil carbon stocks between them. A previous study (Bolívar, 2015) showed that for basin mangroves the total organic carbon storage (TOC) is around  $740 \pm 40 \text{ Mg C ha}^{-1}$ , while for the fringe mangroves this value is only  $95 \pm 9 \text{ Mg C ha}^{-1}$ . These numbers, particularly for the basin mangroves, are in the upper range of values observed for other systems (Donato et al, 2011; Alongi, 2012; Jardine and Siikamäki, 2014).

It is unknown whether the high levels of soil carbon in Cispatá bay are due to the intrinsically high levels of productivity of these systems or whether this soil carbon has an external source such as transport of fluvial or marine sediments. Given that mangrove productivity is high and decomposition in water saturated soils is slow, carbon stored in these systems may not have any external origin (Lacerda et al, 1995). However, it is also possible that sediments in the delta region may have been deposited by the Sinú river given that before 1938 it discharged in the current mangrove area (Serrano, 2004), in which case the carbon stored in these sediments may have its origins in

soils from the northern Andean mountains. Alternatively, the carbon in these sediments may have been transported by marine tides over the Caribbean.

Different techniques have been used in the past to determine different sources of organic carbon in water saturated ecosystems. For instance, the  $\delta^{13}\text{C}$  isotope has been used to explore different sources of carbon by source partitioning analyses (Bouillon et al, 2008; Spohn and Giani, 2012; Spohn et al, 2013). Also, measurements of the mineralogical composition of the sediments can also give some clues on whether the minerals present in an area are from terrestrial or marine origin.

Here, our main objective was to determine the origin of the relatively high carbon levels in these soils using elemental and isotopic analyses of carbon as well as analyses of the soils' mineralogy in concert with Al- and Fe-oxide measurements. In particular, we expect that: 1) the isotopic composition ( $\delta^{13}\text{C}$ ) of soil carbon provides information on whether riverine sediments are a main source of C in Cisipatá bay, Colombia; and 2) the mineralogical composition of the sediments provides additional information on the origin of the soil carbon and the potential that it is mostly stabilized on the surface of Fe- and Al-oxides. Our main hypothesis is that soils in the basin mangroves are composed mainly by sediments transported by the Sinú river and deposited in the delta region, therefore explaining the relatively large values of TOC stored in these soils.

## 2 Materials and methods

### 2.1 Study site

The study site is located on the northwestern Caribbean coast in Colombia (9°23'N 75°52'W), which is part of the southern extreme of Morrosquillo gulf and it is locally known as Cispatá bay (Fig. 1). The coastal zone is characterized by the Sinú river delta and a complex estuarine lagoon system that covers approximately 5,098 ha. Extensive wetlands and mangroves dominate this area. The Sinú river has its origin in the northern part of the western Andean mountains, and between 1938 and 1945 changed its course creating a new delta (Serrano, 2004). The current estuarine mangrove system was established in the previous river delta. Fringe forests are dominated by *Rhizophora mangle*, basin forests are dominated by *Avicennia germinans*. *Laguncularia racemosa* occurs in both forest types.

### 2.2 Field sampling

Our sampling focused on a set of existing plots previously established to determine the carbon sequestration potential of the mangroves of Cispatá bay (Bolívar, 2015). We sampled 10 plots of 500 m<sup>2</sup> up to 1 m in depth from March 12 to 13, 2016, using a soil corer of 7 cm in diameter (Eijkelpkamp bi-partite gouge auger 04.03, Giesbeek, The Netherlands). We selected five randomly chosen points within each plot to extract soil cores at five fringe mangrove sites (plots P21, R1, R4, R5, R6) and at 5 basin mangrove sites (plots P16,

C1, C2, C3, C4). In addition to the 10 plots sampled across the mangrove area, 3 nearby sand cores at Nisperal coast were collected, and also 3 riverbed cores of the Sinú river near the city of Montería, which is located 70 km south from Cispatá bay (Fig. 1). These river and beach sediment samples were used as end-members in our isotopic analysis. Generally, cores without layer changes were divided into sections every 20 cm to explore differences in carbon concentration with depth. We divided conspicuous layer changes at the boundary, except for the sand and river sediment samples that were analyzed as one single sample for mineralogical and elemental composition.

Additionally, we selected one fringe and one basin mangrove plot (P21 and C4) to measure bulk density. At each site, a soil pit was dug three meters away from one of the corners of the plot and samples were collected using sampling rings with a volume of 98.52 cm<sup>3</sup>. We collected four depth levels at plot P21 (0-20, 20-40, 40-60, 60-80 cm) and five depth levels (+ 80-100 cm) at plot C4. Sampling for bulk density was replicated three times for each depth level. In total, we obtained 60 soil samples out of the mangrove area, 6 end-member samples, and 27 samples for bulk density measurements.

### 2.3 Laboratory analyses

After collection, samples were oven-dried at 70°C for 5 days. Samples for bulk density measurements were oven dried at 105°C. We calculated soil bulk density as dry mass divided by fresh volume ( $V = 98.52 \text{ cm}^3$ ). Each sample

was ground for 3 min at a frequency of 25 Hz using a ball mill (Retsch MM 400, Haan, Germany).

We conducted elemental analyses of percent carbon (%TC) and nitrogen (%TN) in all samples by dry combustion (Vario Max, Elementar Analysensysteme GmbH, Hanau, Germany). Organic carbon was later removed by ignition at 450°C for 16 hours, and inorganic carbon (%IC) was then determined using the same elemental analyzer. Organic carbon concentrations were estimated by subtracting %IC from %TC. TOC contents ( $\text{Mg ha}^{-1}$ ) were calculated using the obtained bulk densities for basin and fringe mangrove soils multiplied by each plot depth interval (cm) and %OC.

We used  $\delta^{13}\text{C}$  values of the sampled material and compared them with the  $^{13}\text{C}/^{12}\text{C}$  ratio of the two chosen end-members as indicators for the origin of the carbon (Fry, 2006). We measured  $^{13}\text{C}$  of all samples using a Finnigan MAT IRMS coupled with an EA 1100 elemental analyzer. Ali-j3 (Acetanilide-Jena3) and Caf-j3 (a caffeine sample from a ‘Traube synthesis’ in large supply) were chosen as internal working standards (Werner and Brand, 2001). All elemental and isotopic analyses were conducted at the Max Planck Institute for Biogeochemistry in Jena, Germany.

We conducted X-ray diffraction (XRD) measurements for qualitative and quantitative phase analyses (Spieß et al, 2009) on 12 representative samples including 4 end-member samples, and 4 samples of basin and fringe mangroves each. Samples were measured 20 min each, from 5 to 60 °2 $\theta$ . We determined each mineral phase using the powder diffraction file (PDF) data. We also



conducted a Rietveld refinement analysis using the Topas software (Bruker Corporation). To define the type of clays included in the samples, we further measured each sample before extracting clay fraction from 3 to 70 °2 $\theta$  using ceramic panels. XRD analyses were conducted at the laboratory for Mineralogy and Geochemistry of the Friedrich-Schiller University in Jena, Germany.

We determined iron and aluminum in acid-ammonium-oxalate extracts (pH 3.0) and in sodium-citrate-dithionite extracts (pH 7.3) (Schwertmann, 1964; Holmgren, 1967). We selected 46 samples and 2 standard soils for these measurements. While sodium dithionite was used to extract both crystalline and amorphous oxides, the oxalate method extracted only amorphous oxides. The actual measurement of crystalline and amorphous iron and aluminium oxides was performed using an atomic emission spectrometer with inductive coupled plasma (ICP-AES, Optima 3300DV, PerkinElmer, Norwalk, USA). These analyses were performed at the SpecLab of the Max Planck Institute for Biogeochemistry.

## 2.4 Data analysis

We performed statistical tests to determine differences in organic carbon concentrations, total organic carbon,  $\delta^{13}\text{C}$ , and Fe- and Al-oxides, among the fringe and basin mangroves. After an initial test for normality (Shapiro-Wilk test), we found little evidence to support the normality assumption required in common tools such as ANOVA or t-tests. We therefore, performed the non-parametric Mann-Whitney U test, which is equivalent to the two-sample

Wilcoxon test (Hollander et al, 2015) under the null hypothesis that the samples from the fringe and basin mangroves differ by a shift location  $\mu = 0$ , and the alternative hypothesis that they are different by some other shift location. In other words, the test helps to determine whether the samples from the two different mangrove types belong to the same statistical distribution as stated in the null hypothesis. Data and code to reproduce all results presented here can be obtained from the following repository <https://github.com/crlsierra/mangroveCstabilization.git>.

### 3 Results

We found important differences between fringe and basin mangroves in terms of %OC ( $p$ -value  $< 0.001$ ; two-sample Wilcoxon  $W$ -test,  $W = 62$ ) and %TN ( $p$ -value  $< 0.001$ ,  $W = 102$ ) (Fig. 2). In general, %OC and %TN decreased with soil depth and were highly correlated among each other (96% correlation).

Both end-members, sampled at the Sinú river in Montería and at Nisperal beach, show %OC and %TN concentrations close to zero, which indicates that they include almost no organic matter. In contrast, sand plots displayed the highest %IC concentration of around 10% (Fig. 2). The lack of organic carbon in the fluvial sediments is evidence against our initial hypothesis of carbon imports to the mangrove system through sedimentation.

We obtained much higher bulk densities for basin than for fringe mangrove soil samples. Average  $\pm$  standard deviation of bulk density for fringe mangrove soils was  $0.15 \pm 0.02 \text{ g cm}^{-3}$ , while for basin mangrove soils it was  $1.07 \pm 0.12$

g cm<sup>-3</sup> (Table 1). These values confirm previous results on the same area obtained by Bolívar (2015).

The different bulk densities between the two forest types, multiplied by their respective % organic carbon, resulted in a completely different distribution of TOC compared to the previous results based on %OC alone (Table 1). A higher carbon storage in the upper layers of basin mangrove soils is clearly outlined (Table 1). Summed across the profile, fringe mangroves had a TOC of  $320.04 \pm 42.61$  Mg C ha<sup>-1</sup>, and basing mangroves an average TOC of  $660.93 \pm 259.18$  Mg C ha<sup>-1</sup>; i.e., average TOC was twice as large in basin than in fringe mangroves. Across the profile, TOC decreased with soil depth within the first four (basin) and three (fringe) layers. There was an increase in TOC for the last measured depth intervals of basin and fringe soils, which can be traced back to higher %OC values of those layers.

We measured a higher proportion of negative  $\delta^{13}\text{C}$  values for fringe soils (-28 to -29 ‰) than for basin mangroves soils (-25 to -29 ‰) (Fig. 3). Depth intervals 20-40 and 40-60 cm of basin soils show outliers with equal <sup>13</sup>C values compared to the Sinú river end-member samples with values of around -25 ‰. The sand end-member samples have the most positive <sup>13</sup>C values with approximately -3 ‰. Strong variations in <sup>13</sup>C are conspicuous for the depth intervals 20-40 and 40-60 cm of basin mangrove boxplots. We found no identifiable continuous trend between <sup>13</sup>C values and depth. However, differences in <sup>13</sup>C mean values between fringe and basin mangroves suggest two different distributions ( $p\text{-value} < 0.001$ ,  $W = 542$ ).

There were no differences between basin and fringe mangroves in terms of the composition of their mineral fraction (Table 2). The proportion of mineral soil is larger in basin than in fringe mangroves. Fringe mangrove soils show in contrast a higher proportion of halite than basin soils.

The XRD pattern of sand samples measured from 5 to 60 °2 $\theta$  provided characteristic °2 $\theta$  intensities for the phases aragonite, calcite and quartz. The XRD measurement combined with a Rietveld refinement yielded a mineralogical composition of 95% aragonite, 4% calcite and 1% quartz. River samples showed high intensities for quartz and sodium feldspar (albite) components, as well as peaks for the clay minerals illite and clinochlore. The semi-quantitative distribution calculated by PDF data indicated that quartz is the main representative of the mineral fraction of the Sinú river soils (Fig. 4).

XRD patterns for both mangrove soils, but in particular for basin soils, showed a similar mineralogical distribution compared to the Sinú river sediments (Fig. 5). XRD patterns in fringe soils showed high intensities for halite, which was also found in basin mangrove soils, but not in a comparable distribution ratio. XRD measurements conducted on the extracted clay mineral fraction yielded peaks for the mineral phases clinochlore, illite, quartz and albite. PDF data additionally identified corundum, which is related to the ceramic panel surface composition. We found major proportions for clinochlore and quartz in the clay size fraction.

The oxalate extraction dissolved much of the poorly crystalline Fe and Al oxides from the amorphous materials, whereas the dithionite extraction dis-

solved the crystalline Fe oxides as well as the amorphous materials (Fig. 6). Oxalate- and dithionite extracted Al showed significant differences among fringe and mangrove forest soils ( $p$ -value = 0.002,  $W = 325$ ). Similarly, oxalate and dithionite extracted Fe showed significant differences between both soils ( $p$ -value < 0.001,  $W = 364$ ). Basin soil samples had two times higher concentrations of Al ( $Al_d + Al_o$ ) than fringe soils, and five times higher Fe values. While riverine samples had similar Al and Fe concentrations than those of basin mangroves in all 4 extraction patterns, metal contents of sand samples were constantly low.  $Fe_o$  contents differed extremely for basin soils, especially for the first 2 depth intervals. Both basin and fringe soils showed an increase of metal oxides within the first depth intervals and in turn a decrease within the deeper layers.

## 4 Discussion

Our results confirmed previously observed differences in %OC, bulk density and %TOC between the basin and the fringe mangrove soils (Bolívar, 2015). Furthermore, our measurements of carbon isotopes and mineralogy helped us to explore the potential origin of the carbon stored in both mangrove types. In the following, we will discuss these difference and the potential implications of our findings.

#### 4.1 Differences in carbon storage

Lower values of bulk density in fringe mangrove soils can be explained by their high organic matter content (wood residues, leaf debris and roots). Roots claim a large proportion of the soil volume, which strongly decreases bulk density (Bolívar, 2015). Instead, basin mangrove samples of Cispatá bay are characterized by a dense silty composition including a small organic part, which results in higher bulk densities.

The higher proportion of organic matter in fringe than in basin soils also leads to higher %OC values for fringe soils. Basin mangrove soils instead, are characterized by a small portion of organic topsoil. Because %TN concentrations correlate with %OC, they also show lower values for basin mangroves. That both end-members (river sediments and sand) are mostly consisting of mineral components is illustrated by their %OC contents of nearly 0 %. Because the %IC concentration of 10 % of sand samples is similar to the used pure calcium carbonate standard, we concluded that the sand end member is mostly composed of carbonates.

The decrease of %OC with soil depth is likely the result of the interaction between decomposition, vertical transport of organic matter, and leaching of dissolved carbon in water (Elzein and Balesdent, 1995; Braakhekke et al, 2013; Mathieu et al, 2015). Because soil microorganisms utilize nitrogen and bacteria fix nitrogen, the concentration of %TN also decreases with depth. The fact that concentrations of %OC and %TN decrease continuously with soil depth, but still show layers with higher concentrations in depths of 80-100 cm

(basin) and 60-80 cm (fringe), may reflect differences in sedimentation rates over time (Bolívar, 2015). In Cispatá bay, silting processes linked to changes in the position of the Sinú river delta, current sea level rise, flooding regime and fluvial inputs (Serrano, 2004), can generate deep organic layers that may cause the increase of %OC with depth for both mangrove types.

Higher TOC values in basin mangrove soils reflect higher rates of organic matter accumulation. According to Bolívar (2015), the percentage of clay is similar between both mangrove types. However, the silt fraction dominates in all soil profiles in basin mangroves, while sand dominates in fringe mangrove soils. It has been well established that soil particles with greater surface area, as typical of finer textures like those found in basin mangroves, decrease drainage and decomposition of organic matter (Prasad and Ramanathan, 2008). Because TOC contents are linked to %OC, we found also an increase of TOC in depth levels of 80-100 cm (basin) and 60-80 cm (fringe).

Our results confirm previous studies that found important differences in TOC between fringe and basin mangrove soils (Bolívar, 2015). Furthermore, basin mangrove soils showed a significantly higher range of in-situ produced carbon than fringe mangrove soils, and with it a higher carbon storage of  $661 \pm 259 \text{ MgC ha}^{-1}$  (0-100 cm) compared to  $320 \pm 43 \text{ MgC ha}^{-1}$  (0-80 cm). Based on the %IC concentration results, we infer that marine sediments across Cispatá bay have little to no influence on additional carbon entering via tidal flooding, which is supported by the lack of %IC content in the analyzed mangrove soil samples compared to the sands of Nisperal beach.

## 4.2 Origin of carbon

$\delta^{13}\text{C}$  values of fringe mangrove sediments were more  $^{13}\text{C}$  depleted than basin sediments, which is a strong indication that this carbon is more plant derived. C3 plants fractionate  $^{13}\text{C}$  during photosynthesis, with values from -22 to -38 ‰, while C4 plants show values between -8 to -15 ‰ (Farquhar et al, 1989). *R. mangle*, a typical C3 species, mostly occurs in the fringe area of Cispatá bay (Bolívar, 2015) and is therefore the main contributor of  $^{13}\text{C}$  in this type of forest. In terms of its origin, this carbon is very likely produced in situ in the area. Basin mangrove sediments instead, show a wider range of  $\delta^{13}\text{C}$  values and more positive values. This could mean either that the basin area has a higher contribution by C4 plants (e.g. grasses), or that there is some contribution from mineral sources. Because the most common basin mangrove species, *A. germinans*, is also a C3 plant and there is likely little contribution by C4 grasses, we assumed that basin mangrove sediments have some influence by deposited sediments from the Sinú river. This assumption is also supported by the fact that basin samples tend to have more enriched  $^{13}\text{C}$  values, close to those found for the Sinú river samples (-25 ‰). According to Ruttenberg and Goni (1997) and Powers and Veldkamp (2005),  $\delta^{13}\text{C}$  values of tropical mineral soils range from -23 to -26 ‰, which would underpin mineral derived  $^{13}\text{C}$  values in Cispatá bay. Because differences in  $^{13}\text{C}$  values were significant between basin and fringe sediments, and because fringe samples only have plant derived  $^{13}\text{C}$ , we conclude that the fringe area is not influenced by the Sinú river delta.



It also does not show any influence through marine sediments, because it does not have any enriched values comparable to the sand end member (-5 ‰).

The  $\delta^{13}\text{C}$  analyses confirmed that additional carbon present in basin soils is only terrestrial and not marine derived. Moreover, it shows that additional terrestrial carbon only influences basin mangrove sediments, while carbon in fringe soils is exclusively produced in situ by the plants.

Using XRD, we found that the mineralogical composition of the sediments in Cispatá bay was similar to the composition of the Sinú river sediments in Montería. We therefore conclude that basin and fringe mangrove sediments were transported by the river and have their distant origin in that river basin. Quartz, albite and clay minerals are the major components of those sediments. Additionally, plot R5 shows intense peaks for the mineral halite in depths between 80-90 cm. Because halite crystallizes by the evaporation of sea water and intense salinization (McCaffrey et al, 1987), its occurrence verifies that the fringe mangrove area has tidal influence of hyper saline sea water. Furthermore, halite confirms the sediment's air exposition, since it needs evaporation to be formed. That halite reaches that intense proportion in depths of 80-90 cm can be attributed to the changing course of the Sinú river. According to Serrano (2004), the river course passed through the northern main land of Cispatá bay between 1849 and 1938, where plot R5 is located. Accordingly, the sedimentation rate increased in that period. However, before that period, this region was more influenced by saline sea water, which results in intense

halite peaks. That basin soils also contain halite, shows that they were also occasionally flooded.

Along with the  $^{13}\text{C}$  results, the mineralogical analyses also confirmed that basin mangrove sediments are terrestrially derived as opposed to marine derived. This finding is also reflected in higher metal oxide and hydroxide contents in basin than in fringe mangrove soils. Concentrations of iron and aluminum oxides in basin mangroves were similar to those of the Sinú river samples, which is a strong indication of fluvial deposition of inland sediments.

That mineral surfaces of Al and Fe oxides and hydroxides adsorb dissolved organic matter (DOM) has been well established (Tipping, 1981; Oades, 1988; Kaiser and Guggenberger, 2000; Mikutta et al, 2006). It is therefore very likely that metal oxides and hydroxides bind and preserve C in basin mangrove soils. According to Kaiser and Guggenberger (2000), the capacity to adsorb DOM relates to the presence of Al and Fe oxides and hydroxides. The sorption of DOM derived from decomposition to Al and Fe oxyhydroxides involves strong complexation bondings between surface metals and acidic organic ligands, particularly with those associated with aromatic structures. The strength of the sorption relates further to the surface properties of the sorbing mineral phase. Kaiser and Guggenberger (2000) found that dissolved organic matter sorption is strongly enhanced by hydrous oxide coatings and particularly by amorphous  $\text{Al}(\text{OH})_3$ , which may indicate that amorphous hydroxides bind C in basin soils of Cispatá bay. Tipping (1981) describes moreover, that the extent of adsorption of DOM increases with decreasing pH. Because mangrove soils at the

Colombian Caribbean coast have an acid character both at *A. germinans* and *R. mangle* forests (Urrego et al, 2014), a stronger C binding onto oxides and hydroxides is substantiated in this region.

All together, we found no evidence for our initial hypothesis that C in mangroves of Cispatá bay, particularly in basin soils, have a large contribution from sediments transported by the Sinú river. Instead, we found that the sediments do play an important role for stabilizing in situ produced carbon, but mostly by providing mineral surfaces for C binding.

#### 4.3 Implications

Our results provide strong evidence for an important role of sediment mineralogy, particularly iron and aluminum oxides, in providing mineral surfaces for the adsorption of dissolved carbon and long-term C retention (Oades, 1988) in mangrove soils . These results add a new dimension to the more traditional studies of carbon origin in mangrove soils where the source of the carbon is considered either marine or terrestrially derived (Lacerda et al, 1995; Bouillon et al, 2008), without considering the role of sediments in dissolved carbon retention. This mechanism may play a large role in explaining observed spatial variability in carbon storage (Alongi, 2012; Jardine and Siikamäki, 2014). Also, since retention of dissolved carbon in mangrove soils can reduce rates of carbon exports to the ocean (Adame and Lovelock, 2011), mineral surfaces of sediments may provide a large potential for carbon sequestration in mangrove ecosystems located around river deltas. According to our results, carbon stor-

age can be twice as high in mangroves with dense aggregation of minerals than in more organic mangrove soils, and therefore it is very relevant to explore this carbon sequestration mechanism in other delta regions of the world.

## 5 Conclusions

Based on analyses of carbon concentration, stable isotopes of carbon, and mineralogy, we found that most carbon stored in soils of Cispatá Bay, Colombia, is produced in situ, with little evidence of carbon imported to the area either by fluvial or marine sedimentation. Interior basin mangroves store significantly more carbon in soils than the more ocean exposed fringe mangroves. Sediments transported by the Sinú river and deposited in the delta region contain negligible amounts of organic carbon, but the mineralogical composition of these sediments favors the adsorption of dissolved carbon on charged mineral surfaces, which explains the larger levels of C storage in this type of mangroves.

Our study highlights the importance of fluvial sediment transport in providing a substrate for carbon stabilization through mineral protection. This mechanism for soil carbon storage has been little studied previously in mangrove ecosystems, but it has large implications for determining their potential for long-term carbon sequestration.

**Acknowledgements** We would like to thank Prof. Dr. Juraj Majzlan for providing mentoring and access to the XRD lab at the Friedrich-Schiller-Universität Jena. Thanks to INVEMAR Colombia, particularly Paula C. Sierra, for facilitating logistics and access to the research site. Financial support was provided by the Alexander von Humboldt Founda-

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406 tion through the International Climate Protection Fellowship, and the Max Planck Institute  
407 for Biogeochemistry.

408 **Figures**

**Fig. 1** Sampling plots in Cispatá Bay and Montería, Colombia, ArcGIS-source: <http://www.diva-gis.org/gdata>; accessed on June 07, 2016; fringe plots: P21, R1, R4, R5, R6; basin plots: P16, C1, C2, C3, C4; end-members: Sand Nisperal, Sinú riverbed

**Fig. 2** Observed values of percent inorganic carbon (%IC) for both mangrove types and end members; and percent organic carbon (%OC) and percent nitrogen (%TN) by sampling depth aggregated across plots.

**Fig. 3** Measured  $\delta^{13}\text{C}$  in a) mangrove types and end members, b) basin mangroves by depth, and c) fringe mangroves by depth.

**Fig. 4** Two exemplary XRD patterns ( $\lambda = 1.5406 \text{ \AA}$ ) of both measured end-members: Nisperal beach and Sinú river; figures also include semi-quantitative distribution of detected minerals

**Fig. 5** Two exemplary XRD patterns ( $\lambda = 1.5406 \text{ \AA}$ ) for the fringe (left) and basin (right) mangrove soils; figures also include semi-quantitative distribution of detected minerals

**Fig. 6** Oxalate (o)- and dithionite (d) extracted metal oxides for each mangrove type and soil depth.

409 **Tables****Table 1** Percent organic carbon, bulk density and total organic carbon by mangrove type and soil depth. Values in parentheses indicate standard deviation

Mangrove type	Depth [cm]	OC [%]	Bulk density [g/cm <sup>3</sup> ]	TOC [MgC/ha]
Basin	0-20	14.63 (10.09)	1.01 (0.06)	295.61 (203.77)
	20-40	7.12 (7.19)	1.25 (0.10)	161.99 (147.07)
	40-60	3.22 (1.93)	1.06 (0.19)	68.35 (40.95)
	60-80	2.96 (1.39)	1.10 (0.16)	65.21 (30.58)
	80-100	4.15 (2.24)	0.84 (0.08)	69.78 (37.60)
Fringe	0-20	31.32 (2.82)	0.16 (0.01)	100.24 (9.03)
	20-40	23.61 (8.70)	0.13 (0.02)	62.79 (22.56)
	40-60	16.12 (10.92)	0.16 (0.05)	51.57 (34.94)
	60-80	29.29 (0.55)	0.18 (0.01)	105.44 (1.99)

**Table 2** General mineralogical composition of sediments in Cispatá Bay as measured by XRD analyses.

Class	Mineral	Formula
Silicates	Clinochlore	$(\text{Mg,Fe}^{2+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$
	Illite	$(\text{K,H}_3\text{O})\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{H}_2\text{O,OH})_2$
	Albite	$\text{NaAlSi}_3\text{O}_8$
Oxides/hydrox.	Quartz	$\text{SiO}_2$
Carbonates	Aragonite	$\text{CaCO}_3$
	Calcite	$\text{CaCO}_3$
Halides	Halite	$\text{NaCl}$

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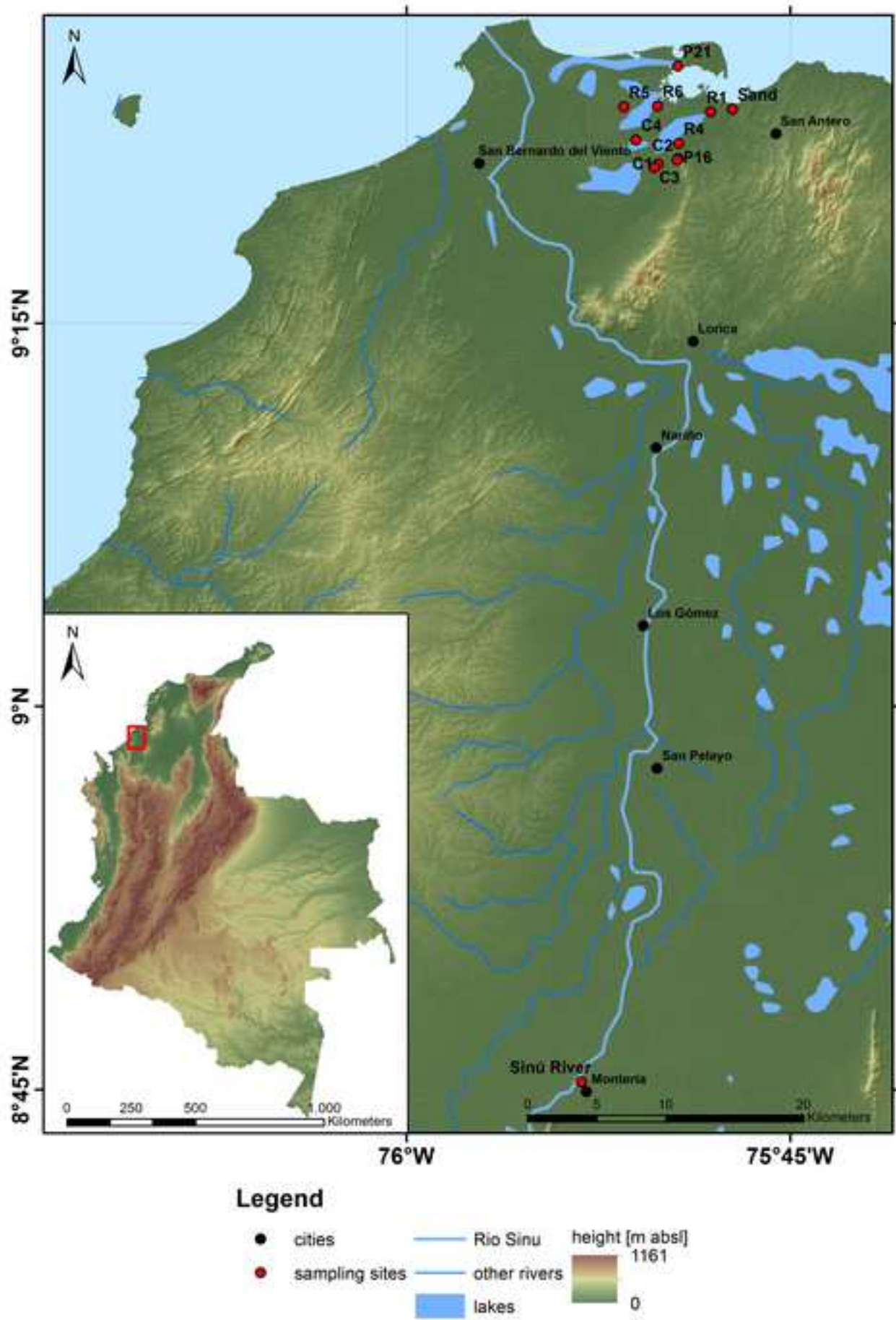
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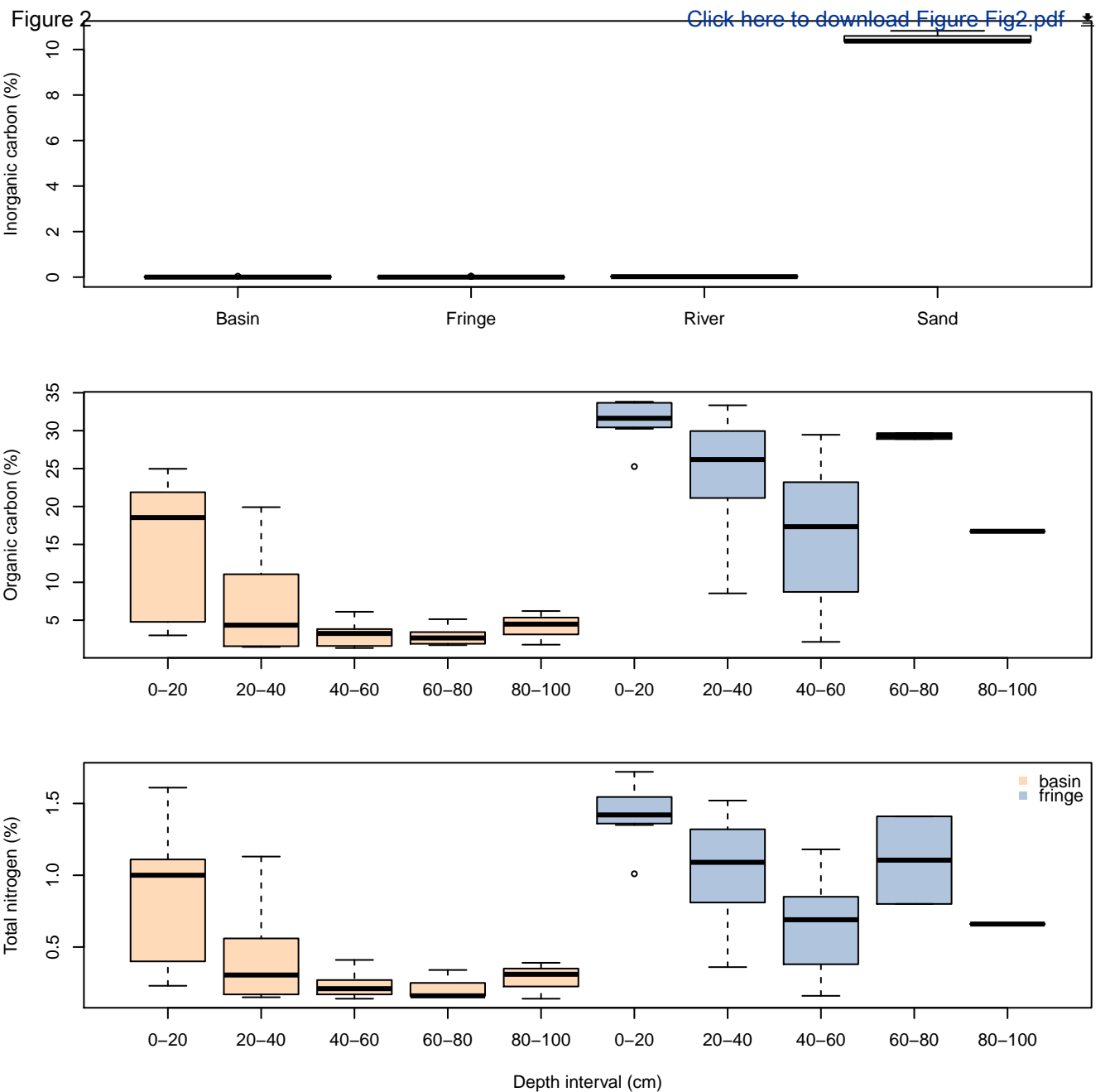
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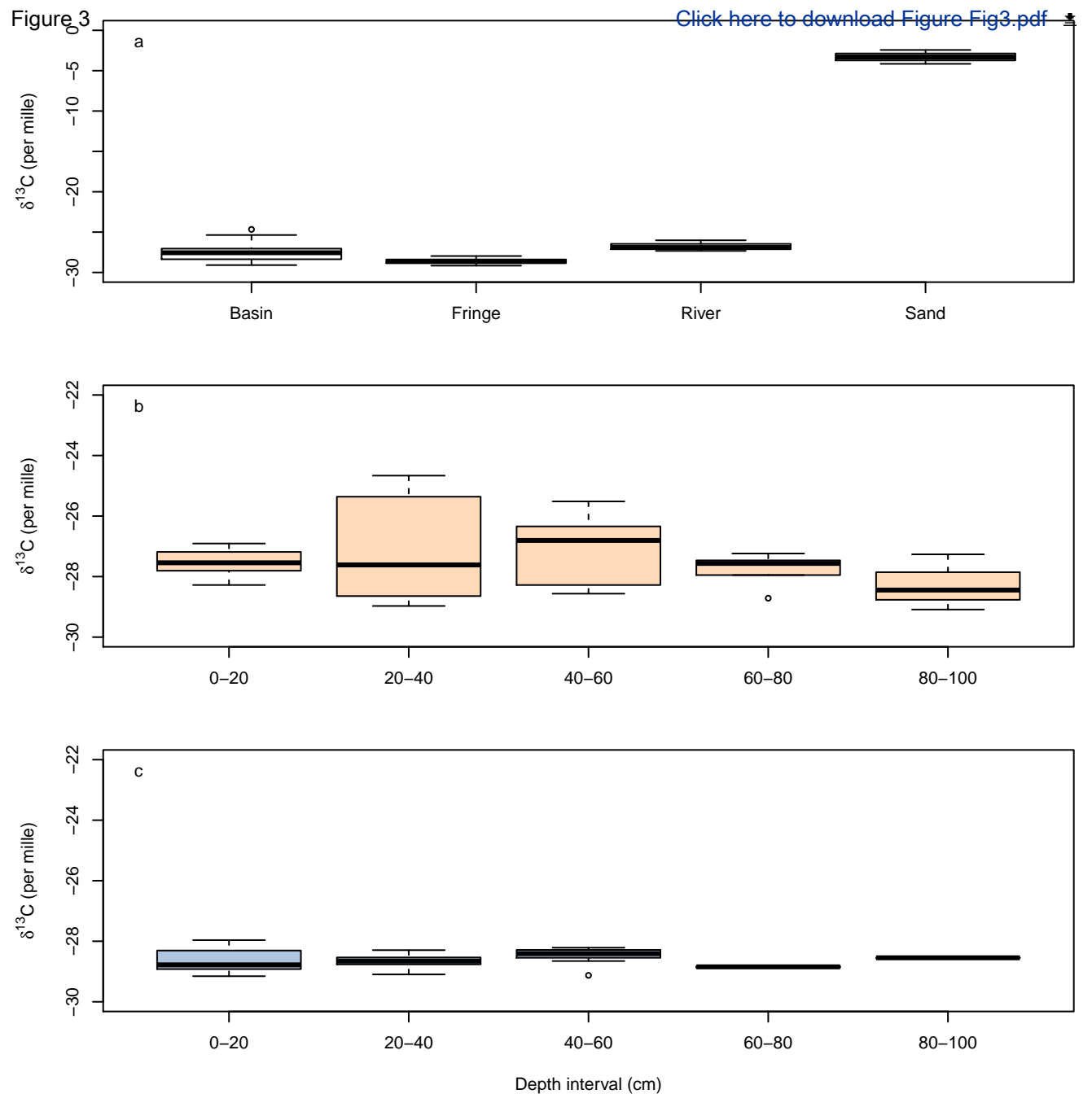
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Figure 1

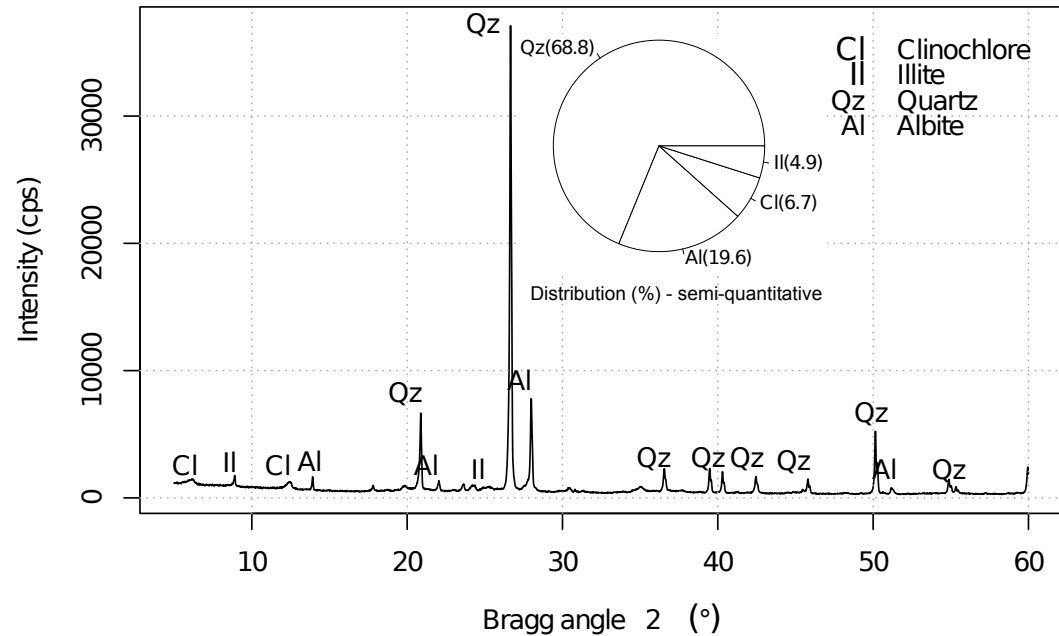
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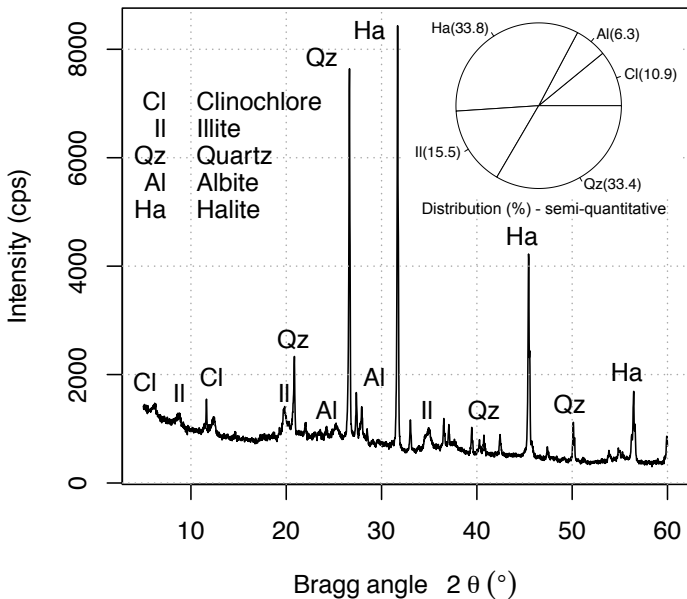


The figure displays an X-ray diffraction (XRD) pattern with the Bragg angle  $2\theta$  (°) on the x-axis, ranging from 10 to 60. The pattern shows several sharp diffraction peaks. An inset pie chart, titled "Distribution (%) - semi-quantitative", provides the relative proportions of the phases: Aragonite (Ar) at 85.2%, Quartz (Qz) at 8.4%, and Calcite (Ca) at 6.4%. A legend in the top right corner identifies the phases: Qz (Quartz), Ar (Aragonite), and Ca (Calcite).

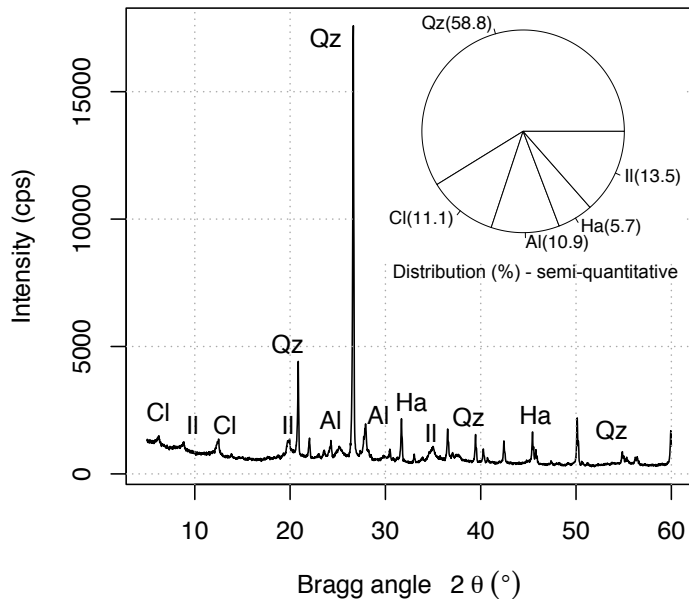


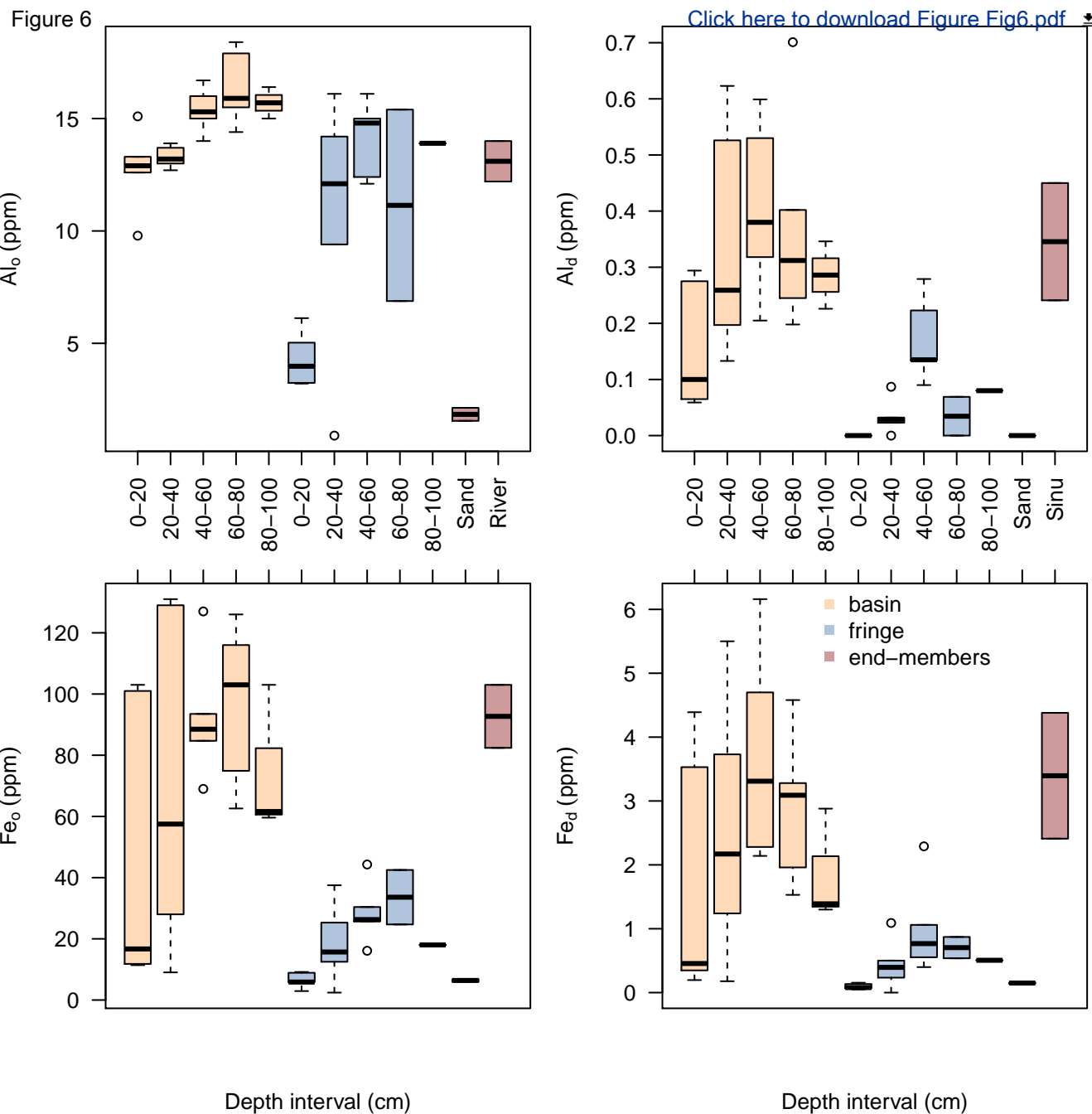


# R5 Fringe / 80–90 cm



# C3 Basin / 80–85 cm





## **Funding sources**

Financial support was provided by the Alexander von Humboldt Foundation through the International Climate Protection Fellowship (KOL 1157857 IKS-2), and the Max Planck Institute for Biogeochemistry.

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2nd July 2018

Dear Dr. Aseda

Thank you very much for your consideration of our manuscript and for the opportunity to submit a revised version. We made several changes to the manuscript based on reviewers' comments. Most changes attempt at increasing clarity addressing reviewers' suggestions. In addition, we changed the statistical test used for comparisons, using now a non-parametric test that does not rely on the assumption of normality of the data. For details, see the answers to the comments below.

In the text below, we provide answers (**blue font**) to all reviewers' comments (*italics font*).

### Reviewer 4

*I recognise the considerable efforts the authors have taken to undertake this study and complete a thorough laboratory analysis of the samples collected. Moreover, I also appreciate the necessity of understanding sediment dynamics and carbon accumulation with respect to mangrove systems, which this study addresses. Overall, what is lacking to me here in this manuscript is a sufficient level of detail in the general presentation and a recognition of the limitations of the study. This extends to a consistent failure to validly support various statements made throughout the manuscript by making appropriate reference to suitable literature sources. Furthermore, the detailed interpretations and contrasts between individual habitat 'zones', which have been inferred from the basic statistical analyses used, are somewhat naïve. The discussions section contains some very confidently-worded interpretations from the results, but does not provide sufficient information to support these (be it either from literature sources or logical argument). Finally, the authors appear to assume, throughout the introduction, methods and results section, that the reader will understand the rationale behind the field sampling and analytical methods used. Links between the hypotheses and why these methods were used are not given until well into the discussion section. The reader is left to try to figure this out for themselves.*



We thank the reviewer for recognizing the value of this study and pointing out different issues such as lack of detailed descriptions and confidence in wording. We have made an effort to address all these issues (see answers below), and as a result the manuscript is now much improved. In some cases however, we think some of the issues raised by the reviewer are due to misunderstandings of the text. In these cases, we made an effort to present a more clear text.

1. Ln. 37 *Describe what habitat or environmental characteristics make up a 'basin', or 'fringe' mangrove. Again - a map of the area would be very helpful here! (Figure 1 is not mentioned in the text).*

Habitat and environmental characteristics of the basing and fringe mangroves are described in the Materials and Methods section. Here in the introduction, we are describing the main motivation of the study and therefore it is not the most appropriate place to describe the study site. Figure 1 is mentioned in the text in the Methods section.

2. Ln. 60-62 *You need to provide information on why this is the case - and what your rationale for this method is. I presume - that  $^{13}\text{C}$  ( $\text{CO}_2$ ) is preferentially taken up by mangrove trees during photosynthesis, therefore accounting for higher ratios in the mangrove sediments? But you haven't given any sort of explanation for this. Your rationale does not seem to explain why allochthonous organic carbon sediments (derived from elsewhere in this catchment would not also be enriched with  $^{13}\text{C}$ ). What is the rationale supporting this line of inquiry - and most importantly - where are the literature sources to validate it?*

We added a new paragraph giving this rationale.

3. Ln 71-73 *A map showing the location might be helpful. (Figure 1 is not mentioned in the manuscript text)*

Figure 1 is a map that shows the location of the study site and the location of the plots. It was initially mentioned in section 2.2, but we added an earlier reference in section 2.1 to address this comment.

4. Ln. 77 *How? Why?*

The cause of the change of the Sinú river course is not well known, however it is well documented in Serrano (2004), which we cite in the manuscript for further information.

5. Ln 86 *Using what apparatus? What diameter? What depth? How were the sample positions determined? How were your sample locations randomised? (This is a FUNDAMENTAL basic requirement for the parametric statistics you have used).*

The diameter and depth were already given in the sentence above. We added a description of the soil corer and information on the random selection of points. We know this is fundamental, and quite obvious, so for this reason we didn't include it in the previous version, but we add it now to address this comment.

6. Ln 87-88 *A map to show the layout of these plots? How big are they? How far are they spaced apart from each other? How were their original positions determined? What do the designations P, R and C actually refer to and why is it necessary to use them?*

The location of the plots is presented in Figure 1. The size of the plots is

500 m<sup>2</sup>. We added this information to the manuscript. Plot designations are relevant for consistency with previously published manuscripts from the same site.

7. *Ln 91-92 Why was this done? What was the rationale for choosing 20cm divisions? Where is a citation to support this?*

This was done to see if we can detect differences by soil depth instead of analyzing the entire soil core. This is commonly done in soil science and usually does not require any specific justification.

8. *Ln 93-96 I can't follow these two sentences. What is an 'end member'? Who or what were 'them'?*

This sentence was reworded for clarity.

9. *Ln 98 Where in the plot? How was this position determined? Was this at a position you simply liked the look of?*

Actually outside the plot to avoid effects on the trees inside the plot. The location was three meters away from a randomly selected corner of the plot.

10. *Ln 101-102 So was a (single) soil pit dug? (Ln. 98) Or were 3 soil pits dug? If these replicates came from a single soil pit - how can they be considered replicates?*

No, two soil pits in plots P21 and C4. This is explicitly mentioned in the manuscript.

11. *Ln 105-107 Why were these protocols chosen? (Citations?)*

These are standard soil processing protocols.

12. *Ln 108 Manufacturer name and location.*

Information add to text.

13. *Ln 118 -120 Do you have a reference to support this inference and further detail to support why it is valid to assume that this method allows for indication of the 'origin of the carbon'?*

This is basic knowledge on isotope source partitioning analysis. We assumed most reads are a familiar with this concept, however we added a reference to a textbook to satisfy reviewer curiosity.

14. *Ln 131 What is this refinement method, why did you use it? Where is the justification in the literature for using it in this way?*

This is simply the name of the technique. See [https://en.wikipedia.org/wiki/Rietveld\\_refinement](https://en.wikipedia.org/wiki/Rietveld_refinement)

15. *Ln 131 "Topas" Is this a citation, a manufacturer name, a piece of software, or an alternative name for the piece of apparatus?*

Topas is a software and Brucker the company who produces it. We added more information to the sentence for clarity.

16. *Ln 132 Measured what of each? The clay? The mass of the sample? The Rietveld / Topas number?*

Each sample.

17. *Ln 136 - 139 I miss a rationale, here or in the introduction section, for why these analyses were necessary. What were you hoping to achieve by doing this? What were your hypotheses?*

The rationale is presented now in the introduction, where we mention that

we use analyses of the structure and composition of the clay minerals to help in determining the origin of the stored carbon.

18. *Ln 157 I remain more than a little confused by your analysis and the conclusions you have made from them. Your statistical analysis (an ANOVA, examining the variance in a range of response variables according to 4 categorical 'zones' within this habitat system: basin, fringe, river, sand) does not allow you to determine the statistical significance of differences between individual habitat zones, even if these contrasts appear (visually) in the figures. You will need to include a Tukey post-hoc HSD analysis of means to be able to validly make such inferences on a pair-wise basis.*

Sorry for the confusion. In the ANOVA we didn't compare four categorical zones as the reviewer thought, but only the two groups of mangrove types: fringe and basin. Therefore the Tukey post-hoc test is not needed. However, given in the new version of the manuscript we do not use ANOVA anymore for comparisons of means. Since the data was not normally distributed, we use now a Wilcoxon test to compare the distribution of the data. Description of statistical analyses was changed accordingly in the text.

19. *Ln 169-170 Error terms for these mean values??*

Standard deviation values were added.

20. *Ln 172-173 How can you make such a definitive inference, based on your observations alone? How do you know that X resulted in Y? (The reader is not convinced - as you haven't provided any explanation why!)*

This is inferred by simply multiplying bulk density by % organic carbon. Also, you can reach this conclusion by simply looking at the results of Table 1. We do not think we need to give a complex argumentation for this result since it is almost trivial. However, in the new version we explain this result better and point the reader to Table 1 to see this in more detail.

21. *Ln 175 -177 I do not see how you can assume to have directly assessed such a contrast, based on the description of the statistical methods and analyses you have used.*

Again, we are not comparing the four groups here, only the two mangrove types, and for this reason it is possible to express the result in the way we do in this paragraph.

22. *Ln 188-190 The statistical test you have described in your methods section did not test for direct differences between your individual habitat zone categories, yet a statistically significant contrast between two individual categories is precisely what you are stating here.*

i.d.e.m.

23. *Ln 229-230 But you haven't at any point described how or why it did this.*

We reworded this paragraph. The point is simply that the results helped us to make an interpretation of the origin of the carbon, but this is analyzed only in the discussion, independent of the results section where we state the result without interpret them.

24. *Ln 236 Reference to support this claim? Surely you were sampling root-free soils? Or did your soil samples also contain live root biomass?*

Reference added.

25. *Ln 239 Wouldn't an increase in bulk density be expected with any soil? Why*

*is this relevant to mangroves? Why is reporting this finding relevant?*

Yes, this happens in most soils, but in mangroves bulk densities increase strongly due to hydrostatic pressure. However, we agree in that this sentence is not very relevant for the discussion on differences in bulk density among the two mangrove types, and therefore we removed it.

26. *Ln 251-254 On what basis? Do you have a references to support these rationales? It is quite a large assumption otherwise!*

This is relatively well known for vertical carbon transport in soils. We added a few references to support this claim.

27. *Ln 281 - 288 Some, if not all of the information in this paragraph needs to be in the introduction / methods section. Without such validating information, until now, what you have done has remained pretty much meaningless to the reader.*

Some of this information was added to the introduction.

28. *Ln 285 What kind of (plant) species - a sunflower? Wheat? Mangrove tree species?*

We do not understand this comment by the reviewer. Line 285 explicitly says *Rizophora mangle*.

29. *Ln 286 - 387 'and is \*likely\* to be' You haven't conducted sufficient analyses to be certain! Here - and elsewhere - there are far too many 'definitive' statements like this in the manuscript, which are either unverifiable the your analyses you have conducted, or unsupported by relevant literature sources. Both these requirements should be the basic minimum for any peer-reviewed scientific study.*

We beg to differ. In this paragraph we do not make any definitive statements as stated by the reviewer. When we use a word such as 'likely', we are actually implying that this might be the case, but there is uncertainty. Notice that we use wording such as 'this assumption is supported', 'this could mean either ... or ...', 'which would underpin', etc. These are all hedged statements that show our interpretation of the results and our favoring for a specific interpretation, but away from a definite true.

Despite our disagreement on this matter, we did try to change the language in several parts of the manuscript to make our statements less 'definite'.

30. *Ln 326 As opposed to being from a marine source? This (implied?) contrast should be made more clear.*

The sentence was completed to make the contrast clear as suggested.

31. *Ln 372 I am perplexed as to how you claim your analyses of bulk density were able to show this. Changes in BD were co-correlated with root density and organic carbon content, that's all. They cannot give any indication of the source of carbon in a soil.*

Sure, bulk density has nothing to do with a determination of the origin of the carbon. Since this was the opening statement of the conclusions, we simply wanted to list all the analyses that were performed in the study. However, we removed bulk density from this paragraph to avoid confusion.



**Reviewer 5**

*The manuscript of Volkel et al. aims to investigate the origin of organic carbon in mangrove ecosystem in Colombia using stable isotopes and mineralogical analyses. The authors improve the manuscript following the suggestions of the reviewers. As the previous reviewers have already marked this article is of interest regionally but also as a contribution in a wider contest. I think that in this form the manuscript is almost ready for publication. I have just few comments.*

*Reviewer 2 highlighted as in the manuscript a statistical section on methodology was missing. The authors add a chapter on statistical methods without explain if before the ANOVA analysis they have checked the population for normality. This is an important point since a normal distribution is an assumption for ANOVA and many soil characters have not a normal distribution. In the file with your codes, I didn't find any code that is usually used to test for normality.*

Thanks for pointing this out. We originally applied an ANOVA test without checking the normality assumption. After checking for normality using the Shapiro-Wilk test, we found that the normally assumption was not met by our data, even after trying different transformations. Therefore, we decided to apply a non-parametric test, the Mann-Whitney U test to determine whether the two independent samples from the fringe and basin mangroves are from the same distributions. After running this test for all the measured variables, we found the same results as with the initial comparison using ANOVA. Therefore, our conclusions are unchanged despite applying a different statistical test.

*Why did you not add data on N/C ratio (or at least C/N ratio) as the reviewer 1 has suggested? You already have values on C and N, adding N/C ration should be a further indicator to support your results and conclusions.*

Organic C concentrations and total N show a very high correlation among each other (0.96 correlation coefficient), and the C:N ratio does not differ between the two forest types. Therefore, the information in the total N variable is redundant with respect to the information in organic C. Therefore, we think that adding an analysis of the C:N ratio does not contribute much to the story, as opposed to using other independent variables such as the isotopic composition of carbon, and the mineralogical composition of the sediments.

We hope this new version adequately addresses reviewer's comments and it is now suitable for publication.

Sincerely,

A handwritten signature in black ink, appearing to read 'Carlos A. Sierra'.

Carlos A. Sierra, PhD

[Click here to view linked References](#)

**Wetlands Ecology and Management manuscript No.**  
(will be inserted by the editor)

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# Stabilization of carbon in mineral soils from mangroves of the Sinú river delta, Colombia

Heidi Völkel · Jhoanata M. Bolivar ·

Carlos A. Sierra

Received: date / Accepted: date

**Abstract** Mangrove forests of the Sinú river delta in Cispatá bay, Colombia, show large differences in soil carbon storage between fringe (oceanic) and basin (estuarine) mangroves. We were interested in testing whether these differences in soil carbon are associated with sediment transport processes or whether most of the carbon is produced in situ within the mangrove system. Given past sedimentation dynamics of the Sinú river, we hypothesized that a large portion of soil carbon in basin mangroves is due to sedimentation. We determined total organic carbon content (TOC) ~~of 661~~ as 660.93  $\pm$  ~~116~~ 259.18 MgC ha<sup>-1</sup> for basin soils up to a sampling depth of 1 m, and ~~320~~ as 259  $\pm$

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~~60~~42.61 MgC ha<sup>-1</sup> for fringe soils up to 80 cm depth (maximum soil depth for fringe soils). Using analyses of mineralogy (Al- and Fe-oxides, clay minerals) as well as isotopic analyses of carbon ( $\delta^{13}\text{C}$ ), the origin of the sediments and their carbon was determined. We found that basin soils in Cispatá bay show similar mineralogical composition than those of fluvial sediments, but the carbon concentration of river sediments was close to zero. Given the large capacity of the Fe and Al oxides in clay minerals to store dissolved carbon, and that the isotopic composition of the carbon is mostly of plant origin, we concluded contrary to our initial hypothesis that the carbon stored in basin mangrove soils are produced in situ. The deposited fluvial sediments do play an important role for carbon storage, but mostly in providing binding surfaces for the stabilization of organic carbon.

**Keywords** soil organic carbon · stable isotopes · iron and aluminum oxides · soil mineralogy · estuarine ecosystems

## 1 Introduction

Although mangroves are ecosystems with some of the largest levels of carbon storage on earth (Donato et al, 2011; Alongi, 2012), there are large variations on the amount of C stored in various systems, particularly soils. For instance, mangrove ecosystems dominated by *Rhizophora* spp. in Peninsular Malaysia store between 479 to 2205 Mg C ha<sup>-1</sup> in the belowground and soil pool (Alongi, 2012), and similar levels of variability have been observed at other sites (Jardine and Siikamäki, 2014). It is unclear however, what are the

main determinants of observed differences in soil C storage across diverse mangrove systems. It is possible that differences in soil carbon storage are due to differences in the level of productivity of different mangrove systems, or due to other external sources such as sediment transport.

This large degree of spatial variability in soil carbon storage is also well expressed in the mangrove forests of Cispatá bay, Colombia. These mangroves consist of two main forest types: basin and fringe systems, which show large differences in terms of soil carbon stocks between them. A previous study (Bolívar, 2015) showed that for basin mangroves the total organic carbon storage (TOC) is around  $740 \pm 40 \text{ Mg C ha}^{-1}$ , while for the fringe mangroves this value is only  $95 \pm 9 \text{ Mg C ha}^{-1}$ . These numbers, particularly for the basin mangroves, are in the upper range of values observed for other systems (Donato et al, 2011; Alongi, 2012; Jardine and Siikamäki, 2014).

It is unknown whether the high levels of soil carbon in Cispatá bay are due to the intrinsically high levels of productivity of these systems or whether this soil carbon has an external source such as transport of fluvial or marine sediments. Given that mangrove productivity is high and decomposition in water saturated soils is slow, carbon stored in these systems may not have any external origin (Lacerda et al, 1995). However, it is also possible that sediments in the delta region may have been deposited by the Sinú river given that before 1938 it discharged in the current mangrove area (Serrano, 2004), in which case the carbon stored in these sediments may have its origins in

soils from the northern Andean mountains. Alternatively, the carbon in these sediments may have been transported by marine tides over the Caribbean.

Different techniques have been used in the past to determine different sources of organic carbon in water saturated ecosystems. For instance, the  $\delta^{13}\text{C}$  isotope has been used to explore different sources of carbon by source partitioning analyses (Bouillon et al, 2008; Spohn and Giani, 2012; Spohn et al, 2013). Also, measurements of the mineralogical composition of the sediments can also give some clues on whether the minerals present in an area are from terrestrial or marine origin.

Here, our main objective was to determine the origin of the relatively high carbon levels in these soils using elemental and isotopic analyses of carbon as well as analyses of the soils' mineralogy in concert with Al- and Fe-oxide measurements. ~~Analyses of stable isotopes are particularly useful to identify the origin of carbon in soils of coastal areas (Bouillon et al, 2008; Spohn and Giani, 2012; Spohn et al, 2013).~~

In particular, we expect that: 1) the isotopic composition ( $\delta^{13}\text{C}$ ) of soil carbon provides information on whether riverine sediments are a main source of C in Cisipatá bay, Colombia; and 2) the mineralogical composition of the sediments provides additional information on the origin of the soil carbon and the potential that it is mostly stabilized on the surface of Fe- and Al-oxides. Our main hypothesis is that soils in the basin mangroves are composed mainly by sediments transported by the Sinú river and deposited in the delta region, therefore explaining the relatively large values of TOC stored in these soils.

## 2 Materials and methods

### 2.1 Study site

The study site is located on the northwestern Caribbean coast in Colombia (9°23'N 75°52'W), which is part of the southern extreme of Morrosquillo gulf and it is locally known as Cispatá bay ~~-(Fig. 1).~~ The coastal zone is characterized by the Sinú river delta and a complex estuarine lagoon system that covers approximately 5,098 ha. Extensive wetlands and mangroves dominate this area. The Sinú river has its origin in the northern part of the western Andean mountains, and between 1938 and 1945 changed its course creating a new delta (Serrano, 2004). The current estuarine mangrove system was established in the previous river delta. Fringe forests are dominated by *Rhizophora mangle*, basin forests are dominated by *Avicennia germinans*. *Laguncularia racemosa* occurs in both forest types.

### 2.2 Field sampling

Our sampling focused on a set of existing plots previously established to determine the carbon sequestration potential of the mangroves of Cispatá bay (Bolívar, 2015). We sampled 10 plots of 500 m<sup>2</sup> up to 1 m in depth from March 12 to 13, 2016, using a soil corer of 7 cm in diameter ~~.-We sampled five (Eijkelpkamp bi-partite gouge auger 04.03, Giesbeek, The Netherlands).~~ We selected five randomly chosen points within each plot to extract soil cores at five fringe mangrove sites (plots P21, R1, R4, R5, R6) and at 5 basin man-

grove sites (plots P16, C1, C2, C3, C4). In addition to the 10 plots sampled across the mangrove area, 3 nearby sand cores at Nisperal coast were collected, and also 3 riverbed cores of the Sinú river near the city of Montería, which is located 70 km south from Cispatá bay (Fig. 1). These river and beach sediment samples were used as end-members in our isotopic analysis. Generally, cores without layer changes were divided into sections every 20 cm to explore differences in carbon concentration with depth. We divided conspicuous layer changes at the boundary. ~~Because only the general mineralogical and elemental composition of the , except for the~~ sand and river ~~samples was important — we considered them as end members — those samples were not divided into segments. Instead, the whole cores down to 1 m were used as individual samples.~~ sediment samples that were analyzed as one single sample for mineralogical and elemental composition.

Additionally, we selected one fringe and one basin mangrove plot (P21 and C4) to measure bulk density. At each site, a soil pit was dug three meters away from one of the corners of the plot and samples were collected using sampling rings with a volume of 98.52 cm<sup>3</sup>. We collected four depth levels at plot P21 (0-20, 20-40, 40-60, 60-80 cm) and five depth levels (+ 80-100 cm) at plot C4. Sampling for bulk density was replicated three times for each depth level. In total, we obtained 60 soil samples out of the mangrove area, 6 end-member samples, and 27 samples for bulk density measurements.

## 2.3 Laboratory analyses

After collection, samples were oven-dried at 70°C for 5 days. Samples for bulk density measurements were oven dried at 105°C. We calculated soil bulk density as dry mass divided by fresh volume ( $V = 98.52 \text{ cm}^3$ ). Each sample was ground for 3 min at a frequency of 25 Hz using a [ball mill](#) (Retsch MM 400 ~~ball-mill~~, [Haan, Germany](#)).

We conducted elemental analyses of percent carbon (%TC) and nitrogen (%TN) in all samples by dry combustion (Vario Max, Elementar Analysensysteme GmbH, Hanau, Germany). Organic carbon was later removed by ignition at 450°C for 16 hours, and inorganic carbon (%IC) was then determined using the same elemental analyzer. Organic carbon concentrations were estimated by subtracting %IC from %TC. TOC contents ( $\text{Mg ha}^{-1}$ ) were calculated using the obtained bulk densities for basin and fringe mangrove soils multiplied by each plot depth interval (cm) and %OC.

We used  $\delta^{13}\text{C}$  values of the sampled material and compared them with the  $^{13}\text{C}/^{12}\text{C}$  ratio of the two chosen end-members as indicators for the origin of the carbon ([Fry, 2006](#)). We measured  $^{13}\text{C}$  of all samples using a Finnigan MAT IRMS coupled with an EA 1100 elemental analyzer. Ali-j3 (Acetanilide-Jena3) and Caf-j3 (a caffeine sample from a ‘Traube synthesis’ in large supply) were chosen as internal working standards (Werner and Brand, 2001). All elemental and isotopic analyses were conducted at the Max Planck Institute for Biogeochemistry in Jena, Germany.



We conducted X-ray diffraction (XRD) measurements for qualitative and quantitative phase analyses (Spieß et al, 2009) on 12 representative samples including 4 end-member samples, and 4 samples of basin and fringe mangroves each. Samples were measured 20 min each, from 5 to 60 °2 $\theta$ . We determined each mineral phase using the powder diffraction file (PDF) data. We also conducted a Rietveld refinement ~~using Topas (Bruker)~~analysis using the Topas software (Bruker Corporation). To define the type of clays included in the samples, we further measured each sample before extracting clay fraction from 3 to 70 °2 $\theta$  using ceramic panels. XRD analyses were conducted at the laboratory for Mineralogy and Geochemistry of the Friedrich-Schiller University in Jena, Germany.

We determined iron and aluminum in acid-ammonium-oxalate extracts (pH 3.0) and in sodium-citrate-dithionite extracts (pH 7.3) (Schwertmann, 1964; Holmgren, 1967). We selected 46 samples and 2 standard soils for these measurements. While sodium dithionite was used to extract both crystalline and amorphous oxides, the oxalate method extracted only amorphous oxides. The actual measurement of crystalline and amorphous iron and aluminium oxides was performed using an atomic emission spectrometer with inductive coupled plasma (ICP-AES, Optima 3300DV, PerkinElmer, Norwalk, USA). These analyses were performed at the SpecLab of the Max Planck Institute for Biogeochemistry.

## 2.4 Data analysis

Comparison of group means for the different measured variables were performed using standard analysis of variance procedures. In all cases, we fitted a linear model between the response and the group variable (mangrove type) using the `lm` function in the R language for statistical computing (The R Foundation, Vienna). Anova tables with summary statistics were obtained using the function `anovain R`, including  $F$ -statistic, degrees of freedom, and  $p$ -values. We performed statistical tests to determine differences in organic carbon concentrations, total organic carbon,  $\delta^{13}\text{C}$ , and Fe- and Al-oxides, among the fringe and basin mangroves. After an initial test for normality (Shapiro-Wilk test), we found little evidence to support the normality assumption required in common tools such as ANOVA or t-tests. We therefore, performed the non-parametric Mann-Whitney U test, which is equivalent to the two-sample Wilcoxon test (Hollander et al, 2015) under the null hypothesis that the samples from the fringe and basin mangroves differ by a shift location  $\mu = 0$ , and the alternative hypothesis that they are different by some other shift location. In other words, the test helps to determine whether the samples from the two different mangrove types belong to the same statistical distribution as stated in the null hypothesis. Data and code to reproduce all results presented here can be obtained from the following repository <https://github.com/crlsierra/mangroveCstabilization>. `git`.

### 3 Results

We found important differences between fringe and basin mangroves in terms of %OC ( $p$ -value  $< 0.001$ ; ~~analysis of variance  $F$~~ two-sample Wilcoxon  $W$ -test,  ~~$F = 54.13$  with 49 degrees of freedom~~ $W = 62$ ) and %TN ( $p$ -value  $< 0.001$ ,  ~~$F = 27.1$  with 49 d.f.~~ $W = 102$ ) (Fig. 2). In general, %OC and %TN decreased with soil depth ~~, with a more clear trend for % OC than % TN~~and were highly correlated among each other (96% correlation).

Both end-members, sampled at the Sinú river in Montería and at Nisperal beach, show %OC and %TN concentrations close to zero, which indicates that they include almost no organic matter. In contrast, sand plots displayed the highest %IC concentration of around 10% (Fig. 2). The lack of organic carbon in the fluvial sediments is evidence against our initial hypothesis of carbon imports to the mangrove system through sedimentation.

We obtained much higher bulk densities for basin than for fringe mangrove soil samples. Average  ~~$\pm$  standard deviation of~~ bulk density for fringe mangrove soils was ~~0.16~~ $0.15 \pm 0.02$  g cm<sup>-3</sup>, while for basin mangrove soils it was ~~1.11~~ $1.07 \pm 0.12$  g cm<sup>-3</sup> (Table 1). These values confirm previous results on the same area obtained by Bolívar (2015).

~~Differences in~~ The different bulk densities between the two forest types, multiplied by their respective % organic carbon, resulted in a completely different distribution of ~~C~~TOC compared to the previous results based on %OC alone (Table 1). A higher carbon storage in the upper layers of basin mangrove soils is clearly outlined (Table 1). ~~The differences in TOC between basin~~

~~and fringe mangrove types are significant according to the one-way analysis of~~  
~~variance test ( $p$ -value = 0.032,  $F$  = 4.88, 48 d.f.).~~ Summed across the profile,  
fringe mangroves had a TOC of  $320.04 \pm 42.61$  Mg C ha<sup>-1</sup>, and basing  
mangroves an average TOC of  $660.93 \pm 259.18$  Mg C ha<sup>-1</sup>; i.e., average TOC  
was twice as large in basin than in fringe mangroves. Across the profile, TOC  
 decreased with soil depth within the first four (basin) and three (fringe) lay-  
 ers. There was an increase in TOC for the last measured depth intervals of  
 basin and fringe soils, which can be traced back to higher %OC values of those  
 layers.

We measured a higher proportion of negative  $\delta^{13}\text{C}$  values for fringe soils  
 (-28 to -29 ‰) than for basin mangroves soils (-25 to -29 ‰) (Fig. 3). Depth  
 intervals 20-40 and 40-60 cm of basin soils show outliers with equal  $^{13}\text{C}$  val-  
 ues compared to the Sinú river end-member samples with values of around  
 -25 ‰. The sand end-member samples have the most positive  $^{13}\text{C}$  values with  
 approximately -3 ‰. Strong variations in  $^{13}\text{C}$  are conspicuous for the depth  
 intervals 20-40 and 40-60 cm of basin mangrove boxplots. We found no iden-  
 tifiable continuous trend between  $^{13}\text{C}$  values and depth. However, differences  
 in  $^{13}\text{C}$  mean values between fringe and basin mangroves ~~were statistically~~  
~~significant~~ suggest two different distributions ( $p$ -value < 0.001,  ~~$F$  = 24.35, 49~~  
~~d.f.~~  $W = 542$ ).

There were no differences between basin and fringe mangroves in terms  
 of ~~their composition of the~~ the composition of their mineral fraction (Table  
 2). The proportion of mineral soil is larger in basin than in fringe mangroves.

Fringe mangrove soils show in contrast a higher proportion of halite than basin soils.

The XRD pattern of sand samples measured from 5 to 60 °2 $\theta$  provided characteristic °2 $\theta$  intensities for the phases aragonite, calcite and quartz. The XRD measurement combined with a Rietveld refinement yielded a mineralogical composition of 95% aragonite, 4% calcite and 1% quartz. River samples showed high intensities for quartz and sodium feldspar (albite) components, as well as peaks for the clay minerals illite and clinochlore. The semi-quantitative distribution calculated by PDF data indicated that quartz is the main representative of the mineral fraction of the Sinú river soils (Fig. 4).

XRD patterns for both mangrove soils, but in particular for basin soils, showed a similar mineralogical distribution compared to the Sinú river sediments (Fig. 5). XRD patterns in fringe soils showed high intensities for halite, which was also found in basin mangrove soils, but not in a comparable distribution ratio. XRD measurements conducted on the extracted clay mineral fraction yielded peaks for the mineral phases clinochlore, illite, quartz and albite. PDF data additionally identified corundum, which is related to the ceramic panel surface composition. We found major proportions for clinochlore and quartz in the clay size fraction.

The oxalate extraction dissolved much of the poorly crystalline Fe and Al oxides from the amorphous materials, whereas the dithionite extraction dissolved the crystalline Fe oxides as well as the amorphous materials (Fig. 6). Oxalate- and dithionite extracted Al showed significant differences among

fringe and mangrove forest soils ( $p$ -value  $< 0.001$ ,  $F = 16.35$ ,  $39$  d.f.,  $W = 0.002$ ,  $W = 325$ ). Similarly, oxalate and dithionite extracted Fe showed significant differences between both soils ( $p$ -value  $< 0.001$ ,  $F = 33.45$ ,  $39$  d.f.,  $W = 364$ ). Basin soil samples had two times higher concentrations of Al ( $Al_d + Al_o$ ) than fringe soils, and five times higher Fe values. While riverine samples had similar Al and Fe concentrations than those of basin mangroves in all 4 extraction patterns, metal contents of sand samples were constantly low.  $Fe_o$  contents differed extremely for basin soils, especially for the first 2 depth intervals. Both basin and fringe soils showed an increase of metal oxides within the first depth intervals and in turn a decrease within the deeper layers.

## 4 Discussion

Our results confirmed previously observed differences in %OC, bulk density and %TOC between the basin and the fringe mangrove soils (Bolívar, 2015). Furthermore, our measurements of carbon isotopes and mineralogy helped us to ~~establish~~ explore the potential origin of the carbon stored in both mangrove types. In the following, we will discuss these difference and the potential implications of our findings.

### 4.1 Differences in carbon storage

Lower values of bulk density in fringe mangrove soils can be explained by their high organic matter content (wood residues, leaf debris and roots). Roots claim a large proportion of the soil volume, which strongly decreases bulk

density ([Bolívar, 2015](#)). Instead, basin mangrove samples of Cispatá bay are characterized by a dense silty composition including a small organic part, which results in higher bulk densities. ~~The increase in bulk density with depth in both mangrove types is likely the result of hydrostatic pressure and time inside the mangrove forest belowground. The~~

~~The~~ higher proportion of organic matter in fringe than in basin soils also leads to higher %OC values for fringe soils. Basin mangrove soils instead, are characterized by a small portion of organic topsoil. Because %TN concentrations correlate with %OC, they also show lower values for basin mangroves. That both end-members (river sediments and sand) are mostly consisting of mineral components is illustrated by their %OC contents of nearly 0 %. Because the %IC concentration of 10 % of sand samples is similar to the used pure calcium carbonate standard, we concluded that the sand end member is mostly composed of carbonates.

The decrease of %OC with soil depth is likely the result of the interaction between decomposition, vertical transport of organic matter, and leaching of dissolved carbon in water ([Elzein and Balesdent, 1995](#); [Braakhekke et al, 2013](#); [Mathieu et al, 2015](#)). Because soil microorganisms utilize nitrogen and bacteria fix nitrogen, the concentration of %TN also decreases with depth. The fact that concentrations of %OC and %TN decrease continuously with soil depth, but still show layers with higher concentrations in depths of 80-100 cm (basin) and 60-80 cm (fringe), may reflect differences in sedimentation rates over time (Bolívar, 2015). In Cispatá bay, silting processes linked to changes in the position of

the Sinú river delta, current sea level rise, flooding regime and fluvial inputs (Serrano, 2004), can generate deep organic layers that may cause the increase of %OC with depth for both mangrove types (Serrano, 2004).

Higher TOC values in basin mangrove soils reflect higher rates of organic matter accumulation. According to Bolívar (2015), the percentage of clay is similar between both mangrove types. However, the silt fraction dominates in all soil profiles in basin mangroves, while sand dominates in fringe mangrove soils. It has been well established that soil particles with greater surface area, as typical of finer textures like those found in basin mangroves, decrease drainage and decomposition of organic matter (Prasad and Ramanathan, 2008). Because TOC contents are linked to %OC, we found also an increase of TOC in depth levels of 80-100 cm (basin) and 60-80 cm (fringe).

Our results confirm previous studies that found important differences in TOC between fringe and basin mangrove soils (Bolívar, 2015). Furthermore, basin mangrove soils showed a significantly higher range of in-situ produced carbon than fringe mangrove soils, and with it a higher carbon storage of  $661 \pm 116$   $\text{MgC ha}^{-1}$  (0-100 cm) compared to  $320 \pm 60$   $\text{MgC ha}^{-1}$  (0-80 cm). Based on the %IC concentration results, we infer that marine sediments across Cispatá bay have little to no influence on additional carbon entering via tidal flooding, which is supported by the lack of %IC content in the analyzed mangrove soil samples compared to the sands of Nisperal beach.



## 4.2 Origin of carbon

$\delta^{13}\text{C}$  values of fringe mangrove sediments were more  $^{13}\text{C}$  depleted than basin sediments, which is a strong indication that this carbon is more plant derived. C3 plants fractionate  $^{13}\text{C}$  during photosynthesis, with values from -22 to -38 ‰, while C4 plants show values between -8 to -15 ‰ (Farquhar et al, 1989). *R. mangle*, a typical C3 species, mostly occurs in the fringe area of Cispatá bay (Bolívar, 2015) and is therefore the main contributor of  $^{13}\text{C}$  in this type of forest. In terms of its origin, this carbon is very likely produced in situ in the area. Basin mangrove sediments instead, show a wider range of  $\delta^{13}\text{C}$  values and more positive values. This could mean either that the basin area has a higher contribution by C4 plants (e.g. grasses), or that there is some contribution from mineral sources. Because the most common basin mangrove species, *A. germinans*, is also a C3 plant and there is likely little contribution by C4 grasses, we assumed that basin mangrove sediments have some influence by deposited sediments from the Sinú river. This assumption is also supported by the fact that basin samples tend to have more enriched  $^{13}\text{C}$  values, close to those found for the Sinú river samples (-25 ‰). According to Ruttenberg and Goni (1997) and Powers and Veldkamp (2005),  $\delta^{13}\text{C}$  values of tropical mineral soils range from -23 to -26 ‰, which would underpin mineral derived  $^{13}\text{C}$  values in Cispatá bay. Because differences in  $^{13}\text{C}$  values were significant between basin and fringe sediments, and because fringe samples only have plant derived  $^{13}\text{C}$ , we conclude that the fringe area is not influenced by the Sinú river delta.

It also does not show any influence through marine sediments, because it does not have any enriched values comparable to the sand end member (-5 ‰).

The  $\delta^{13}\text{C}$  analyses confirmed that additional carbon present in basin soils is only terrestrial and not marine derived. Moreover, it shows that additional terrestrial carbon only influences basin mangrove sediments, while carbon in fringe soils is exclusively produced in situ by the plants.

Using XRD, we found that the mineralogical composition of the sediments in Cispatá bay was similar to the composition of the Sinú river sediments in Montería. We therefore conclude that basin and fringe mangrove sediments were transported by the river and have their distant origin in that river basin. Quartz, albite and clay minerals are the major components of those sediments. Additionally, plot R5 shows intense peaks for the mineral halite in depths between 80-90 cm. Because halite crystallizes by the evaporation of sea water and intense salinization (McCaffrey et al, 1987), its occurrence verifies that the fringe mangrove area has tidal influence of hyper saline sea water. Furthermore, halite confirms the sediment's air exposition, since it needs evaporation to be formed. That halite reaches that intense proportion in depths of 80-90 cm can be attributed to the changing course of the Sinú river. According to Serrano (2004), the river course passed through the northern main land of Cispatá bay between 1849 and 1938, where plot R5 is located. Accordingly, the sedimentation rate increased in that period. However, before that period, this region was more influenced by saline sea water, which results in intense

halite peaks. That basin soils also contain halite, shows that they were also occasionally flooded.

Along with the  $^{13}\text{C}$  results, the mineralogical analyses also confirmed that basin mangrove sediments are terrestrially derived as opposed to marine derived. This finding is also reflected in higher metal oxide and hydroxide contents in basin than in fringe mangrove soils. Concentrations of iron and aluminum oxides in basin mangroves were similar to those of the Sinú river samples, which is a strong indication of fluvial deposition of inland sediments.

That mineral surfaces of Al and Fe oxides and hydroxides adsorb dissolved organic matter (DOM) has been well established (Tipping, 1981; Oades, 1988; Kaiser and Guggenberger, 2000; Mikutta et al, 2006). It is therefore very likely that metal oxides and hydroxides bind and preserve C in basin mangrove soils. According to Kaiser and Guggenberger (2000), the capacity to adsorb DOM relates to the presence of Al and Fe oxides and hydroxides. The sorption of DOM derived from decomposition to Al and Fe oxyhydroxides involves strong complexation bondings between surface metals and acidic organic ligands, particularly with those associated with aromatic structures. The strength of the sorption relates further to the surface properties of the sorbing mineral phase. Kaiser and Guggenberger (2000) found that dissolved organic matter sorption is strongly enhanced by hydrous oxide coatings and particularly by amorphous  $\text{Al}(\text{OH})_3$ , which indicates may indicate that amorphous hydroxides bind C in basin soils of Cispatá bay. Tipping (1981) describes moreover, that the extent of adsorption of DOM increases with decreasing pH. Because mangrove soils at

the Colombian Caribbean coast have an acid character both at *A. germinans* and *R. mangle* forests (Urrego et al, 2014), a stronger C binding onto oxides and hydroxides is substantiated in this region.

All together, we found no evidence for our initial hypothesis that C in mangroves of Cispatá bay, particularly in basin soils, have a large contribution from sediments transported by the Sinú river. Instead, we found that the sediments do play an important role for stabilizing in situ produced carbon, but mostly by providing mineral surfaces for C binding.

#### 4.3 Implications

Our results provide strong evidence for an important role of sediment mineralogy, particularly iron and aluminum oxides, in providing mineral surfaces for the adsorption of dissolved carbon and long-term C retention (Oades, 1988) in mangrove soils . These results add a new dimension to the more traditional studies of carbon origin in mangrove soils where the source of the carbon is considered either marine or terrestrially derived (Lacerda et al, 1995; Bouillon et al, 2008), without considering the role of sediments in dissolved carbon retention. This mechanism may play a large role in explaining observed spatial variability in carbon storage (Alongi, 2012; Jardine and Siikamäki, 2014). Also, since retention of dissolved carbon in mangrove soils can reduce rates of carbon exports to the ocean (Adame and Lovelock, 2011), mineral surfaces of sediments may provide a large potential for carbon sequestration in mangrove ecosystems located around river deltas. According to our results, carbon stor-

age can be twice as high in mangroves with dense aggregation of minerals than in more organic mangrove soils, and therefore it is very relevant to explore this carbon sequestration mechanism in other delta regions of the world.

## 5 Conclusions

Based on analyses of carbon concentration, ~~bulk density~~, stable isotopes of carbon, and mineralogy, we found that most carbon stored in soils of Cispatá Bay, Colombia, is produced in situ, with little evidence of carbon imported to the area either by fluvial or marine sedimentation. Interior basin mangroves store significantly more carbon in soils than the more ocean exposed fringe mangroves. Sediments transported by the Sinú river and deposited in the delta region contain negligible amounts of organic carbon, but the mineralogical composition of these sediments favors the adsorption of dissolved carbon on charged mineral surfaces, which explains the larger levels of C storage in this type of mangroves.

Our study highlights the importance of fluvial sediment transport in providing a substrate for carbon stabilization through mineral protection. This mechanism for soil carbon storage has been little studied previously in mangrove ecosystems, but it has large implications for determining their potential for long-term carbon sequestration.

**Acknowledgements** We would like to thank Prof. Dr. Juraž Majzlan for providing mentoring and access to the XRD lab at the Friedrich-Schiller-Universität Jena. Thanks to INVEMAR Colombia, particularly Paula C. Sierra, for facilitating logistics and access to

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427 the research site. Financial support was provided by the Alexander von Humboldt Founda-  
428 tion through the International Climate Protection Fellowship, and the Max Planck Institute  
429 for Biogeochemistry.

430 **Figures**

**Fig. 1** Sampling plots in Cispatá Bay and Montería, Colombia, ArcGIS-source: <http://www.diva-gis.org/gdata>; accessed on June 07, 2016; fringe plots: P21, R1, R4, R5, R6; basin plots: P16, C1, C2, C3, C4; end-members: Sand Nisperal, Sinú riverbed

**Fig. 2** Observed values of percent inorganic carbon (%IC) for both mangrove types and end members; and percent organic carbon (%OC) and percent nitrogen (%TN) by sampling depth aggregated across plots.

**Fig. 3** Measured  $\delta^{13}\text{C}$  in a) mangrove types and end members, b) basin mangroves by depth, and c) fringe mangroves by depth.

**Fig. 4** Two exemplary XRD patterns ( $\lambda = 1.5406 \text{ \AA}$ ) of both measured end-members: Nisperal beach and Sinú river; figures also include semi-quantitative distribution of detected minerals

**Fig. 5** Two exemplary XRD patterns ( $\lambda = 1.5406 \text{ \AA}$ ) for the fringe (left) and basin (right) mangrove soils; figures also include semi-quantitative distribution of detected minerals

**Fig. 6** Oxalate (o)- and dithionite (d) extracted metal oxides for each mangrove type and soil depth.

431 **Tables****Table 1** Percent organic carbon, bulk density and total organic carbon by mangrove type and soil depth. Values in parentheses indicate standard deviation

Mangrove type	Depth [cm]	OC [%]	Bulk density [g/cm <sup>3</sup> ]	TOC [MgC/ha]
Basin	0-20	14.63 (10.09)	1.01 (0.06)	295.61 (203.77)
	20-40	7.12 (7.19)	1.25 (0.10)	161.99 (147.07)
	40-60	3.22 (1.93)	1.06 (0.19)	68.35 (40.95)
	60-80	2.96 (1.39)	1.10 (0.16)	65.21 (30.58)
	80-100	4.15 (2.24)	0.84 (0.08)	69.78 (37.60)
Fringe	0-20	31.32 (2.82)	0.16 (0.01)	100.24 (9.03)
	20-40	23.61 (8.70)	0.13 (0.02)	62.79 (22.56)
	40-60	16.12 (10.92)	0.16 (0.05)	51.57 (34.94)
	60-80	29.29 (0.55)	0.18 (0.01)	105.44 (1.99)

**Table 2** General mineralogical composition of sediments in Cispatá Bay as measured by XRD analyses.

Class	Mineral	Formula
Silicates	Clinochlore	(Mg,Fe <sup>2+</sup> ) <sub>5</sub> Al(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>8</sub>
	Illite	(K,H <sub>3</sub> O)Al <sub>2</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (H <sub>2</sub> O,OH) <sub>2</sub>
	Albite	NaAlSi <sub>3</sub> O <sub>8</sub>
Oxides/hydrox.	Quartz	SiO <sub>2</sub>
Carbonates	Aragonite	CaCO <sub>3</sub>
	Calcite	CaCO <sub>3</sub>
Halides	Halite	NaCl



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