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Stabilization of carbon in mineral soils from mangroves

of the Sinú river delta, Colombia

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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

4 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

 $_{7}\,\,$  of soil carbon in basin mangroves is due to sedimentation. We determined total

organic carbon content (TOC) of  $661 \pm 116 \; \mathrm{MgC \; ha^{-1}}$  for basin soils up to

a sampling depth of 1 m, and 320  $\pm$  60 MgC ha<sup>-1</sup> for fringe soils up to 80

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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 ( $\delta^{13}$ C), 11 the origin of the sediments and their carbon was determined. We found that basin soils in Cispatá bay show similar mineralogical composition than those 13 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 15 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 17 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 19 providing binding surfaces for the stabilization of organic carbon.

- Keywords soil organic carbon  $\cdot$  stable isotopes  $\cdot$  iron and aluminum oxides  $\cdot$
- $_{22}$  soil mineralogy  $\cdot$  estuarine ecosystems

#### 23 1 Introduction

- 24 Although mangroves are ecosystems with some of the largest levels of carbon
- storage on earth (Donato et al, 2011; Alongi, 2012), there are large varia-
- 26 tions 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  $ha^{-1}$  in the belowground and soil
- 29 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
- $_{31}$  main determinants of observed differences in soil C storage across diverse man-

grove 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±40 Mg C ha<sup>-1</sup>, while for the fringe mangroves this value is only 95±9 Mg C ha<sup>-1</sup>. 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.

Here, our main objective was to determine the origin of the relatively high 55 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 58 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 ( $\delta^{13}$ C) of soil carbon provides information on whether riverine sediments are a main source of C in Cisipatá bay, Colombia; and 2) 62 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.

#### <sup>69</sup> 2 Materials and methods

## 70 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 charac-

74 terized by the Sinú river delta and a complex estuarine lagoon system that

75 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

<sup>81</sup> racemosa occurs in both forest types.

#### 82 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 84 (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 (Eijkelkamp 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 91 cores of the Sinú river near the city of Montería, which is located 70 km south 92 from Cispatá bay (Fig. 1). Generally, cores without layer changes were divided into sections every 20 cm to explore differences of 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.

#### 106 2.3 Laboratory analyses

After collection, samples were oven-dried at  $70^{\circ}$ C for 5 days. Samples for bulk density measurements were oven dried at  $105^{\circ}$ 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 112 (%TN) in all samples by dry combustion (Vario Max, Elementar Analysensys-113 teme GmbH, Hanau, Germany). Organic carbon was later removed by ignition 114 at 450°C for 16 hours, and inorganic carbon (%IC) was then determined using 115 the same elemental analyzer. Organic carbon concentrations were estimated 116 by subtracting %IC from %TC. TOC contents (Mg ha<sup>-1</sup>) were calculated us-117 ing the obtained bulk densities for basin and fringe mangrove soils multiplied 118 by each plot depth interval (cm) and %OC. 119

We used  $\delta^{13}$ C values of the sampled material and compared them with the  $^{13}$ C/ $^{12}$ C ratio of the two chosen end-members as indicators for the origin of the carbon (Fry, 2006). We measured  $^{13}$ 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 128 quantitative phase analyses (Spieß et al, 2009) on 12 representative samples including 4 end-member samples, and 4 samples of basin and fringe mangroves 130 each. Samples were measured 20 min each, from 5 to 60 °2θ. We determined 131 each mineral phase using the powder diffraction file (PDF) data. We also 132 conducted a Rietveld refinement using the Topas software for XRD analysis 133 (Bruker Corporation). To define the type of clays included in the samples, 134 we further measured each sample before extracting clay fraction from 3 to 135 70 °2θ using ceramic panels. XRD analyses were conducted at the laboratory 136 for Mineralogy and Geochemistry of the Friedrich-Schiller University in Jena, 137 Germany. 138

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 nitrogen,  $\delta^{13}$ C, Fe- and Al-oxides, among the fringe and basin 151 mangroves. After an initial test for normality (Shapiro-Wilk test), we found little evidence to support the normality assumption required in common tools 153 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 (Hollan-155 der et al, 2015) under the null hypothesis that the samples from the fringe and 156 basin mangroves differ by a shift location  $\mu = 0$ , and the alternative hypothesis 157 that they different by some other shift location. In other words, the test helps to 158 determine whether the samples from the two different mangrove types belong 159 to the same statistical distribution as stated in the null hypothesis. Data and 160 code to reproduce all results presented here can be obtained from the following 161  $repository\ \verb|https://github.com/crlsierra/mangroveCstabilization.git|.$ 162

#### 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, with a more clear trend for %OC than %TN.

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  $0.15 \pm 0.02$  g cm<sup>-3</sup>, 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).

Differences in bulk densities between the two forest types, multiplied by % organic carbon, resulted in a completely different distribution of C 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  $387.77 \pm 125.77$  Mg C ha<sup>-1</sup>, and basing mangroves an average TOC of  $665.41 \pm 434.65$  Mg C ha<sup>-1</sup>. Given this large variability, we did not find enough evidence to reject the hypothesis

that TOC from these two forest types are sampled from the same distribution (p-value = 0.47, W = 350). 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  $\delta^{13}$ C values for fringe soils 191 (-28 to -29 ‰) than for basin mangroves soils (-25 to -29 ‰) (Fig. 3). Depth 192 intervals 20-40 and 40-60 cm of basin soils show outliers with equal  $^{13}\mathrm{C}$  values 193 compared to the Sinú river end-member samples with values of around -25 \%. 194 The sand end-member samples have the most positive <sup>13</sup>C values with approx-195 imately -3 ‰. Strong variations in <sup>13</sup>C are conspicuous for the depth intervals 196 20-40 and 40-60 cm of basin mangrove boxplots. We found no identifiable 197 continuous trend between <sup>13</sup>C values and depth. However, differences in <sup>13</sup>C 198 mean values between fringe and basin mangroves were statistically significant 199 (p-value < 0.001, F = 24.35, 49 d.f.).

There were no differences between basin and fringe mangroves in terms of their composition of the 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 °2θ provided characteristic °2θ 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).

213 XRD patterns for both mangrove soils, but in particular for basin soils,
214 showed a similar mineralogical distribution compared to the Sinú river sedi215 ments (Fig. 5). XRD patterns in fringe soils showed high intensities for halite,
216 which was also found in basin mangrove soils, but not in a comparable dis217 tribution ratio. XRD measurements conducted on the extracted clay mineral
218 fraction yielded peaks for the mineral phases clinochlore, illite, quartz and
219 albite. PDF data additionally identified corundum, which is related to the ce220 ramic panel surface composition. We found major proportions for clinochlore
221 and quartz in the clay size fraction.

The oxalate extraction dissolved much of the poorly crystalline Fe and Al 222 oxides from the amorphous materials, whereas the dithionite extraction dissolved the crystalline Fe oxides as well as the amorphous materials (Fig. 6). 224 Oxalate- and dithionite extracted Al showed significant differences among 225 fringe and mangrove forest soils (p-value < 0.001, F = 16.35, 39 d.f.). Similarly, 226 oxalate and dithionite extracted Fe showed significant differences between both 227 soils (p-value < 0.001, F = 33.45, 39 d.f.). Basin soil samples had two times 228 higher concentrations of Al  $(Al_d+Al_o)$  than fringe soils, and five times higher 229 Fe values. While riverine samples had similar Al and Fe concentrations than 230 those of basin mangroves in all 4 extraction patterns, metal contents of sand 231

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 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 259 between decomposition, vertical transport of organic matter, and leaching of 260 dissolved carbon in water (Elzein and Balesdent, 1995; Braakhekke et al, 2013; 261 Mathieu et al, 2015). Because soil microorganisms utilize nitrogen and bac-262 teria fix nitrogen, the concentration of %TN also decreases with depth. The fact that concentrations of %OC and %TN decrease continuously with soil 264 depth, but still show layers with higher concentrations in depths of 80-100 cm 265 (basin) and 60-80 cm (fringe), may reflect differences in sedimentation rates 266 over time (Bolívar, 2015). In Cispatá bay, silting processes linked to changes in 267 the position of the Sinú river delta, current sea level rise, flooding regime and 268 fluvial inputs, can generate deep organic layers that may cause the increase of 269 %OC with depth for both mangrove types (Serrano, 2004). 270

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 276 and decomposition of organic matter (Prasad and Ramanathan, 2008). Because TOC contents are linked to %OC, we found also an increase of TOC in 278 depth levels of 80-100 cm (basin) and 60-80 cm (fringe). 279 Our results confirm previous studies that found important differences in 280 TOC between fringe and basin mangrove soils (Bolívar, 2015). Furthermore, 281 basin mangrove soils showed a significantly higher range of in-situ produced 282 carbon than fringe mangrove soils, and with it a higher carbon storage of 283  $661\pm116 \text{ MgC ha}^{-1} \text{ (0-100 cm) compared to } 320\pm60 \text{ MgC ha}^{-1} \text{ (0-80 cm)}.$ 284 Based on the %IC concentration results, we infer that marine sediments across Cispatá bay have no influence on additional carbon entering via tidal flooding, 286 which is supported by the lack of %IC content in the analyzed mangrove soil 287 samples compared to the sands of Nisperal beach.

#### <sup>289</sup> 4.2 Origin of carbon

 $\delta^{13}$ C values of fringe mangrove sediments were more  $^{13}$ C depleted than basin sediments, which is a strong indication that this carbon is more plant derived. C3 plants fractionate  $^{13}$ 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  $^{13}$ 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  $\delta^{13}$ C values and more positive values. This could mean either that the basin area has a 298 higher contribution by C4 plants (e.g. grasses), or that there is some contribution from mineral sources. Because the most common basin mangrove species, 300 A. germinans, is also a C3 plant and there is likely little contribution by C4 301 grasses, we assumed that basin mangrove sediments have some influence by 302 deposited sediments from the Sinú river. This assumption is also supported 303 by the fact that basin samples tend to have more enriched <sup>13</sup>C values, close to 304 those found for the Sinú river samples (-25 ‰). According to Ruttenberg and 305 Goni (1997) and Powers and Veldkamp (2005),  $\delta^{13}$ C values of tropical mineral 306 soils range from -23 to -26 \%, which would underpin mineral derived <sup>13</sup>C val-307 ues in Cispatá bay. Because differences in <sup>13</sup>C values were significant between 308 basin and fringe sediments, and because fringe samples only have plant derived 309 <sup>13</sup>C, we conclude that the fringe area is not influenced by the Sinú river delta. 310 It also does not show any influence through marine sediments, because it does 311 not have any enriched values comparable to the sand end member (-5 \%). 312

The  $\delta^{13}$ 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. 321 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 323 and intense salinization (McCaffrey et al, 1987), its occurrence verifies that the 324 fringe mangrove area has tidal influence of hyper saline sea water. Furthermore, 325 halite confirms the sediment air exposition, since it needs evaporation to be formed. That halite reaches that intense proportion in depths of 80-90 cm can 327 be attributed to the changing course of the Sinú river. According to Serrano (2004), the river course passed the northern main land of Cispatá bay between 329 1849 and 1938, where plot R5 is located. Accordingly, the sedimentation rate increased in that period. However, before that period, this region was more 331 influenced by saline sea water, which results in intense halite peaks. That basin 332 soils also contain halite, shows that they were also occasionally flooded. 333

Along with the <sup>13</sup>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 344 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 346 complexation bondings between surface metals and acidic organic ligands, particularly with those associated with aromatic structures. The strength of the 348 sorption relates further to the surface properties of the sorbing mineral phase. Kaiser and Guggenberger (2000) found that dissolved organic matter sorption 350 is strongly enhanced by hydrous oxide coatings and particularly by amorphous 351 Al(OH)<sub>3</sub>, which indicates that amorphous hydroxides bind C in basin soils of 352 Cispatá bay. Tipping (1981) describes moreover, that the extent of adsorp-353 tion of DOM increases with decreasing pH. Because mangrove soils at the 354 Colombian Caribbean coast have an acid character both at A. germinans and 355 R. mangle forests (Urrego et al, 2014), a stronger C binding onto oxides and 356 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 365 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 367 studies of carbon origin in mangrove soils where the source of the carbon is considered either marine or terrestrially derived (Lacerda et al, 1995; Bouil-369 lon et al, 2008), without considering the role of sediments in dissolved carbon retention. This mechanism may play a large role in explaining observed spa-371 tial variability in carbon storage (Alongi, 2012; Jardine and Siikamäki, 2014). Also, since retention of dissolved carbon in mangrove soils can reduce rates of 373 carbon exports to the ocean (Adame and Lovelock, 2011), mineral surfaces of 374 sediments may provide a large potential for carbon sequestration in mangrove 375 ecosystems located around river deltas. According to our results, carbon stor-376 age can be twice as high in mangroves with dense aggregation of minerals than 377 in more organic mangrove soils, and therefore it is very relevant to explore this 378 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 for long-term carbon sequestration.

fluvial or marine sedimentation. Interior basin mangroves store significantly more carbon in soils than the more ocean exposed fringe mangroves. Sedi-385 ments transported by the Sinú river and deposited in the delta region contain negligible amounts of organic carbon, but the mineralogical composition of 387 these sediments favors the adsorption of dissolved carbon on charged mineral 388 surfaces, which explains the larger levels of C storage in this type of mangroves. 389 Our study highlights the importance of fluvial sediment transport in providing a substrate for carbon stabilization through mineral protection. This 391 mechanism for soil carbon storage has been little studied previously in mangrove ecosystems, but it has large implications for determining their potential 393

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## Figures 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  $\delta^{13}$ 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 ( $\lambda=1.5406$  Å) 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 ( $\lambda = 1.5406$  Å) 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.

# 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	$({\rm Mg,Fe^{2+}})_5{\rm Al}({\rm Si_3Al}){\rm O_{10}}({\rm OH})_8$
	Illite	$(K,\!H_3O)Al_2(Si_3Al)O_{10}(H_2O,\!OH)_2$
	Albite	$NaAlSi_3O_8$
Oxides/hydrox.	Quartz	$SiO_2$
Carbonates	Aragonite	CaCO <sub>3</sub>
	Calcite	$CaCO_3$
Halides	Halite	NaCl

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