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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⁻¹ 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 (δ^{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⁻¹, while for the fringe mangroves this value is only 95±9 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 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.

⁷⁴ 2 Materials and methods

75 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.

87 2.2 Field sampling

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

112 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 118 (%TN) in all samples by dry combustion (Vario Max, Elementar Analysensys-119 teme GmbH, Hanau, Germany). Organic carbon was later removed by ignition 120 at $450^{\circ}\mathrm{C}$ for 16 hours, and inorganic carbon (%IC) was then determined using 121 the same elemental analyzer. Organic carbon concentrations were estimated 122 by subtracting %IC from %TC. TOC contents (Mg ha⁻¹) were calculated us-123 ing the obtained bulk densities for basin and fringe mangrove soils multiplied 124 by each plot depth interval (cm) and %OC. 125

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 140 measured each sample before extracting clay fraction from 3 to 70 °2θ using ceramic panels. XRD analyses were conducted at the laboratory for Mineralogy 142 and Geochemistry of the Friedrich-Schiller University in Jena, Germany. We determined iron and aluminum in acid-ammonium-oxalate extracts 144 (pH 3.0) and in sodium-citrate-dithionite extracts (pH 7.3) (Schwertmann, 145 1964; Holmgren, 1967). We selected 46 samples and 2 standard soils for these 146 measurements. While sodium dithionite was used to extract both crystalline 147 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 150 coupled plasma (ICP-AES, Optima 3300DV, PerkinElmer, Norwalk, USA). 151 These analyses were performed at the SpecLab of the Max Planck Institute 152 for Biogeochemistry. 153

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.

169 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 ± 0.02 g cm⁻³, while for basin mangrove soils it was 1.07 ± 0.12

 $_{183}$ 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 185 their respective % organic carbon, resulted in a completely different distribution of TOC compared to the previous results based on %OC alone (Table 1). 187 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 189 $387.77 \pm 125.77 \,\mathrm{Mg}\,\mathrm{C}\,\mathrm{ha}^{-1}$, and basing mangroves an average TOC of 665.41 \pm 434.65 Mg C $\rm ha^{-1}.$ Given this large variability, and deespite average TOC 191 being almost twice as high in the basing than in the fringe mangroves, we did 192 not find enough evidence to reject the hypothesis that TOC from these two for-193 est 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) 195 layers. There was an increase in TOC for the last measured depth intervals 196 of basin and fringe soils, which can be traced back to higher %OC values of 197 those layers. 198

We measured a higher proportion of negative δ^{13} 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 C values compared to the Sinú river end-member samples with values of around -25 ‰. The sand end-member samples have the most positive 13 C values with approximately -3 ‰. Strong variations in 13 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 C values and depth. However, differences in 13 C mean values between fringe and basin mangroves suggest two different distributions (p-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 °20 provided characteristic °20 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 ce-

ramic 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 230 oxides from the amorphous materials, whereas the dithionite extraction dis-231 solved the crystalline Fe oxides as well as the amorphous materials (Fig. 6). 232 Oxalate- and dithionite extracted Al showed significant differences among 233 fringe and mangrove forest soils (p-value = 0.002, W = 325). Similarly, oxalate and dithionite extracted Fe showed significant differences between both soils 235 (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. 237 While riverine samples had similar Al and Fe concentrations than those of basin mangroves in all 4 extraction patterns, metal contents of sand samples 239 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 241 of metal oxides within the first depth intervals and in turn a decrease within the deeper layers. 243

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 bac-

teria 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, 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 279 matter accumulation. According to Bolívar (2015), the percentage of clay is similar between both mangrove types. However, the silt fraction dominates in 281 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 283 typical of finer textures like those found in basin mangroves, decrease drainage 284 and decomposition of organic matter (Prasad and Ramanathan, 2008). Be-285 cause TOC contents are linked to %OC, we found also an increase of TOC in 286 depth levels of 80-100 cm (basin) and 60-80 cm (fringe). 287

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±116 MgC ha⁻¹ (0-100 cm) compared to 320±60 MgC ha⁻¹ (0-80 cm).
Based on the %IC concentration results, we infer that marine sediments across

Cispatá bay have 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

 δ^{13} C values of fringe mangrove sediments were more 13 C depleted than basin 298 sediments, which is a strong indication that this carbon is more plant derived. C3 plants fractionate ¹³C during photosynthesis, with values from -22 to -38 ‰, 300 while C4 plants show values between -8 to -15 % (Farguhar et al, 1989). R. 301 mangle, a typical C3 species, mostly occurs in the fringe area of Cispatá bay 302 (Bolívar, 2015) and is therefore the main contributor of ¹³C in this type of forest. In terms of its origin, this carbon is very likely produced in situ in the 304 area. Basin mangrove sediments instead, show a wider range of δ^{13} C values 305 and more positive values. This could mean either that the basin area has a 306 higher contribution by C4 plants (e.g. grasses), or that there is some contribution from mineral sources. Because the most common basin mangrove species, 308 A. germinans, is also a C3 plant and there is likely little contribution by C4 309 grasses, we assumed that basin mangrove sediments have some influence by 310 deposited sediments from the Sinú river. This assumption is also supported 311 by the fact that basin samples tend to have more enriched ¹³C values, close to 312 those found for the Sinú river samples (-25 ‰). According to Ruttenberg and 313 Goni (1997) and Powers and Veldkamp (2005), δ^{13} C values of tropical mineral 314 soils range from -23 to -26 ‰, which would underpin mineral derived ¹³C val-315

ues in Cispatá bay. Because differences in ¹³C values were significant between
basin and fringe sediments, and because fringe samples only have plant derived
¹³C, 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 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 325 in Cispatá bay was similar to the composition of the Sinú river sediments in Montería. We therefore conclude that basin and fringe mangrove sediments 327 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. 329 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 331 and intense salinization (McCaffrey et al, 1987), its occurrence verifies that the 332 fringe mangrove area has tidal influence of hyper saline sea water. Furthermore, 333 halite confirms the sediment air exposition, since it needs evaporation to be 334 formed. That halite reaches that intense proportion in depths of 80-90 cm can 335 be attributed to the changing course of the Sinú river. According to Serrano 336 (2004), the river course passed the northern main land of Cispatá bay between 337 1849 and 1938, where plot R5 is located. Accordingly, the sedimentation rate 338

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 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 348 organic matter (DOM) has been well established (Tipping, 1981; Oades, 1988; Kaiser and Guggenberger, 2000; Mikutta et al, 2006). It is therefore very likely 350 that metal oxides and hydroxides bind and preserve C in basin mangrove soils. 351 According to Kaiser and Guggenberger (2000), the capacity to adsorb DOM 352 relates to the presence of Al and Fe oxides and hydroxides. The sorption of 353 DOM derived from decomposition to Al and Fe oxyhydroxides involves strong 354 complexation bondings between surface metals and acidic organic ligands, par-355 ticularly with those associated with aromatic structures. The strength of the 356 sorption relates further to the surface properties of the sorbing mineral phase. 357 Kaiser and Guggenberger (2000) found that dissolved organic matter sorption 358 is strongly enhanced by hydrous oxide coatings and particularly by amorphous 359 Al(OH)₃, which indicates that amorphous hydroxides bind C in basin soils of 360 Cispatá bay. Tipping (1981) describes moreover, that the extent of adsorp-361

tion 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.

71 4.3 Implications

Our results provide strong evidence for an important role of sediment mineral-372 ogy, particularly iron and aluminum oxides, in providing mineral surfaces for 373 the adsorption of dissolved carbon and long-term C retention (Oades, 1988) 374 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 376 considered either marine or terrestrially derived (Lacerda et al, 1995; Bouil-377 lon et al, 2008), without considering the role of sediments in dissolved carbon 378 retention. This mechanism may play a large role in explaining observed spa-379 tial variability in carbon storage (Alongi, 2012; Jardine and Siikamäki, 2014). 380 Also, since retention of dissolved carbon in mangrove soils can reduce rates of 381 carbon exports to the ocean (Adame and Lovelock, 2011), mineral surfaces of 382 sediments may provide a large potential for carbon sequestration in mangrove 383

ecosystems located around river deltas. According to our results, carbon storage 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 min-389 eralogy, we found that most carbon stored in soils of Cispatá Bay, Colombia, is 390 produced in situ, with little evidence of carbon imported to the area either by fluvial or marine sedimentation. Interior basin mangroves store significantly 392 more carbon in soils than the more ocean exposed fringe mangroves. Sedi-393 ments transported by the Sinú river and deposited in the delta region contain 394 negligible amounts of organic carbon, but the mineralogical composition of 395 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. 397 Our study highlights the importance of fluvial sediment transport in pro-398 viding a substrate for carbon stabilization through mineral protection. This 399 mechanism for soil carbon storage has been little studied previously in mangrove ecosystems, but it has large implications for determining their potential 401 for long-term carbon sequestration.

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408 for Biogeochemistry.

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 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.

410 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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