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## Mineralization of soil organic matter from equatorial giant podzols submitted to drier pedoclimate: A drainage topochronosequence study

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1        **Mineralization of soil organic matter from**  
2        **equatorial giant podzols submitted to drier**  
3        **pedoclimate: a drainage**  
4        **topochronosequence study**

5

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18

19

20 **Hightlights**

21

22 • Active hydromorphic podzol in the area store around 63 kgC

23 m<sup>2</sup>

24 • Erosive incision by a river meander resulted in air entry and

25 oxygenation of the Bh

26 • C content in the Bh of a podzol truncated due to meander

27 diminished by 70%

28 • Drier climate would induce C emission from Amazonian

29 podzol Bhs

30

31

32

33 **Abstract**

34

35 Podzol soils are an important carbon pool in the Amazon, due to  
36 the high organic matter (OM) content in their topsoil horizons and  
37 deep Bh. To quantify the evolution of the stock and the lability of  
38 this carbon pool in the hypothesis of the onset of drier climates, we  
39 studied a soil toposequence at the end of which the incision of a river  
40 meander lowered the water table, as would result from a drier  
41 climate, allowing oxidation the Bh horizons. The soil OM was  
42 quantified and characterized (physical fractionation, humification  
43 indexes,  $^{14}\text{C}$  average age) and its lability under oxic conditions was  
44 estimated by measuring respiration during a 660-days experiment.  
45 Podzol genesis time was calculated by constraining the carbon fluxes  
46 using both C stock and  $^{14}\text{C}$  average age. The results confirmed that  
47 the studied podzols store large amounts of carbon ( $62.8 \text{ kgC m}^{-2}$  on  
48 average). They resulted from a long genesis time, probably greater  
49 than 30-50 ky. Topsoil OM is very labile with a residence time of  
50 about 100 y; Bh OM is highly humified with a high C/N (62.7 on  
51 average) related to low respiration rates. The measured respiration  
52 rates were used to estimate the C emission that would result from  
53 drier climates at  $55 \text{ gC m}^{-2} \text{ y}^{-1}$  on average during the first 100 y,  
54 which would correspond, by extrapolation, to  $8.5 \cdot 10^{12} \text{ gC y}^{-1}$  for all  
55 Amazonian podzols.

56

57

58        Keywords: Amazon podzol; Soil organic matter; Humification  
59        index; Soil carbon storage and loss; Climate change; Soil formation  
60        rate

61

62

## 63    **1. Introduction**

64

65

66        Equatorial podzols are characterized by upper organic matter  
67        (OM)- rich horizons and thick sandy eluviated horizons (E horizons,  
68        also called white sands) overlying deep OM-rich horizons called Bh.  
69        In these soils, the dissolved organic matter (DOM) produced in the  
70        topsoil is transferred at depth, through the E horizons, by the  
71        percolating waters (Lucas, 2001). Part of this DOM is directly  
72        exported to the river network by the lateral flow of the groundwater  
73        perched on the Bh horizons and circulating in the E horizons. The  
74        other part enters the Bh horizons where it can be immobilized as soil  
75        organic matter (SOM), remobilized in the perched groundwater  
76        (Bardy et al., 2011), mineralized by microbial activity or transferred  
77        towards deeper horizons and deep groundwater (Lucas et al., 2012).

78        Despite their very low fertility, equatorial podzols are of interest  
79        because, on the one hand, they release large amounts of dissolved  
80        organic carbon (DOC) in the river sytem (Leenheer, 1980), most of  
81        which is transferred to the sea, participating to the storage of carbon  
82        on the scale of geological time (Tardy et al., 2009). On the other  
83        hand, since most of them are giant podzols compared to podzols of  
84        cold regions, i.e. with E or Bh horizon thicknesses that can reach

85 several meters, they store large amounts of carbon in their upper and  
86 Bh horizons: hydromorphic podzols can store more than 100 kgC m<sup>-2</sup>  
87 in the whole profile and more than 80 kgC m<sup>-2</sup> in the only deep Bh  
88 (Montes et al., 2011). These soil systems therefore contribute  
89 significantly to the global CO<sub>2</sub> cycle (Marquez et al., 2016, 2017).  
90 The dynamics of DOM transfer and SOM accumulation, however,  
91 are still poorly understood.

92 Carbon accumulation in deep Bh horizons is due to the acidic and  
93 water-saturated conditions found there. It should be noted that in  
94 most areas the hydromorphic podzols are not situated in the bottom  
95 of valleys but in a plateau position or on slopes, higher than the  
96 phreatic base level (Lucas et al., 1987). As the Bhs have low  
97 hydraulic conductivity, they support a perched water-table that joins  
98 the deep water-table in restricted parts of the landscape. As a result,  
99 the upper part of the Bh is always in waterlogged conditions, which  
100 prevents the entry of air from the E horizon into the Bh (Ishida et al.,  
101 2014), It can be drained if the climate turns drier, allowing  
102 oxygenation of the underlying Bh. For the Upper Rio Negro Basin,  
103 where most of the Amazonian podzols are found, climate change  
104 modelling predictions point to the gradual onset of a drier season  
105 centered around October (Gutiérrez et al., 2021; Iturbide et al., 2021).  
106 The CMIP6 model predicted a negligible decrease in annual rainfall,  
107 but an increase in the number of consecutive dry days. These were on  
108 average 15 days during the 1986-2005 reference period; forecasts  
109 were 19 and 31 days for SSP2, near-term period (2021-2040) and  
110 SSP5, long-term period (2081-2100), respectively. The CORDEX  
111 South America model predicted no change for either scenarios; the  
112 CORDEX Central America model predicted 28 and 39 days

113 respectively. An increase in the number of consecutive dry days  
114 would alter the dynamics of the water tables perched on the Bh,  
115 which could temporarily disappear, allowing air to penetrate into  
116 OM-rich horizons that are generally waterlogged. This can lead to  
117 increased C mineralization through better aeration satisfying the O<sub>2</sub>  
118 demand of microorganisms. Increased in dry/wet cycles is also likely  
119 to have an impact on the mineralization of C: rewetting of the soil  
120 after a period of drying has long been known to cause a burst of  
121 respiration (Birch, 1958), so that dry/wet cycles can accelerate soil C  
122 loss relative to what would be lost under constant conditions (Miller  
123 et al. 2005). Tadini et al. (2018) showed significant compositional  
124 changes in the humic acid (HA) fractions of Bh SOM throughout the  
125 horizon, with four types of organic matter: recalcitrant, humified, and  
126 old dating; labile and young dating; humified and young dating; and  
127 little humified and old dating. This suggests a different sensitivity of  
128 these organic matters to mineralization processes.

129 In such a context, a first objective of the present work was to  
130 evaluate the sensibility to mineralization of the OM issued of  
131 hydromorphic podzols to predict the kinetics of CO<sub>2</sub> release after  
132 oxygenation.

133 Another way to evaluate the evolution of podzolic OM in a  
134 context of climate change is to study a chronosequence where the  
135 hydromorphic podzols were progressively submitted to a drier  
136 pedoclimate. Two types of such chronosequence can be identified:  
137 (1) a Bh formed beneath permanent water table then was submitted to  
138 alternating dry and wet conditions due to an external change in  
139 drainage conditions and (2) podzols were formed under humid  
140 climates then subjected to dryer climates. We have identified in the

141 Amazon a topochronosequence of the first type, for which the change  
142 in drainage conditions was a lowering of the water table caused by  
143 the erosive incision of a river. The second objective of the present  
144 study was therefore to compare the rates of Bh mineralization along  
145 this topochronosequence.

146

147

## 148 **2. Material and methods**

149

### 150 *2.1. Study area and sampling*

151

152 The study area is situated in Brazilian Amazonia, north of the city  
153 of Barcelos, at the edge of the Demini River at the central  
154 coordinates 0°17'30"N and 62°48'0"W (Fig. 1). Landscape is a flat  
155 area whose altitude is 3 to 15 m over the Demini River higher level.  
156 Annual rainfall is around 2600 mm (Reboita et al., 2010) without a  
157 marked dry season. The geological substratum, previously considered  
158 as a part of the Içá sedimentary formation (Reis et al., 2006), was  
159 more recently reclassified as late Pleistocene (129 to 11.7 ky BP) Rio  
160 Negro – Rio Branco sedimentary formation, that mainly consists in  
161 unconsolidated sands with some clay-silt and conglomerate layers  
162 (IBGE, 2011). These sediments were deposited as a megafan  
163 following the slow subsidence of the Guyana Shield, giving the  
164 largest wetland area of the Amazon (Cremon et al., 2012). After these  
165 authors, the studied soils are located on one of the oldest deposit of  
166 the megafan whose age, however, is not precisely known. Soils in the  
167 area are mainly typical tropical podzols and hydromorphic podzols



168 (Lucas et al., 1996; Dubroeuq and Volkoff, 1998; Montes et al.,  
169 2011) associated to some ferralsols which can occur occasionally on  
170 scattered hills 2 to 10 m higher than the flat, hydromorphic podzolic  
171 inter-hill surface (Pereira et al., 2015). The forest on well-drained  
172 podzols is a forest of tall trees, but with low species diversity  
173 (Adeney et al., 2016; García-Villacorta et al., 2016); over the  
174 hydromorphic podzols is a specific vegetation named campinarana,  
175 characterized by a high density of smaller trees (20 to 30 m) that are  
176 adapted to physiological stress caused either by waterlogging when  
177 the water table is near the surface, or by drought when the water table  
178 is further from the surface (Anderson, 1981). In the lowest areas  
179 which are always waterlogged, hydromorphic podzols are observed  
180 under an herbaceous vegetation forming clumps 20-30 cm high, with  
181 the presence of bare patches of white sand.

182 The study area was chosen on the convex side of a meander of the  
183 Demini River (Fig. 1), out of the meandering channel in an area  
184 where erosion cut directly in the Rio Negro – Rio Branco  
185 sedimentary formation, in order to observe the podzol evolution after  
186 the lowering of the water table related to the river incision.

187 Soils were studied and sampled by the mean of hand-auger  
188 drilling, using casing in the E horizons to avoid sand collapsing in the  
189 borehole. Samples for microbial respiration measurements were  
190 maintained in the dark at temperature below 5° until analyzed, which  
191 occurred within 2 weeks, such a procedure was shown not to affect  
192 respiration measurements (Lucas et al., 2020). Samples for soil  
193 organic matter (SOM) characterization were frozen and maintained  
194 frozen until analyzed. Undisturbed samples for bulk dry density were

195 taken in boreholes by hammering a cylindrical Ø 3 cm piston  
196 sampler.

197

198

## 199 *2.2. Laboratory characterizations*

200

### 201 *2.2.1. Soil characterization*

202 Soil particle size distribution was performed using the Robinson  
203 pipette method. Total organic carbon (TOC) was determined using a  
204 LECO CR-412 TOC analyser. No carbonates minerals were found in  
205 these very acid soils (pH<5) so that in the following "C content" refer  
206 to "organic C content". A SOM humification index ( $H_{LIF}$ ) was  
207 obtained by Laser Induced Fluorescence Spectroscopy (LIFS) after  
208 Milori et al. (2006): the bulk sample grinded to pass a 250- $\mu$ m mesh  
209 was pressed in pellets and the fluorescence emission spectra between  
210 420 and 800 nm under a 405 nm excitation was obtained using a  
211 Hamamatsu photomultiplier. The  $H_{LIF}$  index was calculated dividing  
212 the area of the LIF spectrum by the C content of the sample.

213 The HA fractions were isolated and characterized in a previous  
214 work (Tadini et al., 2018) using the procedure recommended by the  
215 International Humic Substances Society (Swift, 1996). Here we used  
216 the humification index ( $A_{465}$ ) of HA determined as the total area  
217 under the fluorescence emission spectrum recorded at the excitation  
218 wavelength of 465 nm (Milori et al., 2002).

219 All mineralogical determinations were performed after organic  
220 matter removing with  $H_2O_2$ . Main minerals were identified by XRD  
221 (X-ray diffraction) of Cu  $K\alpha$  radiation on powder samples using a  
222 Philips PW 1877 diffractometer. Kaolinite and gibbsite were

223 confirmed by FTIR (Fourier-transformed Infra-Red spectrometry) on  
224 sample-KBr pellets using a Shimadzu IR Prestige-21 spectrometer.  
225 Differential thermal analysis (DTA) and thermogravimetric analysis  
226 (TGA) were undertaken with a DTG-60H-Simultaneous DTA-TG  
227 (Shimadzu, Kyoto, Japan). Goethite was identified using the 488 and  
228 413 nm absorption bands (Scheinost et al., 1998) by DRS (Diffuse  
229 Reflectance Spectroscopy, Varian Cary 5 spectrometer)

230 Saturated hydraulic conductivity ( $K_{sat}$ ) was measured on  
231 undisturbed samples taken with a  $\varnothing$  37 mm piston sampler  
232 hammered in boreholes. Samples were sealed in a polycarbonate  
233 tube, led to water saturation by a 24-h progressive rise of water level  
234 from the base of the cylinder, then remained 48 hours for dissolution  
235 of the air possibly trapped in the porosity. The water used was  
236 previously brought to pH 4 (Lucas et al., 2012) with  $H_2SO_4$  to avoid  
237 any dispersion of the organic matter likely to modify the value of  
238  $K_{sat}$ .

239 Physical fractionation of the organic matter was realized in  
240 triplicate using the procedure described in Sohi et al. (2001). Five  
241 grams of soil sieved at 2 mm were placed in centrifuge bottles  
242 containing 35 mL of  $1.8 \text{ g cm}^{-3}$   $NaIO_3$  solution, manually stirred  
243 during 30s then centrifugated at 8000 g during 30 mn. The floating  
244 particles, that corresponded to the light free fraction (LFF), were  
245 separated by filtration on a GF/A 1.6  $\mu\text{m}$  filter. The filtrate was  
246 returned to the corresponding centrifuge bottle containing the soil  
247 residue and sonicated. Floating particles corresponded to a light intra-  
248 aggregate fraction, the light occluded fraction (LOF), they were  
249 separated by centrifugation and filtration as for LFF. The OM  
250 remaining in the centrifugation pellet corresponded to the heavy

251 fraction (HF). C on the filters and on the final centrifugation pellets  
252 was quantified as for TOC.

253

#### 254 *2.2.2. Basal respiration*

255 Soil respiration was determined using the method described in  
256 Paul et al. (2001). The respiration gas samples were analyzed for CO<sub>2</sub>  
257 concentrations using a GC-17A Shimadzu gas chromatograph  
258 equipped with a flame ionization detector. After extraction, jars were  
259 opened for 5 mn for equilibrating with external atmosphere.

260 Sampling was done twice a week during the 2 first weeks, then thrice  
261 a week until 3 months, then weekly until 4 months, then monthly  
262 until the end of experiment that was stopped after 660 days. Detailed  
263 data are given in supplementary material; they were used to calculate  
264 the cumulative respiration during the 660 days long experiment and  
265 the SOM respiration rates using a 2 pools model, each pool having a  
266 first order kinetics. The respiration curves were fitted by the Excel  
267 Solver using the Evolutionary algorithm to find the parameters values  
268 that minimized the normalized root mean square deviation (RMSD).  
269 Examples of respiration curves and processing are given in Lucas et  
270 al. (2020).

271

#### 272 *2.2.3. Isotopic measurements*

273 After freeze drying, soil samples were ground to pass a 106- $\mu$ m  
274 mesh. Between 35 to 90 mg of the sample, depending on carbon  
275 concentration, was transferred to a tin capsule for elemental and  
276 isotopic analysis. The isotope ratios of carbon (<sup>13</sup>C/<sup>12</sup>C) and nitrogen  
277 (<sup>15</sup>N/<sup>14</sup>N) of each sample were determined using a continuous-flow  
278 isotope ratio mass spectrometer (Delta Plus, ThermoFisher Scientific,

279 Bremen, Germany) coupled to an elemental analyzer (CHN-1110,  
280 Carlo Erba, Rodano, Italy). Carbon and nitrogen isotope  
281 compositions were calculated as:

282

$$283 \quad \delta (\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$$

284

285 where R is the ratio of  $^{13}\text{C}/^{12}\text{C}$  or  $^{15}\text{N}/^{14}\text{N}$ . Stable isotope ratios for  
286 C were measured using internationally standard PDB (Limestone  
287 from the Grand Canyon region, USA) while the standard for nitrogen  
288 was atmospheric air.

289

#### 290 *2.2.4. Radiocarbon measurement*

291 Radiocarbon measurements were carried out at the Poznań  
292 Radiocarbon Laboratory, Poland. Radiocarbon dating of organic  
293 matter must be corrected for "bomb carbon", the atmospheric  $^{14}\text{C}$   
294 peak brought by the tropospheric nuclear tests of the 1960s  
295 (Trumbore, 2000). In the Bh, we assumed that the proportion of  
296 bomb carbon in the Bh organic matter was negligible and we  
297 calculated a conventional, uncalibrated age from the radiocarbon  
298 pMC (percent modern carbon) value. This age is an apparent age  
299 because the Bh are open systems mixing organic carbon of different  
300 ages. The topsoil organic matter, however, was very younger and had  
301 a significant amount of post-bomb carbon, giving a pMC higher than  
302 100 %. In such case, we assumed that the topsoil horizons reached a  
303 steady state before 1950 and calculated an apparent age using the  
304 method given in Doupoux et al. (2017).

305

306

307 2.3. *Statistical analysis and modelling*

308 Statistical analysis was performed using XLSTAT2017. We chose  
309 a correlation-type PCA on standardized variables to avoid sensitivity  
310 to the scaling of the variables. Modelling was realized using the  
311 method developed in Doupoux et al. (2017), in which the podzol  
312 profile genesis time is constrained by both total carbon and  
313 radiocarbon. For a given C pool, assuming a constant input of C and  
314 a constant rate for C outflow, the relationships between total carbon  
315 and radiocarbon can be calculated analytically. This allows the  
316 calculation of the minimum time required to form the carbon pool.  
317 The authors applied this method to give an estimate of the minimum  
318 time required to form a given profile by considering three carbon  
319 pools: a topsoil C pool and two pools in the Bh: a fast Bh pool (high  
320 C turn-over) and a slow Bh pool (low turn-over).

321 The model required knowing the radiocarbon and total carbon  
322 values in each pool. Total carbon was calculated from carbon weight  
323 % and bulk density. Radiocarbon and carbon % were measured; the  
324 bulk density was measured for some samples and, for the others,  
325 estimated using the following equation proposed by Pereira et al.  
326 (2016):

327

$$\begin{aligned} 328 \quad \rho_p = & 1.463 + 0.1998 \tan[1.044 - 0.002 (\text{clay})] \cos[0.125 + \\ 329 \quad & 0.135(C/N) + (3.543 \cdot 10^{-5}) (\text{silt})^2 - 0.013 (\text{silt})] \cos[0.004 (\text{fine sand}) \\ 330 \quad & \cos(0.315 + \tan[0.005 (\text{clay}) - 2.317]) - 1.065 \cos[0.315 + \tan(0.005 \\ 331 \quad & (\text{clay}) - 2.317])] - 0.144 (\text{total } N) \end{aligned}$$

332

333 where *clay*, *silt*, *fine sand*, *C*, *N* and *total N* are expressed in  $\text{g kg}^{-1}$   
334 <sup>1</sup>. Total carbon stock as well as apparent <sup>14</sup>C age was calculated  
335 using linear interpolation between sampled depth.

336

337

### 338 **3. Results and discussion**

339

#### 340 *3.1. Soils description and main characteristics*

341

342 The soils presented and discussed here (BAR1 to BAR6) are  
343 located in Fig. 1. The BAR1, BAR2 and BAR4 soil are situated on a  
344 toposequence (Fig. 2) starting from a waterlogged zone, in which the  
345 water table is all the time near or above the soil surface, until at the  
346 bank of the Demini River. BAR3 is in a position equivalent to that of  
347 BAR2 (Fig. 1), but in a more hydromorphic zone characterized by  
348 Campinarana-type forest and "murundus" micro-relief, i.e. earth  
349 mounds, about 0.6 m high and 2-10 m wide, separated by U-shaped  
350 channels, as described in Ishida et al. (2014). Soils BAR5 and 6 are  
351 located further towards the centre of the highly hydromorphic area,  
352 which is waterlogged most of the year (Fig. 1). BAR1 to BAR4 soils  
353 have been studied analytically in detail; all laboratory analysis are  
354 given in Supplementary material (Tab. S1).

355 All the soils were sand to loamy sand over the whole profile,  
356 except BAR1 mainly sandy loam, and BAR3, sandy loam in the  
357 upper part of Bh (Fig. 3). In all soils, apart from a few heavy  
358 minerals as zircon and ilmenites, the identifiable minerals were  
359 quartz, kaolinite, gibbsite and goethite (Fig. 4). In all E horizons,

360 quartz was the only mineral observed. Kaolinite was observed in  
361 trace amounts (<0.5%) in other horizons and in quantifiable amounts  
362 at depth. Goethite and gibbsite were observed at depth in BAR1 and  
363 along the whole profile in BAR4.

364 The upper soil horizons varied according to local waterlogging  
365 conditions. In the mostly waterlogged areas (BAR1, BAR3, BAR5  
366 and BAR6), the surface horizon was a sticky, very fine-grained black  
367 peat (P horizons). In better drained areas, it was an A horizon. E  
368 horizons were well expressed and light in color (grey to light grey)  
369 except for BAR1, where it was weakly expressed, and BAR4, where  
370 it was absent. In the Bh horizons the C content ranged between 0.25  
371 and 3.28 % (average 1.09%), unrelated with soil colour darkness  
372 (hue) (Munsell, 1990). The C content varied with depth but was  
373 higher in the upper indurated part of BAR2 and BAR3 Bhs.

374 Considering all Bhs together, there was surprisingly no correlation  
375 between C content and clay, silt, (clay + silt) or kaolinite content ( $R^2$   
376 values < 0.13), while several studies point to the role of absorption  
377 on clay and oxide surfaces in immobilization of DOM (Kaiser and  
378 Zech, 2000; Merdy et al., 2021). Considering the soils separately,  
379 however, a correlation was observed between C content and clay  
380 content for BAR2 and BAR3 soil ( $R^2$  equal to 0.56 and 0.50,  
381 respectively) and between C content and silt content in the BAR1 soil  
382 ( $R^2$  equal to 0.39), which indicates that in these sandy materials the  
383 SOM tends to accumulate at the finest grain size levels.

384 A perched water table was observed above the Bh in the BAR2  
385 and BAR3 soils. The saturated hydraulic conductivity  $K_{sat}$  was  
386 determined on three samples from the upper part of the BAR3 Bh (at  
387 165-170 cm depth for each sample). The results gave a very low



388 average value ( $7.7 \cdot 10^{-9} \pm 2.3 \cdot 10^{-9} \text{ m s}^{-1}$ ), which corresponds to an  
389 impervious material, in accordance with the presence of perched  
390 groundwater. A hydrogen sulfide odor, indicating reducing  
391 conditions, was detected during drilling of the Bh horizons of all  
392 profiles except BAR4.

393 BAR2 and BAR3 soils are typical giant equatorial podzols, with a  
394 bleached sandy E horizon more than 1 m thick overlying a thick Bh.  
395 In areas that are mostly waterlogged, podzols profiles are either  
396 thinner (BAR5 and BAR6 soils) or less developed, such as BAR1  
397 soil where the E horizon is not bleached, probably because the lateral  
398 throughflow of the perched groundwater is slower. In the BAR4  
399 profile, the E horizons and the indurated upper part of the Bh have  
400 been removed by erosion due to the meanders of the Demini river.  
401 The % carbon in the topsoil horizon as well as in the Bh are  
402 significantly lower than in the BAR2 and BAR3 profile, indicating  
403 that profile truncation likely resulted in a loss of carbon throughout  
404 the profile. It should be noticed that the horizon situated beneath the  
405 Bh was not reached for the BAR2 and BAR3 profiles despite the  
406 casing of the borehole: the groundwater sapping in depth resulted in  
407 the rise in the borehole of a mixture of groundwater and Bh material.

408

409

## 410 *3.2. Soil organic matter*

411

### 412 *3.2.1. Fractionation and humification indexes*

413 The results of the organic matter fractionation of the BAR1,  
414 BAR3 and BAR4 soils are given in Fig. 5. Uncomplexed OM (LFF  
415 and LOF fractions) is usually considered as a transient pool between

416 undecomposed litter and mineral-associated OM (HF fraction), with  
417 the turnover of LFF and HF respectively being the faster and the  
418 lower (Christensen, 2001). Here the highest LFF percentages were  
419 observed in the topsoil horizons and decreased in the top 50 cm while  
420 the LOF and HF percentages increased, indicating progressively  
421 stronger bonds with mineral material, although it was very sandy. In  
422 these horizons, a strong negative correlation was observed between  
423 LFF and LOF (Fig. 6), suggesting that LFF transformed into LOF  
424 with depth. In BAR1 and BAR3 Bhs, the HF percentage in SOM  
425 increased rapidly with depth, up to more than 70% around 2 m in  
426 depth, then gradually decreased. The positive correlation between  
427 LFF and LOF in BAR1 suggests that these fractions were both  
428 transformed to HF in the upper 2 m of Bh, and both produced from  
429 HF or brought by percolating solutions or deep groundwater to the  
430 transition towards the C horizon. A part of the highly humified OM  
431 can however appear in the LFF fraction (Cadisch et al., 1996). In  
432 BAR4 Bh, the SOM fractions are from 50 cm depth similar to those  
433 observed at depth in BAR3 Bh, which is consistent with the  
434 hypothesis of a truncated soil.

435       There was no significant correlation between the humification  
436 index  $A_{465}$  (Tadini et al., 2018) and any of the LFF, LOF and HF  
437 fractions, indicating that aromaticity was not related to a specific  
438 fraction. The  $A_{465}$  index was however higher in the BAR4 soil than in  
439 other soils, which indicates that since the lowering of the water table,  
440 the less aromatic compounds have been preferentially leached or  
441 mineralized.

442       Considering all the samples, there was no correlation between the  
443  $H_{LIFS}$  index and the  $A_{465}$  index (Table 1). As pointed out by Tadini et

444 al. (2018), this is probably due to fluorescence self-absorption of  
 445 dark Bh samples and these authors proposed a colour-corrected index  
 446 ( $H_{LIFS-M}$ ) calculated by dividing the  $H_{LIFS}$  index by the Munsell colour  
 447 value of the bulk sample. The correlation, however, was also very  
 448 weak between the colour-corrected index  $H_{LIFS-M}$  and the  $A_{465}$  index  
 449 (Table 1). By gradually restricting the sample population to samples  
 450 belonging to narrower colour range, the correlations between  $H_{LIFS}$   
 451 and  $H_{LIFS-M}$  indexes and the  $A_{465}$  index become progressively higher:  
 452  $R^2$  between  $H_{LIFS-M}$  and  $A_{465}$  was 0.79 when considering only samples  
 453 with a colour value  $<4$ . This indicates that the  $H_{LIFS}$  signal is indeed  
 454 dependent on the degree of humification, but that the colour  
 455 interference masks this dependence: black material lowered the  
 456 fluorescence signal by absorption when white material exhausted the  
 457 fluorescence signal by diffusion. The correction proposed by Tadini  
 458 et al. (2018) was insufficient for our sample set. Pending the  
 459 development of an effective correction, it is therefore advisable to  
 460 restrict the use of the  $H_{LIFS}$  or  $H_{LIFS-M}$  indexes to samples belonging to  
 461 a restricted colour range.

462

463 **Table 1**

464 Pearson coefficient of determination  $R^2$  between  $A_{465}$  index and  $H_{LIFS}$ ,  
 465  $H_{LIFS-M}$  indexes

466

	$H_{LIFS}$	$H_{LIFS-M}$
All samples (n = 20)	0.06	0.12
Samples with colour value $<5$ (n = 13)	0.47	0.73
Samples with colour value $<4$ (n = 11)	0.65	0.79

467

468

469 *3.2.2. Apparent age, C/N, respiration and isotopic data*

470 The SOM of all topsoil horizons had a low apparent  $^{14}\text{C}$  age (<110  
471 y), indicating an average C turnover around 100 y (Trumbore, 2000),  
472 and a C/N < 25 (Fig. 7). Cumulative respiration was very high for the  
473 more hydromorphic P horizons (BAR1 and BAR3). In the well-  
474 expressed E horizons (BAR2 and BAR3), ages ranged from 205 to  
475 830 y, C/N from 32 to 37 and cumulative respiration was high. In the  
476 Bh horizons, the apparent ages were variable but all high, ranging  
477 from 2510 to 9980 y. The C/N was higher than 40 (62,7 cm on  
478 average) in all the Bhs of untruncated podzols, that is to say profiles  
479 BAR1, -2, -3 where the water table have not been lowered. In BAR4,  
480 it ranged from 21 to 31. There were no significant differences  
481 between the profiles for  $\delta^{13}\text{C}$ , which increased slightly with depth,  
482 whereas the values of  $\delta^{15}\text{N}$  were more discriminating with higher  
483 values for the BAR4 whole profile and the BAR2 topsoil (Fig. 8).

484 A principal component analysis (PCA) was performed on all  
485 the parameters discussed above, to which were added the values of  
486 the N % in the SOM humic acid fractions (%N HA, data from Tadini  
487 et al., 2018) (Fig. 9). It showed a positive Pearson correlation ( $R >$   
488 0.65) between  $^{14}\text{C}$  age,  $A_{465}$  index, depth,  $\delta^{13}\text{C}$  on one side and  
489 between N(%), %N HA on the other, the variables from one group  
490 having negative correlations ( $R < -0.65$ ) with those from the other  
491 group. It also showed a very negative correlation between  $\delta^{15}\text{N}$  and  
492 C/N.

493 These relationships indicate that, on the one hand, the increase in  
494 age is related to the increase in aromaticity and  $\delta^{13}\text{C}$  and the decrease  
495 in N%, especially in HA, which is the expected SOM evolution in the  
496 Bh, resulting in a C/N greater than 45. In the BAR4 profile and the

497 BAR2 topsoil, the lower C/N and higher  $\delta^{15}\text{N}$  indicate that the  
498 lowering of the water table has resulted in a better oxygenation and N  
499 supply from the topsoil, promoting microbial activity which  
500 consumed C and increased  $^{15}\text{N}$  (Kamer et al., 2003; Dijkstra et al.,  
501 2006).

502

### 503 3.2.3. *Respiration kinetics*

504 Results of the modelling of the respiration data are given in Fig.  
505 10. Topsoil horizons were characterized by a fast pool having a larger  
506 relative size when hydromorphic (BAR3), and smaller when better  
507 drained (BAR2 and BAR4). Well expressed E horizons (BAR2 and  
508 BAR3) showed a large relative size of the fast pool and high  
509 respirations rates in fast and slow pools. Bh horizons showed a low  
510 relative size of the fast pool and low respiration rates of the slow  
511 pool, consistent with high aromaticity and high C/N. In the BAR4  
512 profile these latter characteristics were observed up to the topsoil,  
513 indicating that over the entire profile the slow pool has not, or very  
514 little, rejuvenated after truncation.

515 The respiration rates obtained here can be compared to respiration  
516 rates obtained for other soils with similar methods at a temperature  
517 comprised between 25 and 30° (Fig. 11). Yang et al. (2007), Haddix  
518 et al. (2011) and Kern et al. (2019) provided data from topsoil  
519 horizons of a variety of soil types from cold to hot, and humid to dry  
520 climates; Lucas et al. (2020) provided data from topsoil and Bh  
521 horizons of other Amazonian podzols. The respiration rates obtained  
522 here are in the same range that those obtained for the topsoil of other  
523 soil types regarding the fast pool, but lower regarding the slow pool.  
524 For the latter, the respiration rate were in the range  $[2.4 \cdot 10^{-2} - 5.0 \cdot 10^{-2}]$

525  $^1] \text{ y}^{-1}$  for topsoil of other soil types,  $[2.4 \cdot 10^{-3} - 1.8 \cdot 10^{-2}] \text{ y}^{-1}$  for topsoil  
526 of untruncated podzols and  $[6.8 \cdot 10^{-4} - 2.4 \cdot 10^{-3}] \text{ y}^{-1}$  for the Bh  
527 horizons. The respiration rate of the Bh slow pool is therefore on  
528 average about 2 orders of magnitude lower than that observed for the  
529 topsoil of most soils.

530

### 531 3.3. Carbon stock and soil genesis

532

#### 533 3.3.1. Profile genesis

534 The untruncated podzol profiles, where the water table has not  
535 been lowered, store large amount of C (at least 67.9, 73.7 and 56.8 kg  
536  $\text{C m}^{-2}$  for profiles BAR1, -2 and -3, respectively). The average is 62.8  
537  $\text{kg ha}^{-1}$ , which is consistent with the results of previous studies  
538 (Montes et al., 2012; Pereira et al., 2016; Doupoux et al., 2017). We  
539 calculated the minimum time required to form the presently observed  
540 BAR1, BAR2 and BAR3 profiles and the time required to reach 99%  
541 of the observed  $^{14}\text{C}$  age and Bh C pool, considering that these values  
542 correspond to a steady state (Fig. 11 and Table 2). The calculations  
543 gave a range of time according to assumptions about the size of the  
544 fast Bh pool. The minimum time to form the profile is a lower bound  
545 but not likely, because it corresponds to a scenario with no C outflux  
546 from the Bh and in which the profile evolves very quickly (Fig. 12).  
547 The time needed to reach 99% of the steady state gives a more  
548 probable order of magnitude of the minimum genesis time. The  
549 BAR4 profile was not considered because, truncated, it does not meet  
550 the conditions of constant flux rates with time.

551 The order of magnitude of the time to reach 99% of steady state is  
552 around 30000 y for the BAR1 and BAR2 profiles and around 50000

553 years for the BAR3 profile (Table 2). For the BAR2 and BAR3  
 554 profiles these times are certainly underestimated because the horizon  
 555 located beneath the Bh was not reached during the drilling so that the  
 556 Bh total C stock and therefore the genesis time were underestimated.  
 557 Regardless, these results are consistent with the late Pleistocene age  
 558 of the parent material and show that these podzols accumulated  
 559 organic carbon for a very long time.

560

561 **Table 2**

562 Carbon stock, apparent age and time required to form the profiles

Profile	P or A horizons		Bh horizon		Minimum time to form the profile (y)	Time to reach 99% of steady state (y)
	Carbon stock (kg m <sup>-2</sup> )	Apparent age (y BP)	Carbon stock (kg m <sup>-2</sup> )	Apparent age (y BP)		
BAR1	29.59	110	35.58	4785	9690 – 11400	29250 – 30380
BAR2	6.71	105	59.95	4689	9830 – 10550	28700 – 29400
BAR3	7.84	108	37.51	6699	14800 – 18260	48640 – 54215
BAR4	3.73	106	19.28			

563

564

565 *3.3.2. Soil OM dynamics after truncation*

566 How much and at what rate was the organic carbon of the BAR4  
 567 profile mineralized after truncation of the profile and corresponding  
 568 oxygenation of the Bh? To obtain an order of magnitude, the initial C  
 569 content of the BAR4 profile can be assumed to be the same as that  
 570 currently observed in the untruncated podzol, which will be  
 571 represented here by the average of the BAR2 and BAR3 profiles.  
 572 Measured respiration rates allow calculation of how long it takes to  
 573 decrease the C content of untruncated podzol to the BAR4 values and  
 574 how much C would be released into the atmosphere after the perched  
 575 groundwater disappears and oxygenated air enters the Bh. The

576 calculation was performed using the following equation, and the data  
577 used for the calculation is given in Table 3.

578

$$579 \quad C = C_0 \left( f_{Fp} (e^{-k_{Fp}t}) + (1 - f_{Fp}) (e^{-k_{Sp}t}) \right)$$

580

581 Where  $C$  is the carbon pool at time  $t$ ,  $C_0$  the initial carbon pool,  $f_{Fp}$   
582 the initial fast pool fraction,  $k_{Fp}$  and  $k_{Sp}$  the respiration rate of the fast  
583 and the slow pool, respectively. The results are that it takes about 10  
584 and 1220 y for topsoil horizon and Bh, respectively, to derive BAR4  
585 values from untruncated podzol values. The latter seems consistent  
586 with the rate of bank erosion by an Amazonian meander, estimated  
587 at, in  $\text{m y}^{-1}$ , 0.008 to 0.015 of the meander width (Constantine et al.,  
588 2014), which would give a displacement of 1 to 2  $\text{m y}^{-1}$  for the  
589 Demini meander. It should be noted, however, that the lateral  
590 widening of the flood plain is slower than the displacement of a  
591 meander (Camporeale et al., 2006).

592 Assuming that the disappearance due to climate change of the  
593 permanent water-table perched above the Bh would have the same  
594 consequence as what was observed in the toponosequence, we  
595 can extrapolate the measured mineralization rate to the Amazonian  
596 podzol area. The carbon pools decrease being exponential, the  
597 emission of C per year decreases over time: it is on average about 63  
598  $\text{gC m}^{-2} \text{y}^{-1}$  during the first 10 years, 54  $\text{gC m}^{-2} \text{y}^{-1}$  during the  
599 following 90 years and 41  $\text{gC m}^{-2} \text{y}^{-1}$  during the following 400 years.  
600 These values, related to the 155000  $\text{km}^2$  of the Amazonian podzol  
601 area (Montes et al., 2011), would correspond to an emission of C into  
602 the atmosphere about  $9.8 \cdot 10^{12}$ ,  $8.4 \cdot 10^{12}$ ,  $6.3 \cdot 10^{12}$   $\text{gC y}^{-1}$  for the 0-10 y,



603 10-100 y, 100-500 y periods, respectively. These values, however,  
604 remain low compared to current carbon emission by fossil fuels  
605 (about  $9 \cdot 10^{15} \text{ g y}^{-1}$ , IEA (2020)). It should also be noted that other  
606 processes may arise after Bh oxygenation begins. Some can  
607 accelerate degradation, such as the addition of nitrogen from the  
608 surface horizons (Qiao et al., 2016) or fluctuating water content (Van  
609 Gestel et al., 1993), others can slow it down, such as substrate  
610 availability (Wei et al., 2015). **Table 3**  
611 Data for calculation of SOM mineralization after truncation.  
612 Untruncated podzol values are the average of values obtained for the  
613 BAR2 and BAR3 profiles.

	C content		Fast pool fraction	Respiration rate ( $\text{y}^{-1}$ )	
	$\text{kg m}^{-2}$	$\text{kg m}^{-3}$		Fast pool	Slow pool
Topsoil horizons					
Untruncated podzol	7.27	11.88	$1.25 \cdot 10^{-3}$	7.70	$1.01 \cdot 10^{-2}$
BAR4	3.73	10.68	$5.04 \cdot 10^{-3}$	6.96	$7.72 \cdot 10^{-4}$
Bh					
Untruncated podzol	48.73	19.43	$1.25 \cdot 10^{-3}$	4.54	$1.18 \cdot 10^{-3}$
BAR4	19.28	4.59	$1.22 \cdot 10^{-3}$	7.08	$6.76 \cdot 10^{-4}$

614

615

## 616 **4. Conclusions**

617

618 The studied topochronosequence comprised typical equatorial  
619 giant podzol and equatorial hydromorphic podzols, both of which  
620 with a perhumid Bh under reducing conditions. They store large  
621 amounts of C ( $62.8 \text{ kg m}^{-2}$  on average) and result from a long  
622 genesis time the minimum estimate of which is around 10-20 ky, but  
623 which is very probably greater than 30-50 ky. The organic matter of  
624 topsoil had a rapid average turnover, about 100 y, therefore likely to  
625 mineralize very quickly in the event of a change towards a drier

626 climate. In the Bh of these podzols, increased OM age was related to  
627 increased heavy fraction, aromaticity, C/N and  $\delta^{13}\text{C}$ . The  $H_{\text{LIFS}}$   
628 humification index was found to be inappropriate for these soils, due  
629 to interference with the soil colour.

630 The lowering of the water table in part of the topochronosequence  
631 and the subsequent oxygenation of the Bh resulted in a decrease in  
632 the Bh C stock from about  $19 \text{ kgC m}^{-3}$  to  $5 \text{ kgC m}^{-3}$  that requires,  
633 according to measured respiration rates, a duration of around 1200 y.

634 Applying these respiration rates to the Bh oxygenation that would  
635 result from climate change gives a rough estimate of subsequent C  
636 emission, around  $55 \text{ gC m}^{-2} \text{ y}^{-1}$  on average during the first 100 years.  
637 Extrapolated to all Amazonian podzols, and regardless of other  
638 processes that may be involved, this value would correspond to  $8.5$   
639  $10^{12} \text{ gC y}^{-1}$ .

640

641

## 642 **CRedit authorship contribution statement**

643

644 **Célia R. Montes:** Conceptualization, Methodology, Writing -  
645 Original Draft, Investigation, Supervision, Project administration,  
646 Funding acquisition. **Patricia Merdy:** Methodology, Formal  
647 analysis, Writing – review & Editing. **Wilson T.L. da Silva:**  
648 Investigation, Supervision. **Débora Ishida:** Investigation,  
649 Ressources. **Adolpho J. Melfi:** Investigation, Writing – review &  
650 Editing. **Roberta C. Santin:** Investigation. **Yves Lucas:**  
651 Conceptualization, Methodology, Data Curation, Writing - Original  
652 Draft, Supervision, Project administration, Funding acquisition.

653

## 654 **Declaration of Competing Interest**

655

656 The authors declare that they have no known competing financial  
657 interests or personal relationships that could have appeared to  
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669

670

## 671 **Appendix A. Supplementary data**

672

673

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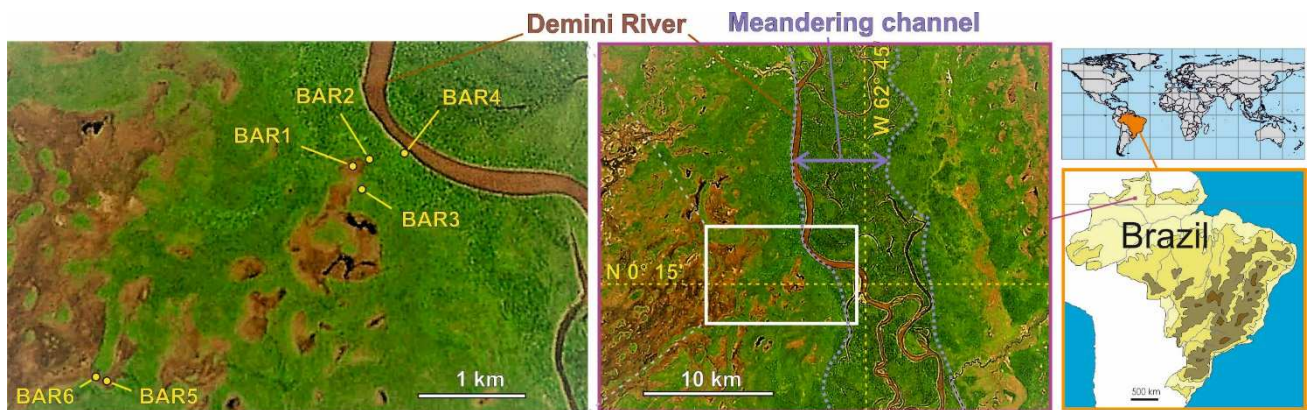
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905 **Fig. 1**

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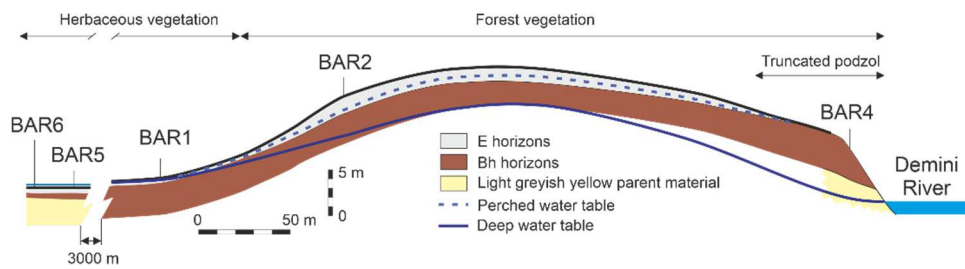


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910 **Fig. 2**

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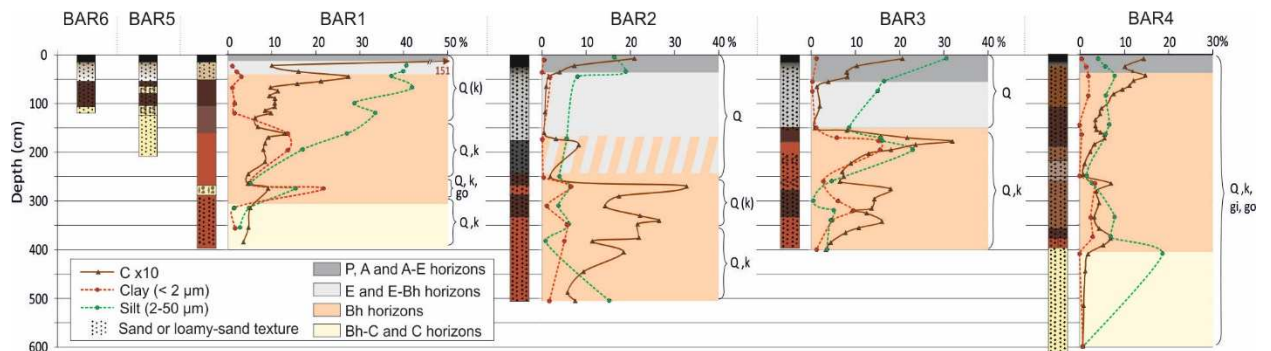
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915 **Fig. 3**

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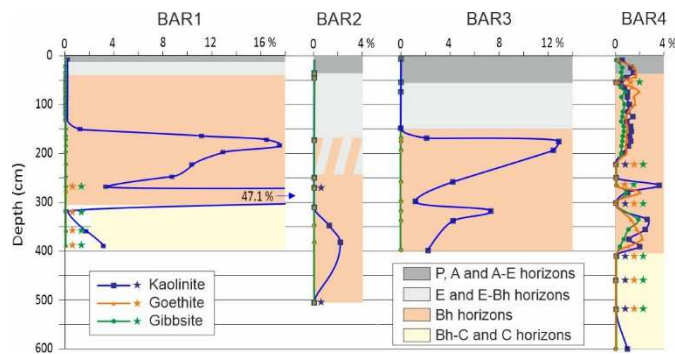


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920 **Fig. 4**

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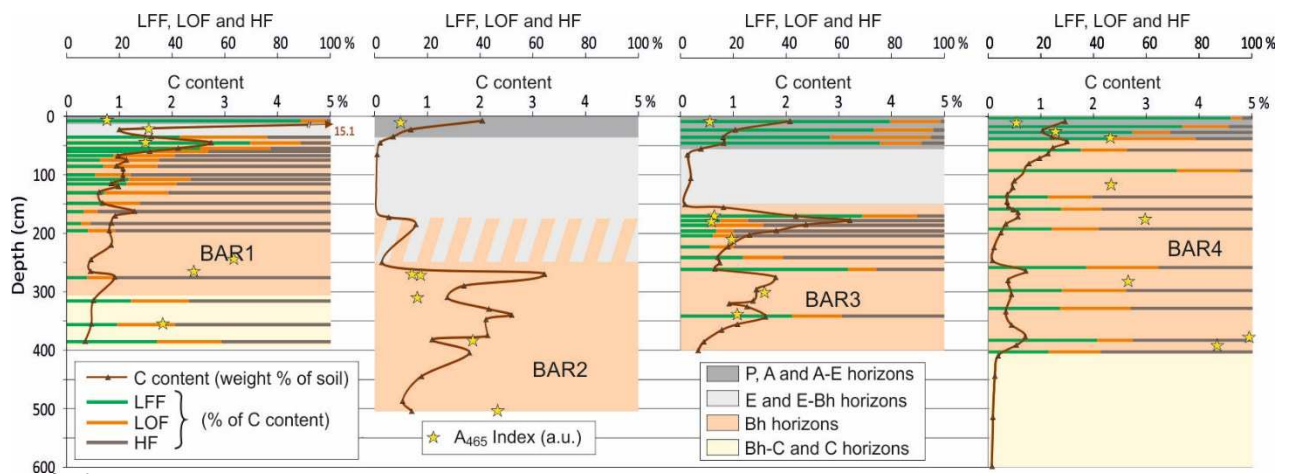
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925 **Fig. 5**

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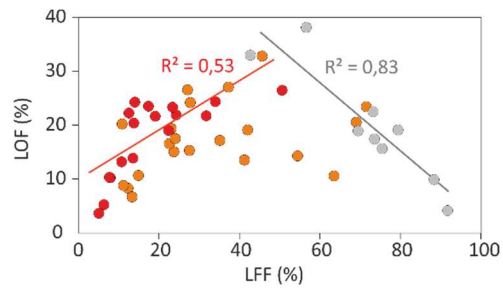
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932 **Fig. 6**

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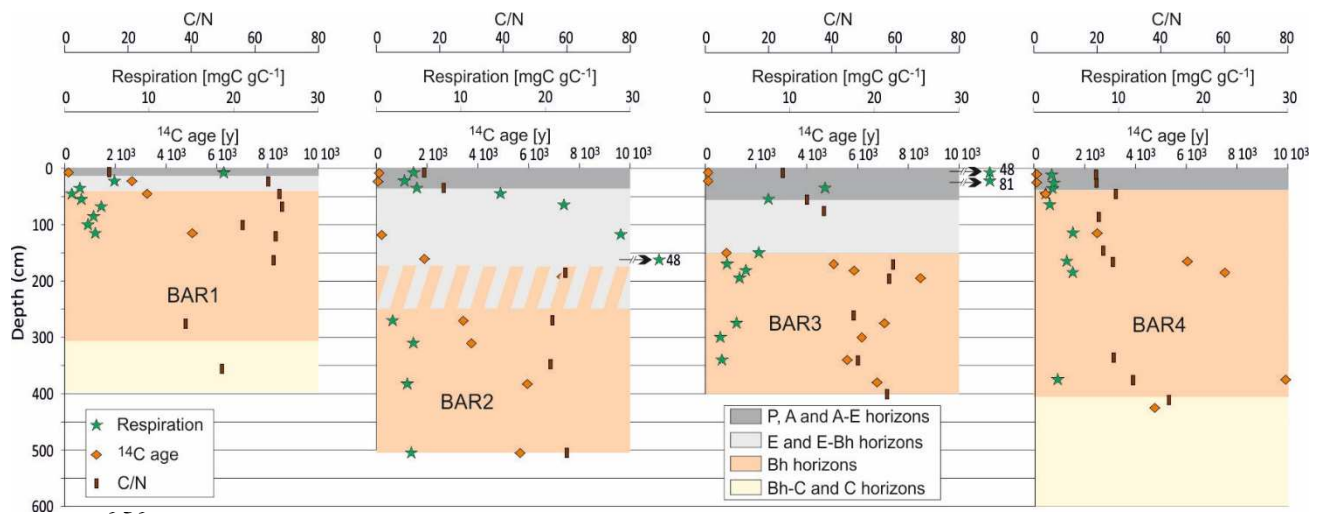
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937 **Fig. 7**

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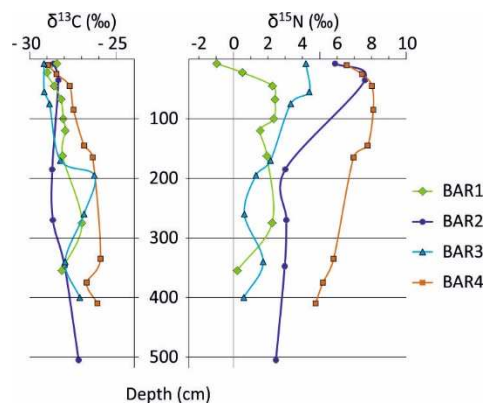
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943 **Fig. 8**

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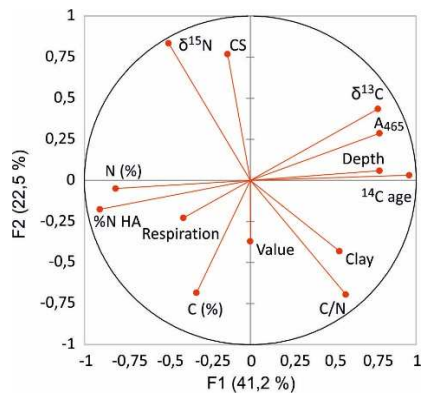
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948 **Fig. 9**

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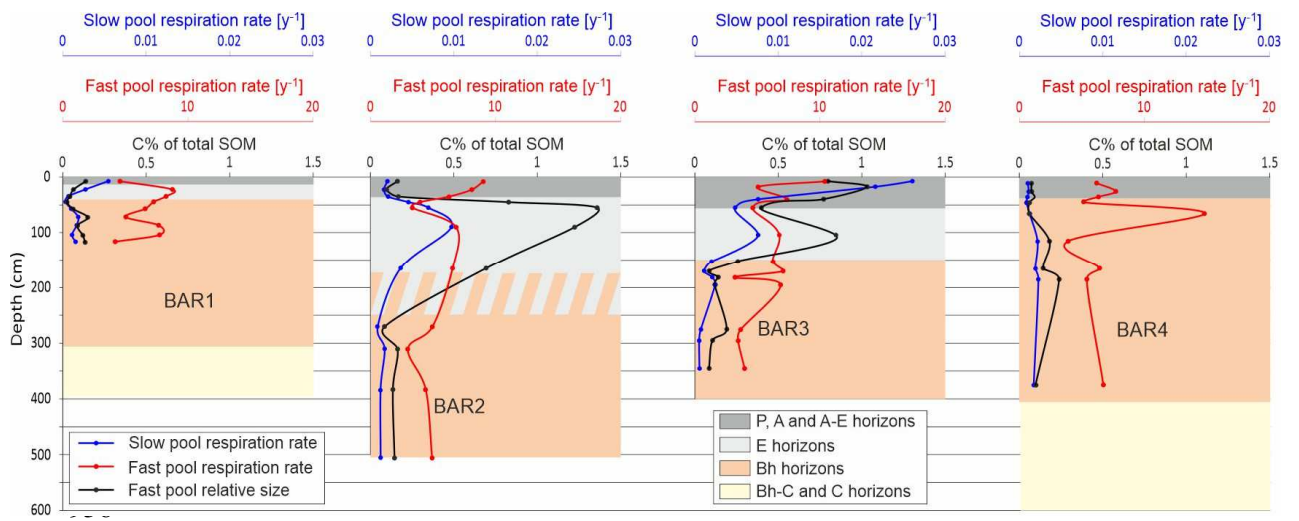
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954 **Fig. 10**

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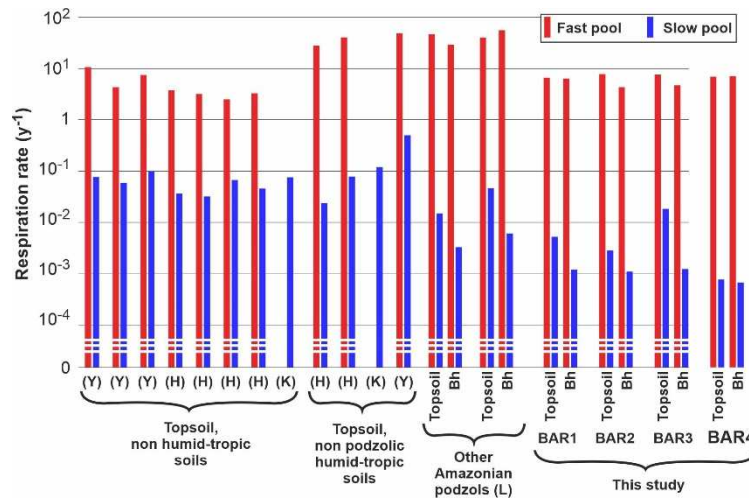


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959 **Fig. 11**

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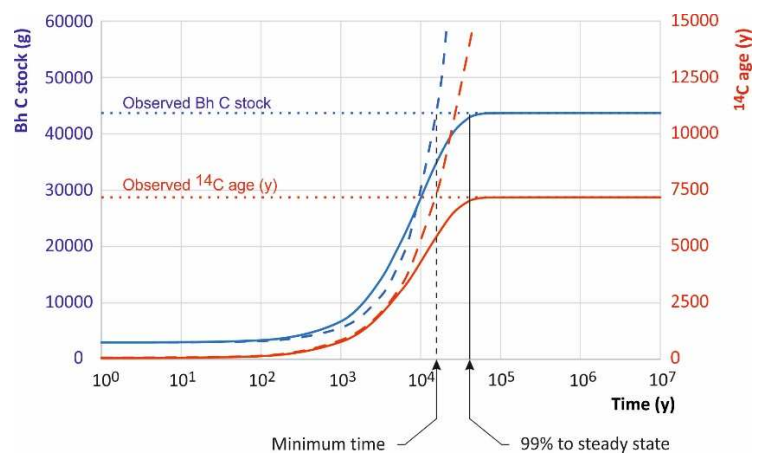
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964 **Fig. 12**

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969 **Figure caption**

970

971 **Fig. 1.** Location of the studied site

972

973 **Fig. 2.** Situation of the soil profiles with regard to topography and  
974 sketch of the horizon geometry.

975

976 **Fig. 3.** The studied profiles: borehole logs (colours seek to reflect  
977 actual colours); C (carbon), clay and silt in %; mineralogy. Q: quartz,  
978 k: kaolinite, gi: gibbsite, go: goethite (uppercase: dominant mineral;  
979 lowercase in parentheses: trace mineral only). E-Bh horizons:  
980 transition between E and Bh horizons; Bh-C horizons: transition  
981 between Bh and C horizons.

982

983 **Fig. 4.** Quantifiable kaolinite, goethite and gibbsite in the BAR1  
984 to BAR4 profiles. A star indicates that the given mineral has been  
985 identified but in a quantity too small to be quantified.

986

987 **Fig. 5.** Organic matter fractionation and  $A_{465}$  humification index.  
988 LFF: light free fraction, LOF: light occluded fraction, HF: heavy  
989 fraction.

990

991 **Fig. 6.** Relationships between LFF and LOF % in SOM. Grey  
992 points: P, A and A-E horizons; red and orange points: Bh and B-C  
993 horizons. Red points refer to the BAR1 profile.

994

995 **Fig. 7.** SOM apparent  $^{14}\text{C}$  age, C/N values and cumulative  
996 respiration at 660 days.

997

998 **Fig. 8.** SOM isotopic data

999

1000 **Fig. 9.** PCA correlation circles on the first two factorial axes.

1001 Percent on each factorial axis gives the explained variance. Value:

1002 value of the horizon Munsell color; %N HA: % of N in the extracted

1003 humic acid fraction of the SOM (data from Tadini et al., 2018). CS:

1004 coarse sand.

1005

1006 **Fig. 10.** Relative size of the SOM fast pool (C% of the total SOM)  
1007 and respiration rates of the slow and fast pool.

1008

1009 **Fig. 11.** Respiration rates of fast and slow pools of soil organic  
1010 matter. (Y): Yang et al., 2007; (H): Haddix et al., 2011; (K) : Kern et  
1011 al., 2019 ; (L): Lucas et al., 2020.

1012

1013 **Fig. 12.** Modelling the time of genesis. Dashed lines: scenario for  
1014 minimum time; plain lines: scenario for steady state.

1015

