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

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| Abstract: | <p>Mangrove forests of the Sinú river delta in Cispatá bay, Colombia, show large differences in soil carbon storage between fringe (oceanic) and basin (estuarine) mangroves. We were interested in testing whether these differences in soil carbon are associated with sediment transport processes or whether most of the carbon is produced in situ within the mangrove system. Given past sedimentation dynamics of the Sinú river, we hypothesized that a large portion of soil carbon in basin mangroves is due to sedimentation.</p> <p>We determined total organic carbon content (TOC) of $591 \pm 92 \text{ MgC ha}^{-1}$ for basin soils, and $320 \pm 17 \text{ MgC ha}^{-1}$ for fringe soils up to a sampling depth of 80 cm. Using analyses of mineralogy (Al- and Fe-oxides, clay minerals) as well as isotopic analyses of carbon ($\delta^{13}\text{C}$), the origin of the sediments and their carbon was determined. We found that basin soils in Cispatá bay show similar mineralogical composition than those of fluvial sediments, but the carbon concentration of river sediments was close to zero.</p> <p>Given the large capacity of the Fe oxides in clay minerals to store dissolved carbon, and that the isotopic composition of the carbon is mostly of plant origin, we concluded contrary to our initial hypothesis that the carbon stored in basin mangrove soils are produced in situ. The deposited fluvial sediments do play an important role for carbon storage, but mostly in providing binding surfaces for the stabilization of organic carbon.</p> |

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

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¹ **Abstract** Mangrove forests of the Sinú river delta in Cispatá bay, Colombia,
² show large differences in soil carbon storage between fringe (oceanic) and basin
³ (estuarine) mangroves. We were interested in testing whether these differences
⁴ in soil carbon are associated with sediment transport processes or whether
⁵ most of the carbon is produced in situ within the mangrove system. Given
⁶ past sedimentation dynamics of the Sinú river, we hypothesized that a large
⁷ portion of soil carbon in basin mangroves is due to sedimentation. We deter-
⁸ mined total organic carbon content (TOC) of $591 \pm 92 \text{ MgC ha}^{-1}$ for basin
⁹ soils, and $320 \pm 17 \text{ MgC ha}^{-1}$ for fringe soils up to a sampling depth of 80

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

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

1 Introduction

Although mangroves are ecosystems with some of the largest levels of carbon storage on earth (Donato et al, 2011; Alongi, 2012), there are large variations on the amount of C stored in various systems, particularly for 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 pool (Alongi, 2012), and similar levels of variability have been observed at other sites (Jardine and Siikamäki, 2014). It is unclear however, what are the main determinants on observed differences in soil C storage across diverse

32 mangrove systems. It is possible that differences in soil carbon storage are due
33 to differences in the level of productivity of different mangrove systems, or due
34 to other external sources such as sediment transport.

35 This large degree of spatial variability in soil carbon storage is also well
36 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
38 differences in terms of soil carbon stocks between them. A previous study
39 (Bolívar, 2015) showed that for basin mangroves the total organic carbon
40 storage (TOC) is around $740 \pm 40 \text{ Mg C ha}^{-1}$, while for the fringe mangroves
41 this value is only $95 \pm 9 \text{ Mg C ha}^{-1}$. These numbers, particularly for the basin
42 mangroves, are in the upper range of values observed for other systems (Donato
43 et al, 2011; Alongi, 2012; Jardine and Siikamäki, 2014).

44 It is unknown whether the high levels of soil carbon in Cispatá bay are
45 due to the intrinsically high levels of productivity of these systems or whether
46 this soil carbon has an external source such as transport of fluvial or marine
47 sediments. Given that mangrove productivity is high and decomposition in
48 water saturated soils is slow, carbon stored in these systems may not have
49 any external origin. However, it is also possible that sediments in the delta
50 region may have been deposited by the Sinú river (Serrano, 2004), in which
51 case the carbon stored in these sediments may have its origins in soils from
52 the northern Andean mountains. Alternatively, the carbon in these sediments
53 may have been transported by marine tides over the Caribbean.

54 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
56 as well as analyses of the soils' mineralogy in concert with Al- and Fe-oxide
57 measurements. Analyses of stable isotopes are particularly useful to identify
58 the origin of carbon in soils of coastal areas (Spohn and Giani, 2012; Spohn
59 et al, 2013). In particular, we expect that: 1) the isotopic composition ($\delta^{13}\text{C}$)
60 of soil carbon provides information on whether riverine sediments are a main
61 source of C in Cisipatá bay, Colombia; and 2) the mineralogical composition of
62 the sediments provides additional information on the origin of the soil carbon
63 and the potential that it is mostly stabilized on the surface of Fe- and Al-oxides.
64 Our main hypothesis is that soils in the basin mangroves are composed mainly
65 by sediments transported by the Sinú river and deposited in the delta region,
66 therefore explaining the relatively large values of TOC stored in these soils.

67 2 Materials and methods

68 2.1 Study site

69 The study site is located on the northwestern Caribbean coast in Colombia
70 ($9^{\circ}23'\text{N}$ $75^{\circ}52'\text{W}$), which is part of the southern extreme of Morrosquillo gulf.
71 ~~Scenically~~, the coastal zone is characterized by the Sinú river delta and a
72 complex estuarine lagoon  Extensive wetlands and mangroves dominate
73 this area. The Sinú river, which has changed its flow direction in the last
74 decades (Serrano, 2004), has its origin in the northern part of the western

75 Andean mountains. ~~The area includes mainly 3 mangrove species.~~ While fringe
76 forests are dominated by ~~the species~~ *Rhizophora mangle*, basin forests are
77 dominated by *Avicennia germinans*. *Laguncularia racemosa* occurs in both
78 forest types.

79 2.2 Field sampling

80 We sampled 10 plots up to 1 m in depth from March 12 to 13, 2016, using a soil
81 corer of 7 cm in diameter. We sampled five soil cores at five fringe mangrove
82 sites (plots P21, R1, R4, R5, R6) and at 5 basin mangrove sites (plots P16, C1,
83 C2, C3, C4). In addition to the 10 plots sampled across the mangrove area, 3
84 nearby sand cores at Nisperal coast were collected, and ~~also~~ 3 riverbed cores
85 of the Sinú river near the city of Montería, which is located 70 km south from
86 Cispatá bay (Fig. 1). Generally, cores without layer changes were divided into
87 sections every 20 cm. We divided conspicuous layer changes at the boundary.
88 Because only the general mineralogical and elemental composition of the sand
89 and river samples was important - we considered them as end members - those
90 samples were not divided into segments. Instead, the whole cores down to 1
91 m were used as individual samples.

92 Additionally, we selected one fringe and one basin mangrove plot (P21 and
93 C4) to measure bulk density. At each site, a soil pit was dug and samples were
94 collected using sampling rings with a volume of 98.52 cm³. We collected four
95 depth levels at plot P21 (0-20, 20-40, 40-60, 60-80 cm) and five depth levels (+
96 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.

99 2.3 Laboratory analyses

100 After collection, samples were oven-dried at 70°C for 5 days. Samples for
101 bulk density measurements were oven dried at 105°C. We calculated soil bulk
102 density as dry mass divided by fresh volume, ~~which matches the used sampling~~
~~rings~~ ($V = 98.52 \text{ cm}^3$). Each sample was ground for 3 min at a frequency of
104 25 Hz using a Retsch MM 400 ball mill.

105 We conducted elemental analyses of percent carbon (%TC), nitrogen (%TN)
106 and inorganic carbon (%IC) in all samples using a vario MAX elemental ana-
107 lyzer for samples with high concentrations, and a vario EL analyzer for sam-
108 ples with low concentrations. We filled precisely weighed sample quantities
109 into pre-weighed tin capsules or ceramic pots for vario EL measurements. Or-
110 ganic carbon concentrations were estimated by subtracting %IC from %TC.
111 TOC ~~contents~~ (Mg ha^{-1}) were calculated using the obtained bulk densities for
112 basin and fringe mangrove soils multiplied by each plot depth interval (cm)
113 and %OC.

114 We used $\delta^{13}\text{C}$ signatures of the sampled material and compared the values
115 with the $^{13}\text{C}/^{12}\text{C}$ ratio of the two chosen end-members as indicators for the
116 origin of the carbon. We measured ^{13}C of all samples using a Finnigan MAT
117 IRMS coupled with an EA 1100 elemental analyzer. Ali-j3 (Acetanilide-Jena3)

¹¹⁸ and Caf-j3 (a caffeine sample from a ‘Traube synthesis’ in larger supply) were
¹¹⁹ chosen as internal working standards.

¹²⁰ We conducted X-ray diffraction (XRD) measurements for qualitative and
¹²¹ quantitative phase analyses on 12 representative samples including ~~4 end-~~
~~122 member samples, and 4 samples of basin and fringe mangroves each.~~ Samples
¹²³ were measured 20 min each, from 5 to 60 ° 2θ . We determined each mineral
¹²⁴ phase using the powder diffraction file (PDF) data. We also conducted a Ri-
¹²⁵ etveld refinement using Topas (Bruker). To define the type of clays included
¹²⁶ in the samples, we further measured each before extracting clay fraction from
¹²⁷ 3 to 70 ° 2θ using ceramic panels.

¹²⁸ We determined iron and aluminum in acid-ammonium-oxalate extracts (pH
¹²⁹ 3.0) and in sodium-citrate-dithionite extracts (pH 7.3). We selected 46 samples
¹³⁰ and 2 standard soils for these measurements. While sodium dithionite was
¹³¹ used to extract both crystalline and amorphous oxides, the oxalate method
¹³² extracted only amorphous oxides. The actual measurement of crystalline and
¹³³ amorphous iron and aluminium oxides was performed using ICP-AES.

¹³⁴ **3 Results**

¹³⁵ We found important differences in %OC and %TN between fringe (Fig. 2, ~~blue~~
~~136 bars~~) and basin (~~orange bars~~) mangrove soils, which overall had much higher
¹³⁷ %OC and %TN concentrations in fringe (P21 - R6) than in basin mangroves
¹³⁸ (P16 - C4). These differences in %OC and %TN between basin and fringe
¹³⁹ mangrove soils were statistically significant according to a one-way ANOVA

¹⁴⁰ test (p -value <0.001). In general, %OC and %TN decreased with soil depth,
¹⁴¹ with a more clear trend for %OC than %TN.

¹⁴² Both end-members, sampled at the Sinú river in Montería and at Nisperal
¹⁴³ beach, show %OC and %TN concentrations close to zero, which indicates that
¹⁴⁴ they include almost no organic matter. In contrast, sand Nisperal plots display
¹⁴⁵ the highest %IC concentration of around 10% compared to the other plots. The
¹⁴⁶ lack of organic carbon in the fluvial sediments is evidence against our initial
¹⁴⁷ hypothesis of carbon imports to the mangrove system through sedimentation.

¹⁴⁸ We calculated much higher bulk densities for basin than for fringe mangrove
¹⁴⁹ soil samples: While P21 (fringe) samples only had an average bulk density of
¹⁵⁰ 0.16 g/cm³, plot C4 (basin) samples had an average bulk density of 1.11 g/cm³
¹⁵¹ (Table 1) .

¹⁵² Differences in bulk densities between the two forest types resulted in a
¹⁵³ completely different distribution of C compared to the previous results based
¹⁵⁴ on %OC alone. A higher carbon storage in the upper layers of basin mangrove
¹⁵⁵ soils is clearly outlined (Table 1). The differences in TOC between basin and
¹⁵⁶ fringe mangrove types ~~are~~ significant according to the one-way ANOVA test
¹⁵⁷ (p -value <0.05). TOC ~~decreases~~ with soil depth within the first four (basin)
¹⁵⁸ and three (fringe) layers. There was an increase in TOC for the last measured
¹⁵⁹ depth intervals of basin and fringe soils, which can be traced back to higher
¹⁶⁰ %OC values of those layers.

¹⁶¹ We measured a higher proportion of negative $\delta^{13}\text{C}$ values for fringe soils
¹⁶² (-28 to -29 ‰) than for basin mangroves soils (-25 to -29 ‰) (Fig. 3). Depth

163 intervals 20-40 and 40-60 cm of basin soils show outliers with equal ^{13}C signa-
164 tures compared to the Sinú river end-member samples with values of around
165 -25 ‰. The carbonate sand end-member samples have the most positive ^{13}C
166 values with approximately -3 ‰. This value is the closest to the ^{13}C VPDB
167 standard (0.01118 ‰) with regard to our samples. Strong variations in ^{13}C
168 are conspicuous for the depth intervals 20-40 and 40-60 cm of basin man-
169 grove boxplots. We found no identifiable continuous trend between ^{13}C values
170 and depth. However, differences in ^{13}C mean values between fringe and basin
171 mangroves were statistically significant (p -value <0.001).

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

176 The XRD pattern of Nisperal samples measured from 5 to 60 $^{\circ}2\theta$ provided
177 characteristic $^{\circ}2\theta$ intensities for the phases aragonite, calcite and quartz. The
178 XRD measurement combined with a Rietveld refinement yielded a mineralogi-
179 cal composition of 95% aragonite, 4% calcite and 1% quartz. Sinú river samples
180 showed high intensities for quartz and sodium feldspar (albite) components, as
181 well as peaks for the clay minerals illite and clinochlore. The semi-quantitative
182 distribution calculated by PDF data indicated that quartz is the main repre-
183 sentative of the mineral fraction of the Sinú river soils (Fig. 4).

184 XRD patterns for both mangrove soils, but in particular for basin soils,
185 showed a similar mineralogical distribution compared to the Sinú river sedi-

186 ments (Fig. 5). XRD patterns in fringe soils showed high intensities for halite,
187 which was also found in basin mangrove soils, but not in a comparable dis-
188 tribution ratio. XRD measurements conducted on the extracted clay mineral
189 fraction yielded peaks for the mineral phases clinochlore, illite, quartz and
190 albite. PDF data additionally identified corundum, which is related to the ce-
191 ramic panel surface composition. We found major proportions for clinochlore
192 and quartz in the clay size fraction.

193 The oxalate extraction dissolved much of the iron and aluminum from the
194 amorphous materials, whereas the dithionite extraction dissolved only little of
195 the crystalline iron oxides as well as little of the amorphous materials (Fig. 6).

196 Oxalate- and dithionite extracted Al and Fe showed statistically significant
197 differences between basin and fringe mangrove soils (p -value <0.001). Basin
198 soil samples had 2 times higher ppm values of Al ($\text{Al}_d + \text{Al}_o$) than fringe soils,
199 and 5 times higher Fe values. While Sinú river samples had similar Al and
200 Fe concentrations than those of basin mangroves in all 4 extraction patterns,
201 metal contents of sand Nisperal samples were constantly low. Fe_o contents
202 differed extremely for basin soils, especially for the first 2 depth intervals.
203 Both basin and fringe soils showed an increase of metal oxides within the first
204 depth intervals and in turn a decrease within the deeper levels.

205 4 Discussion

206 Lower values of bulk density in fringe mangrove soils can be explained by their
207 high organic matter content (wood residues, leaf debris and roots). Roots claim

208 a large proportion of the soil volume, which strongly decreases bulk density.
209 Instead, basin mangrove samples of Cispatá bay are characterized by a dense
210 silty composition including a small organic part, which results in higher bulk
211 densities. The increase in bulk density with depth in both mangrove types is
212 likely the result of hydrostatic pressure and time inside the mangrove forest
213 belowground.

214 The higher proportion of organic matter in fringe than in basin soils also
215 leads to higher %OC values for fringe soils. Basin mangrove soils instead, are
216 characterized by a small portion of organic topsoil. Because %TN concentra-
217 tions correlate with %OC, they also show lower values for basin mangroves.
218 That both end-members (Sinú river and sand Nisperal samples) are mostly
219 consisting of mineral components is illustrated by their %OC contents of nearly
220 0 %. Because the %IC concentration of 10 % of sand Nisperal samples is similar
221 to the used pure calcium carbonate standard, we concluded that the Nisperal
222 beach is mostly composed of carbonates.

223 The decrease of %OC with soil depth is likely the result of the interaction
224 between heterotrophic consumption by microorganisms, vertical transport of
225 organic matter, and leaching of dissolved carbon in water. Because soil mi-
226 croorganisms utilize nitrogen and bacteria fix nitrogen, the concentration of
227 %TN also decreases with depth. The fact that concentrations of %OC and
228 %TN decrease continuously with soil depth, but still show layers with higher
229 concentrations in depths of 80-100 cm (basin) and 60-80 cm (fringe), may re-
230 flect differences in sedimentation rates over time (Bolívar, 2015). In Cispatá

231 bay, silting processes linked to changes in the position of the Sinú river delta,
232 current sea level rise, flooding regime and fluvial inputs, can generate deep or-
233 ganic layers that may cause the increase of %OC with depth for both mangrove
234 types (Serrano, 2004).

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

245 Our results confirm previous studies that found important differences in
246 TOC between fringe and basin mangrove soils (Bolívar, 2015). Furthermore,
247 basin mangrove soils showed a significantly higher range of in-situ produced
248 carbon than fringe mangrove soils, and with it a higher carbon storage of
249 $661 \pm 92 \text{ MgC ha}^{-1}$ (0-100 cm) compared to $320 \pm 17 \text{ MgC ha}^{-1}$ (0-80 cm).
250 Based on the %IC concentration results, we infer that marine sediments across
251 Cispatá bay have no influence on additional entered carbon via tidal flooding,
252 which is supported by the lack of %IC content in the analyzed mangrove soil
253 samples compared to the coral sands of Nisperal beach.

254 $\delta^{13}\text{C}$ signatures of fringe mangrove sediments were more ^{13}C depleted than
255 basin sediments, which is a strong indication that this carbon is more plant
256 derived. C3 plants fractionate ^{13}C during photosynthesis, with values from
257 -22 to -38 ‰, while C4 plants show values between -8 to -15 ‰ (Farquhar
258 et al, 1989). *R. mangle*, a typical C3 species, mostly occurs in the fringe area
259 of Cispatá bay (Bolívar, 2015) and is therefore the main producer of ^{13}C in
260 this type of forest. In terms of its origin, this carbon is very likely produced
261 in situ in the area. Basin mangrove sediments instead, show a wider range of
262 $\delta^{13}\text{C}$ signatures and more positive values. This could mean either, that the
263 basin area has a higher contribution by C4 plants (e.g. grasses), or that there
264 is some contribution from mineral sources. Because the most common basin
265 mangrove species, *A. germinans*, is also a C3 plant and there is likely little
266 contribution by C4 grasses, we assumed that basin mangrove sediments are
267 mostly influenced by deposited sediments from the Sinú river. This assumption
268 is also supported by the fact that basin samples tend to have more enriched
269 ^{13}C values, close to those found for the Sinú river samples (-25 ‰). According
270 to Ruttenberg and Goni (1997) and Powers and Veldkamp (2005), $\delta^{13}\text{C}$ signa-
271 tures of tropical mineral soils range from -23 to -26 ‰, which would underpin
272 mineral derived ^{13}C values in Cispatá bay. Because ^{13}C values are significant
273 between basin and fringe sediments, and because fringe samples only have
274 plant derived ^{13}C , we conclude that the fringe area is not influenced by the
275 Sinú river delta. It also does not show any influence through marine sediments,

276 because it does not have any enriched signatures comparable to the Nisperal
277 sand (-5 ‰).

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

282 Using XRD, we found that the mineralogical composition of the sediments
283 in Cispatá bay was similar to the composition of the Sinú river sediments in
284 Montería. We therefore conclude that basin and fringe mangrove sediments
285 were transported by the river and have their distant origin in that river basin.
286 Quartz, albite and clay minerals are the major components of those sediments.
287 Additionally, plot R5 shows intense peaks for the mineral halite in depths
288 between 80-90 cm. Because halite crystallizes by the evaporation of sea water
289 and intense salinization, its occurrence verifies that the fringe mangrove area
290 has tidal influence of hyper saline sea water. Furthermore, halite confirms the
291 sediment air exposition, since it needs evaporation to be formed. That halite
292 reaches that intense proportion in depths of 80-90 cm can be attributed to
293 the changing course of the Sinú river. According to Serrano (2004), the river
294 course passed the northern main land of Cispatá bay between 1849 and 1938,
295 where plot R5 is located. Accordingly, the sedimentation rate increased in that
296 period. However, before that period, this region was more influenced by saline
297 sea water, which results in intense halite peaks. That basin soils also contain
298 halite, shows that they were also occasionally flooded.

299 Depending on their cation-exchange capacity, clay minerals are able to bind
300 metal oxides. Because cation-exchange sites on clay and humic colloids have
301 negative charge, cations (metals) from the soil solution must satisfy this charge,
302 so that mineral and organic surfaces appear to be charged neutral. Cations are
303 retained on these clay sites by electrostatic force. At the same time, Al and
304 Fe oxide interactions with clays are pH dependent (variable charges). At low
305 pH, where the oxides carry sufficient positive charge, they precipitate on clay
306 surfaces. These coatings, once formed, are stable at higher pHs. Precipitation
307 of oxides at high pH occurs as phases separated from the clays (Goldberg,
308 1989). According to Goldberg (1989), observed precipitation of oxides showed
309 that only amorphous Fe-precipitates were obtained with the clay substrate.
310 However, in the case of quartz, precipitated oxides had increased crystallinity,
311 particularly for the samples with high iron concentrations. Transferred to our
312 study sites, these previous results help to explain that the increased proportion
313 of metal oxides in basin soils goes together with a more mineralogical composed
314 soil.

315 Along with the ^{13}C results, the mineralogical analyses also confirm that
316 basin mangrove sediments are terrestrially derived. This finding is also re-
317 flected in higher metal oxide and hydroxide contents compared to fringe man-
318 grove soils, with ppm contents similar to those of the Sinú river samples.
319 Because basin mangroves have much older and more compact sediments with
320 a greater proportion of mineral layers, the alteration of minerals and the for-
321 mation of metal oxides, hydroxides and clay minerals is supported in their

soils. The contents of metal oxides in Cispatá bay are generally low, compared to other soil studies (McKeague and Day, 1966). Also, mangrove soils in Cispatá bay do not show typical reddish colour changes, which are an indication for the presence of iron oxides (especially hematite). A continuous grey colouring of all non-humus layers shows further the only presence of clay minerals (Ségalen, 1971). Only plot C1 contains yellow and beige coloured layers in depths of 40-80 cm, which indicates the occurrence of goethite ($\alpha\text{-Fe}^{3+}\text{O(OH)}$). Beside goethite, also gibbsite (Al(OH)_3), indicated by a white colour, is a typical hydroxide for mangrove sediments (Souza-Júnior et al, 2008) and soils of warm and humid areas of the world (Ségalen, 1971). Al and Fe are mostly present as amorphous products, e.g. as alumino- or ferrogels. The negligible small amounts of metal oxides and hydroxides in all 3 sand samples indicate furthermore, that those transported as well as in situ produced oxides get fixed in mangrove soils. An increase of Al and Fe is apparent within the first depth intervals, but there is no continuos trend with depth. Again, this shows the connection between mineral soil horizons and Al and Fe bonding and the smaller amount of Al and Fe in humus layers.

That mineral surfaces of Al and Fe oxides and hydroxides adsorb dissolved organic matter (DOM) has been well established (Kaiser and Guggenberger, 2000; Tipping, 1981). It is therefore very likely that metal oxides and hydroxides bind and preserve C in basin mangrove soils. According to Kaiser and Guggenberger (2000), the capacity to adsorb DOM relates to the presence of Al and Fe oxides and hydroxides. The sorption of DOM derived from decom-

345 position to Al and Fe oxyhydroxides involves strong complexation bondings
346 between surface metals and acidic organic ligands, particularly with those asso-
347 ciated with aromatic structures. The strength of the sorption relates further to
348 the surface properties of the sorbing mineral phase. Kaiser and Guggenberger
349 (2000) found that dissolved organic matter sorption is strongly enhanced by
350 hydrous oxide coatings and particularly by amorphous Al(OH)_3 , what under-
351 pins that amorphous hydroxides bind C in basin soils of Cispatá bay. Tipping
352 (1981) describes moreover, that the extent of adsorption of DOM increases
353 with decreasing pH. Because mangrove soils at the Colombian Caribbean coast
354 have an acid character both at *A. germinans* and *R. mangle* forests (Urrego
355 et al, 2014), a stronger C binding onto oxides and hydroxides is substantiated
356 in this region.

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

362 **5 Conclusions**

363 Based on analyses of carbon concentration, bulk density, stable isotopes of
364 carbon, and mineralogy, we found that most carbon stored in soils of Cispatá
365 Bay, Colombia, is produced in situ, with little evidence of carbon imported to
366 the area either by fluvial or marine sedimentation. Interior basin mangroves

367 store significantly more carbon in soils than the more ocean exposed fringe
368 mangroves. Sediments transported by the Sinú river and deposited in the delta
369 region contain negligible amounts of organic carbon, but the mineralogical
370 composition of these sediments favors the adsorption of dissolved carbon on
371 charged mineral surfaces, which explains the larger levels of C storage in this
372 type of mangroves.

373 Our study highlights the importance of fluvial sediment transport in pro-
374 viding a substrate for carbon stabilization through mineral protection. This
375 mechanism for soil carbon storage has been little studied previously in man-
376 grove ecosystems, but it has large implications for determining their potential
377 for long-term carbon sequestration.

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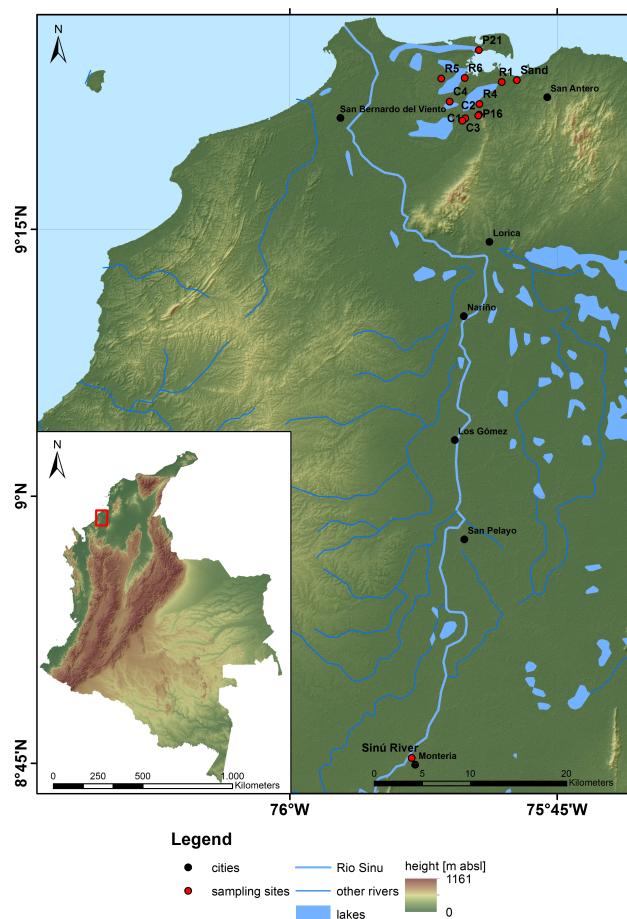
384 **Figures**

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

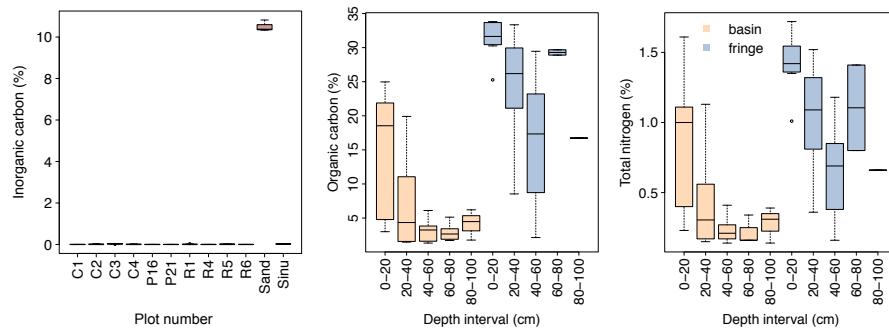


Fig. 2 Observed values of percent inorganic carbon (%IC) for each sampled plot; and percent organic carbon (%OC) and percent nitrogen (%TN) by sampling depth averaged across plots.

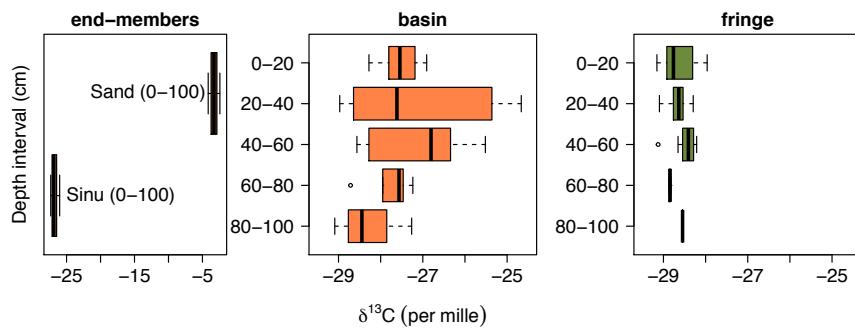


Fig. 3 Measured $\delta^{13}\text{C}$ signatures for both end-members and both mangrove types related to each sampling depth

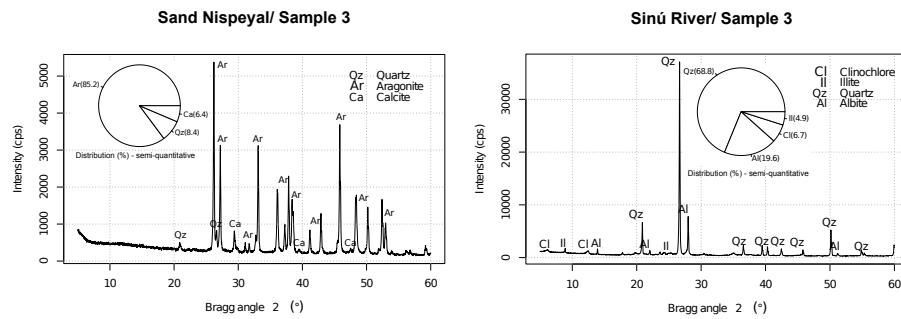


Fig. 4 Two exemplary XRD patterns ($\lambda = 1.5406 \text{ \AA}$) of both measured end-members: Nisperal beach and Sinú river; figures also include semi-quantitative distribution of detected minerals

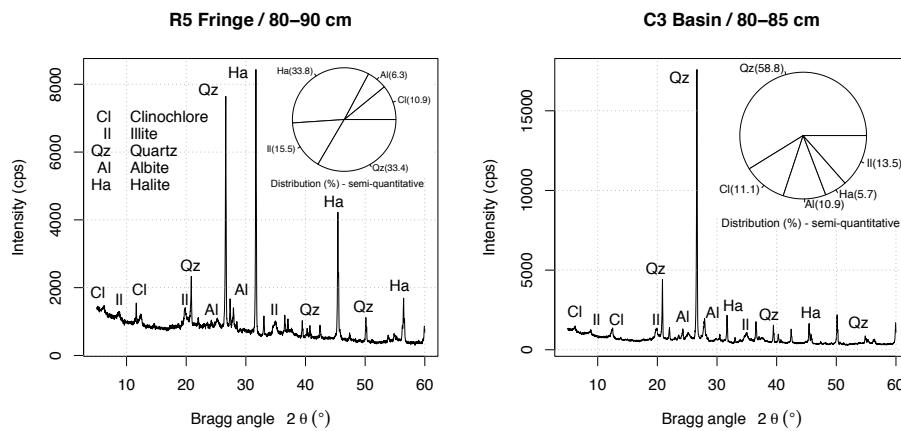


Fig. 5 Two exemplary XRD patterns ($\lambda = 1.5406 \text{ \AA}$) for the fringe (left) and basin (right) mangrove soils; figures also include semi-quantitative distribution of detected minerals

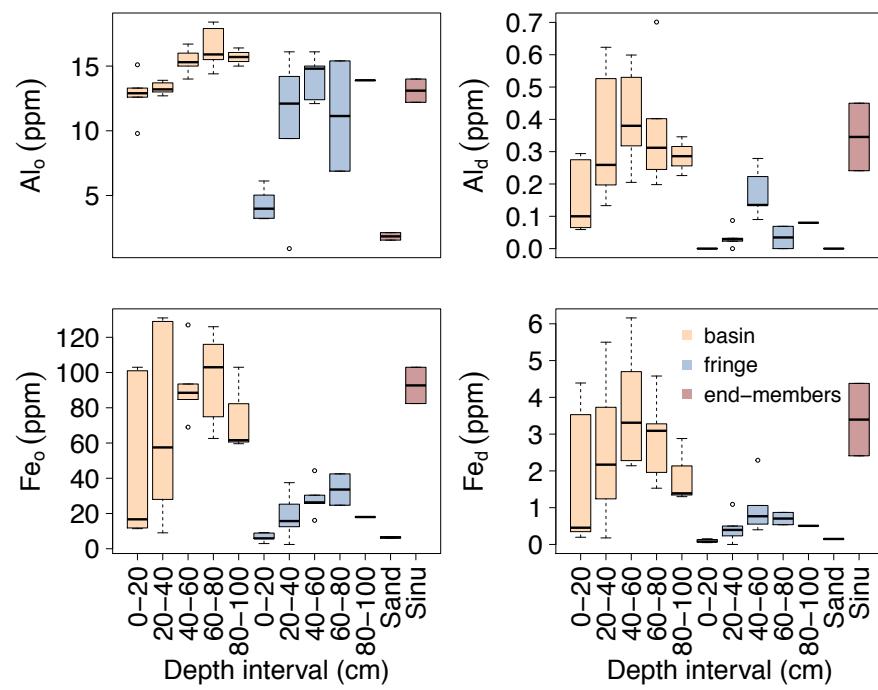


Fig. 6 Oxalate (o)- and dithionite (d) extracted metal oxides for each mangrove type and soil depth (figures in ppm)

385 **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⁺) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈ |
| | Illite | (K,H ₃ O)Al ₂ (Si ₃ Al)O ₁₀ (H ₂ O,OH) ₂ |
| | Albite | NaAlSi ₃ O ₈ |
| Oxides/hydrox. | Quartz | SiO ₂ |
| Carbonates | Aragonite | CaCO ₃ |
| | Calcite | CaCO ₃ |
| Halides | Halite | NaCl |

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