

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

Célia R Montes, Patricia Merdy, Wilson T.L. da Silva, Débora Ishida, Adopho

J Melfi, Roberta C Santin, Yves Lucas

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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	
6	Célia R. Montes ^a , Patricia Merdy ^b , Wilson T.L. da Silva ^c , Débora
7	Ishida ^a , Adopho J. Melfi ^a , Roberta C. Santin ^d , Yves Lucas ^{b*}
8	
9	^a IEE, NUPEGEL, Universidade de São Paulo, São Paulo 05508-
10	010, Brazil
11	^b Université de Toulon, Aix Marseille Université, CNRS, IM2NP,
12	83041 Toulon CEDEX 9, France
13	^c Embrapa Instrumentation, São Carlos 13560-970, Brazil.
14	^d CENA, Universidade de São Paulo, Piracicaba 13400-970,
15	Brazil
16	
17	*Corresponding author (lucas@univ-tln.fr)
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19	

20 Hightlights

21		
22	•	Active hydromorphic podzol in the area store around 63 kgC
23		m ⁻²
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 29 30	•	Drier climate would induce C emission from Amazonian podzol Bhs
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 indexes, ¹⁴C average age) and its lability under oxic conditions was 43 44 estimated by measuring respiration during a 660-days experiment. 45 Podzol genesis time was calculated by constraining the carbon fluxes using both C stock and ¹⁴C average age. The results confirmed that 46 47 the studied podzols store large amounts of carbon (62.8 kgC m⁻² on average). They resulted from a long genesis time, probably greater 48 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 drier climates at 55 gC m⁻² y⁻¹ on average during the first 100 y, 53 which would correspond, by extrapolation, to 8.5 10^{12} gC y⁻¹ for all 54 55 Amazonian podzols. 56

58	Keywords: Amazon podzol; Soil organic matter; Humification
59	index; Soil carbon storage and loss; Climate change; Soil formation
60	rate
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63	1. Introduction
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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⁻² in the whole profile and more than 80 kgC m^{-2} in the only deep Bh 87 88 (Montes et al., 2011). These soil systems therefore contribute 89 significantly to the global CO₂ 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 ₂
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 ₂ 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.
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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 at 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; Dubroeucq 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

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-µm 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 (A₄₆₅) 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 H₂O₂. Main minerals were identified by XRD 221 (X-ray diffraction) of Cu Ka radiation on powder samples using a 222 Philips PW 1877 diffractometer. Kaolinite and gibbsite were

taken in boreholes by hammering a cylindrical \emptyset 3 cm piston

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 $Ø$ 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 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 μ 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

fraction (HF). C on the filters and on the final centrifugation pelletswas 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_2 257 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

After freeze drying, soil samples were ground to pass a 106-µm
mesh. Between 35 to 90 mg of the sample, depending on carbon
concentration, was transferred to a tin capsule for elemental and
isotopic analysis. The isotope ratios of carbon (¹³C/¹²C) and nitrogen
(¹⁵N/¹⁴N) of each sample were determined using a continuous-flow
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	δ (% <i>o</i>) = [(Rsample/Rstandard) – 1] × 1000
284	
285	where R is the ratio of ${}^{13}C/{}^{12}C$ or ${}^{15}N/{}^{14}N$. 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 ${}^{14}C$
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	
328	$\rho_p = 1.463 + 0.1998 \tan[1.044 - 0.002 \ (clay)] \cos[0.125 + 0.002 \ (clay)] \cos[0.125 \ (cl$
329	$0.135(C/N) + (3.543 \ 10^{-5}) \ (silt)^2 - 0.013 \ (silt)] \cos[0.004 \ (fine \ sand)]$
330	$\cos(0.315 + \tan[0.005 \ (clay) - 2.317)] - 1.065 \ \cos[0.315 + \tan(0.005 \ clay) - 2.317)]$
331	(clay) - 2.317])] - 0.144 (total N)
222	

333	where <i>clay</i> , <i>silt</i> , <i>fine sand</i> , <i>C</i> , <i>N</i> and <i>total N</i> are expressed in g kg ⁻
334	¹ . Total carbon stock as well as apparent ¹⁴ 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 $10^{-9} \pm 2.3 \ 10^{-9} \text{ m s}^{-1}$), 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	$(H_{\text{LIFS-M}})$ 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 $H_{\text{LIFS-M}}$ 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 $H_{\text{LIFS-M}}$ indexes and the A_{465} index become progressively higher:
452	R^2 between $H_{\text{LIFS-M}}$ 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 $H_{\text{LIFS-M}}$ 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 $H_{\text{lifs}}\text{,}$
465	H _{LIFS-M} indexes
466	
	All samples (n = 20) H_{LIFS} H_{LIFS-M} Samples with colour value <5 (n = 13)

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

470	The SOM of all topsoil horizons had a low apparent ¹⁴ 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 δ^{13} C, which increased slightly with depth,
482	whereas the values of $\delta^{15}N$ 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 C age, A ₄₆₅ index, depth, δ^{13} 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 $\delta^{15}N$ 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 $\delta^{13}C$ 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 δ¹⁵N 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 ¹⁵N (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. For the latter, the respiration rate were in the range $[2.4 \ 10^{-2} - 5.0 \ 10^{-1}]$ 524

525	¹] y^{-1} for topsoil of other soil types, [2.4 $10^{-3} - 1.8 10^{-2}$] y^{-1} for topsoil
526	of untruncated podzols and $[6.8 \ 10^{-4} - 2.4 \ 10^{-3}] \ y^{-1}$ 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	C m ⁻² for profiles BAR1, -2 and -3, respectively). The average is 62.8
537	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 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

Table 2

Profile	P or A horizons		Bh horizon		Minimum	Time to reach
	Carbon stock (kg m ⁻²)	Apparent age (y BP)	Carbon stock (kg m ⁻²)	Apparent age (y BP)	time to form the profile (y)	99% of steady state (y)
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					

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

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 groudwater disappears and oxygenated air enters the Bh. The

576 calculation was performed using the following equation, and the data577 used for the calculation is given in Table 3.

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

581	Where <i>C</i> is the carbon pool at time <i>t</i> , 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 poll, 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 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 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 topochronosequence, 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	gC m ⁻² y ⁻¹ during the first 10 years, 54 gC m ⁻² y ⁻¹ during the
599	following 90 years and 41 gC m ⁻² y ⁻¹ during the following 400 years.
600	These values, related to the 155000 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 10^{12} , 8.4 10^{12} , 6.3 10^{12} gC y ⁻¹ for the 0-10 y,

- 604 remain low compared to current carbon emission by fossil fuels
- 605 (about 9 10^{15} 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	t	Fast pool fraction	Respirati	on rate (y ⁻¹)
	kg m ⁻²	kg m ⁻³		Fast	Slow pool
				pool	
Topsoil horizons					
Untruncated podzol	7.27	11.88	1.25 10-3	7.70	1.01 10-2
BAR4	3.73	10.68	5.04 10-3	6.96	7.72 10-4
Bh					
Untruncated podzol	48.73	19.43	1.25 10-3	4.54	1.18 10-3
BAR4	19.28	4.59	1.22 10-3	7.08	6.76 10-4

614

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 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

⁶¹⁵

626	climate. In the Bh of these podzols, increased OM age was related to
627	increased heavy fraction, aromaticity, C/N and $\delta^{13}C.$ The H_{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 kgC m ⁻³ to 5 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 gC m ⁻² 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. Adopho J. Melfi: Investigation, Writing – review &
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651	Conceptualization, Methodology, Data Curation, Writing - Original
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653

654 Declaration of Competing Interest

655

656	The authors declare that they have no known competing financial
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659

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Fig. 1



910 Fig. 2





920 Fig. 4



Fig. 5







- 937 Fig. 7











Fig. 10







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959 Fig. 11
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Fig. 12



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 A₄₆₅ 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 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	

