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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

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 deter-

mined total organic carbon content (TOC) as $660.93 \pm 259.18 \,\mathrm{MgC} \,\mathrm{ha}^{-1}$ for

basin soils up to a sampling depth of 1 m, and as $259 \pm 42.61 \,\mathrm{MgC} \,\mathrm{ha}^{-1}$ 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 11 analyses of carbon (δ^{13} C), the origin of the sediments and their carbon was determined. We found that basin soils in Cispatá bay show similar mineralog-13 ical 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 15 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 17 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. 21

- Keywords soil organic carbon \cdot stable isotopes \cdot iron and aluminum oxides \cdot
- 23 soil mineralogy · estuarine ecosystems

24 1 Introduction

- 25 Although mangroves are ecosystems with some of the largest levels of carbon
- 26 storage on earth (Donato et al, 2011; Alongi, 2012), there are large varia-
- 27 tions on the amount of C stored in various systems, particularly soils. For
- 28 instance, mangrove ecosystems dominated by Rhizophora spp. in Peninsular
- ²⁹ Malaysia store between 479 to 2205 Mg C ha⁻¹ 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

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- 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 33 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 37 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⁻¹, while for the fringe mangroves this value is only $95\pm9~\mathrm{Mg~C~ha^{-1}}$. These numbers, particularly for the basin mangroves, are in the upper range of values observed for other systems (Donato 43 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 δ^{13} 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 (δ^{13} 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.

⁷⁵ 2 Materials and methods

76 2.1 Study site

77 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 81 this area. The Sinú river has its origin in the northern part of the western 82 Andean mountains, and between 1938 and 1945 changed its course creating a 83 new delta (Serrano, 2004). The current estuarine mangrove system was established in the previous river delta. Fringe forests are dominated by Rhizophora 85 mangle, basin forests are dominated by Avicennia germinans. Laguncularia racemosa occurs in both forest types.

88 2.2 Field sampling

- Our sampling focused on a set of existing plots previously established to de-
- 50 termine the carbon sequestration potential of the mangroves of Cispatá bay
- 91 (Bolívar, 2015). We sampled 10 plots of 500 m² up to 1 m in depth from March
- 92 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
- 95 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 cm³. 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.

113 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 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 (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 δ^{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 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 °2θ. 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 141 measured each sample before extracting clay fraction from 3 to 70 °2θ using ceramic panels. XRD analyses were conducted at the laboratory for Mineralogy 143 and Geochemistry of the Friedrich-Schiller University in Jena, Germany. We determined iron and aluminum in acid-ammonium-oxalate extracts 145 (pH 3.0) and in sodium-citrate-dithionite extracts (pH 7.3) (Schwertmann, 146 1964; Holmgren, 1967). We selected 46 samples and 2 standard soils for these 147 measurements. While sodium dithionite was used to extract both crystalline 148 and amorphous oxides, the oxalate method extracted only amorphous oxides. The actual measurement of crystalline and amorphous iron and aluminium 150 oxides was performed using an atomic emission spectrometer with inductive 151 coupled plasma (ICP-AES, Optima 3300DV, PerkinElmer, Norwalk, USA). 152 These analyses were performed at the SpecLab of the Max Planck Institute 153 for Biogeochemistry. 154

155 2.4 Data analysis

We performed statistical tests to determine differences in organic carbon concentrations, total organic carbon, δ^{13} 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.

170 3 Results

We found important differences between fringe and basin mangroves in terms 171 of %OC (p-value < 0.001; two-sample Wilcoxon W-test, W = 62) and %TN 172 (p-value < 0.001, W = 102) (Fig. 2). In general, %OC and %TN decreased 173 with soil depth and were highly correlated among each other (96% correlation). 174 Both end-members, sampled at the Sinú river in Montería and at Nisperal 175 beach, show %OC and %TN concentrations close to zero, which indicates that 176 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 178 in the fluvial sediments is evidence against our initial hypothesis of carbon imports to the mangrove system through sedimentation. 180

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 ± 0.02 g cm⁻³, while for basin mangrove soils it was 1.07 ± 0.12

 $_{184}$ g cm $^{-3}$ (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 186 their respective % organic carbon, resulted in a completely different distribution of TOC compared to the previous results based on %OC alone (Table 1). 188 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 190 $320.04 \pm 42.61 \,\mathrm{Mg} \,\mathrm{C} \,\mathrm{ha}^{-1}$, and basing mangroves an average TOC of 660.93 191 \pm 259.18 Mg C ha⁻¹; i.e., average TOC was twice as large in basin than in 192 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 194 for the last measured depth intervals of basin and fringe soils, which can be traced back to higher %OC values of those layers. 196

We measured a higher proportion of negative δ^{13} C values for fringe soils 197 (-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 ¹³C val-199 ues compared to the Sinú river end-member samples with values of around 200 -25 \%. The sand end-member samples have the most positive ¹³C values with 201 approximately -3 \%. Strong variations in \(^{13}\text{C}\) are conspicuous for the depth 202 intervals 20-40 and 40-60 cm of basin mangrove boxplots. We found no iden-203 tifiable continuous trend between ¹³C values and depth. However, differences 204 in ¹³C mean values between fringe and basin mangroves suggest two different 205 distributions (p-value < 0.001, W = 542). 206

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 °2θ provided 211 characteristic °2θ intensities for the phases aragonite, calcite and quartz. The 212 XRD measurement combined with a Rietveld refinement yielded a mineralog-213 ical composition of 95% aragonite, 4% calcite and 1% quartz. River samples 214 showed high intensities for quartz and sodium feldspar (albite) components, as 215 well as peaks for the clay minerals illite and clinochlore. The semi-quantitative 216 distribution calculated by PDF data indicated that quartz is the main repre-217 sentative of the mineral fraction of the Sinú river soils (Fig. 4). 218

219 XRD patterns for both mangrove soils, but in particular for basin soils,
220 showed a similar mineralogical distribution compared to the Sinú river sedi221 ments (Fig. 5). XRD patterns in fringe soils showed high intensities for halite,
222 which was also found in basin mangrove soils, but not in a comparable dis223 tribution ratio. XRD measurements conducted on the extracted clay mineral
224 fraction yielded peaks for the mineral phases clinochlore, illite, quartz and
225 albite. PDF data additionally identified corundum, which is related to the ce226 ramic panel surface composition. We found major proportions for clinochlore
227 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 231 fringe and mangrove forest soils (p-value = 0.002, W = 325). Similarly, oxalate and dithionite extracted Fe showed significant differences between both soils 233 (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. 235 While riverine samples had similar Al and Fe concentrations than those of basin mangroves in all 4 extraction patterns, metal contents of sand samples 237 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 239 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 257 characterized by a small portion of organic topsoil. Because %TN concentrations correlate with %OC, they also show lower values for basin mangroves. 250 That both end-members (river sediments and sand) are mostly consisting of 260 mineral components is illustrated by their %OC contents of nearly 0 %. Be-261 cause the %IC concentration of 10 % of sand samples is similar to the used 262 pure calcium carbonate standard, we concluded that the sand end member is 263 mostly composed of carbonates. 264

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

272 (basin) and 60-80 cm (fringe), may reflect differences in sedimentation rates 273 over time (Bolívar, 2015). In Cispatá bay, silting processes linked to changes 274 in the position of the Sinú river delta, current sea level rise, flooding regime 275 and fluvial inputs (Serrano, 2004), can generate deep organic layers that may 276 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, 287 basin mangrove soils showed a significantly higher range of in-situ produced 288 carbon than fringe mangrove soils, and with it a higher carbon storage of 289 $661 \pm 259 \; \mathrm{MgC \; ha^{-1}} \; (0\text{-}100 \; \mathrm{cm}) \; \mathrm{compared \; to \; 320 \, \pm \, 43 \; MgC \; ha^{-1}} \; (0\text{-}80 \; \mathrm{cm})$ 290 cm). Based on the %IC concentration results, we infer that marine sediments 291 across Cispatá bay have little to no influence on additional carbon entering via 292 tidal flooding, which is supported by the lack of %IC content in the analyzed 293 mangrove soil samples compared to the sands of Nisperal beach.

295 4.2 Origin of carbon

 δ^{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. 297 C3 plants fractionate ¹³C during photosynthesis, with values from -22 to -38 ‰, while C4 plants show values between -8 to -15 \% (Farguhar et al, 1989). R. 299 mangle, a typical C3 species, mostly occurs in the fringe area of Cispatá bay (Bolívar, 2015) and is therefore the main contributor of ¹³C in this type of 301 forest. In terms of its origin, this carbon is very likely produced in situ in the 302 area. Basin mangrove sediments instead, show a wider range of δ^{13} C values 303 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 contribu-305 tion from mineral sources. Because the most common basin mangrove species, 306 A. germinans, is also a C3 plant and there is likely little contribution by C4 307 grasses, we assumed that basin mangrove sediments have some influence by 308 deposited sediments from the Sinú river. This assumption is also supported 309 by the fact that basin samples tend to have more enriched ¹³C values, close to 310 those found for the Sinú river samples (-25 %). According to Ruttenberg and 311 Goni (1997) and Powers and Veldkamp (2005), δ^{13} C values of tropical mineral 312 soils range from -23 to -26 %, which would underpin mineral derived $^{13}\mathrm{C}$ val-313 ues in Cispatá bay. Because differences in ¹³C values were significant between 314 basin and fringe sediments, and because fringe samples only have plant derived 315 ¹³C, we conclude that the fringe area is not influenced by the Sinú river delta. 316

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 δ^{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 323 in Cispatá bay was similar to the composition of the Sinú river sediments in Montería. We therefore conclude that basin and fringe mangrove sediments 325 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. 327 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 329 and intense salinization (McCaffrey et al, 1987), its occurrence verifies that the fringe mangrove area has tidal influence of hyper saline sea water. Furthermore, 331 halite confirms the sediment's air exposition, since it needs evaporation to 332 be formed. That halite reaches that intense proportion in depths of 80-90 333 cm can be attributed to the changing course of the Sinú river. According to 334 Serrano (2004), the river course passed through the northern main land of 335 Cispatá bay between 1849 and 1938, where plot R5 is located. Accordingly, 336 the sedimentation rate increased in that period. However, before that period, 337 this region was more influenced by saline sea water, which results in intense 338

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

Along with the ¹³C 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; 348 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. 350 According to Kaiser and Guggenberger (2000), the capacity to adsorb DOM 351 relates to the presence of Al and Fe oxides and hydroxides. The sorption of 352 DOM derived from decomposition to Al and Fe oxyhydroxides involves strong complexation bondings between surface metals and acidic organic ligands, par-354 ticularly with those associated with aromatic structures. The strength of the 355 sorption relates further to the surface properties of the sorbing mineral phase. 356 Kaiser and Guggenberger (2000) found that dissolved organic matter sorption 357 is strongly enhanced by hydrous oxide coatings and particularly by amorphous 358 Al(OH)₃, which may indicate that amorphous hydroxides bind C in basin soils 359 of Cispatá bay. Tipping (1981) describes moreover, that the extent of adsorption of DOM increases with decreasing pH. Because mangrove soils at the 361

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.

370 4.3 Implications

Our results provide strong evidence for an important role of sediment mineral-371 ogy, particularly iron and aluminum oxides, in providing mineral surfaces for 372 the adsorption of dissolved carbon and long-term C retention (Oades, 1988) 373 in mangrove soils . These results add a new dimension to the more traditional 374 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-376 lon et al, 2008), without considering the role of sediments in dissolved carbon 377 retention. This mechanism may play a large role in explaining observed spa-378 tial variability in carbon storage (Alongi, 2012; Jardine and Siikamäki, 2014). 379 Also, since retention of dissolved carbon in mangrove soils can reduce rates of 380 carbon exports to the ocean (Adame and Lovelock, 2011), mineral surfaces of 381 sediments may provide a large potential for carbon sequestration in mangrove 382 ecosystems located around river deltas. According to our results, carbon stor-383

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 389 produced in situ, with little evidence of carbon imported to the area either by 390 fluvial or marine sedimentation. Interior basin mangroves store significantly 391 more carbon in soils than the more ocean exposed fringe mangroves. Sedi-392 ments transported by the Sinú river and deposited in the delta region contain 393 negligible amounts of organic carbon, but the mineralogical composition of 394 these sediments favors the adsorption of dissolved carbon on charged mineral 395 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 398 mechanism for soil carbon storage has been little studied previously in mangrove ecosystems, but it has large implications for determining their potential 400 for long-term carbon sequestration.

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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 δ^{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.

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 ³]	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	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$
	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 ₃
	Calcite	$CaCO_3$
Halides	Halite	NaCl

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