## **BG-2016-545** Response to referees and marked-up manuscript

## **Response to Referee #1 (Dr. C.A. Sierra)**

## Response to the general comments

First, we would like to thank Dr. Sierra for his constructive remarks and reassure him about the interpretation of radiocarbon data. We used the  $F_a$  radiocarbon data for modelling. In order to compare the Bh between profiles, we calculated a conventional, uncalibrated apparent age from the  $F_a$  radiocarbon values. The paragraph from line 86 to 91 is actually confusing: the Poznań Radiocarbon Laboratory has indeed provided both the values of  $F_a$  and calibrated ages, the latter having not been used. Regarding the topsoil horizons, the bomb carbon should not be neglected so that we retrocalculated a pre-1950  $F_a$  value that we used for modelling. The paragraph has been modified (lines 90-97), as well some column legends in Table 1 that were incorrect, and we added the reference to Sierra, 2014 because of the good synthesis given in this paper. The  $F_a$  values were added in Tables 1 and 2.

Regarding the second concern, and as was pointed out by the reviewer, we used the concept of minimum time and time to steady-state to compare the different soils within the context of this analysis.

- The value we used for the minimum time ( $\beta_{Bh} = 10^{-10}$ ) is not arbitrary: we used a value different from zero for numerical reasons, in order to avoid denominators equal to zero (see for example equ. 12). We checked that the difference between the minimum times obtained using  $\beta_{Bh} = 10^{-10}$  and  $\beta_{Bh} = 10^{-20}$  is negligible (lower than 0.0005%). We clarified this point in the new version of the manuscript (lines 227-229).
- We agree with the reviewer that the proportion of the steady-state value set to 99% is arbitrary. Values closer to 100% would give a dramatic increase of the time needed to form the profile, as shown on Fig. 8. We used 99% because, as shown on Fig. 8, this value gives a result sufficiently close to the horizontal asymptote to give a reasonable evaluation of the time necessary to reach a steady state. This is now explained on lines 209-211.

### *Response to the technical comments.*

Reviewer comments are given in bold, our response in normal font

• The 14C ages presented in the abstract are misleading because you do not meet the closed system assumption. I would rather not present these values, or if you decide to present them, mention that you calculated them even though you do not meet the assumptions of the dating method.

We specified in the abstract that the given ages are calculated apparent ages.

• Line 63. What database? Is it publicly available? Can you provide a reference or a doi? This is a database of 80 podzol profiles which have been studied in detail and of which 11 have been dated, this database will be the subject of a further publication. This is now indicated on lines 61-65.

• Line 75. 'Conventional age calibration' is a contradiction. Conventional radiocarbon age is the age assuming Libby's half life, and does not use a calibration curve. What you probably mean is

# 'age calibration', but as I mentioned above, this step is not needed for your modeling setup so you may consider eliminating this section from your methods.

This was corrected – see response above.

# • Line 112. I had problems understanding this step and the corresponding Fig 5. You may need to provide additional details.

We explained better this step: in eq (7), we give the expression of the  $F_{at_i}$  value ( $F_a$  value of the topsoil OM on year *i*) as a function of the  $F_{at_{i+1}}$  value ( $F_a$  value of the topsoil OM on year *I*+1), and we explained on lines 146-148 the iterative retrocalculation.

• Section 2.3. It is not clear from the description of the simulation setup what is the calendar year corresponding to t = 0. In other words, did you always started your simulations at a specific calendar year or did this varied for the different soils. This information is important because the atmospheric radiocarbon value corresponding to t = 0 influence the forward trajectories for the soil radiocarbon values.

The simulations did not started at a specific year. We used the present day atmospheric carbon value to simulate the Bh formation. This is an approximation, as it is known that atmospheric radiocarbon value was higher than at present (see for example Kitagawa and Van der Plicht, 1998; Reimer et al., 2009), which likely leads to a systematic underestimation of development durations, although this underestimation remains low compared to uncertainty. We addressed this question in section 3.3, lines 349-352.

### • Equation 8. Why is P a subscript of \_ and C? Is this a typo?

It was a "copy and paste" error and was corrected.

• Line 171. These numbers are in reverse order. Curve 1 in Fig 7 has a time required to reach 99% of the steady state of 43 103, while curve 2, 345 103. This also makes sense since Montes et al. suggests a much higher value of vertical C C3 transfers than Sierra et al., therefore the values from Montes et al. should reach the steady-state faster. OK, this was corrected.

• Line 184. This is a very arbitrary definition of minimum time. if \_Bh is 10–20, or 10–30, the 'minimum time' would change drastically, and there is not any relevant reason for why it should be 10–10. I would recommend not using this concept of minimum time.

See explanation above – this minimum time is really significant, we used  $10^{-10}$  in place of 0 for numerical reasons but the result is the same as if 0 is used. We also checked this using equations rewritten for  $\beta_{Bh} = 0$ .

• Line 189. What is this maximum absolute error propagation? Did you define this before? This is the maximum absolute error, this was corrected in the text (line 241).

• Lines 247 and 252. Are these decimal numbers? Change comma for point. This was corrected.

• Tables. I'm missing a table with the obtained values of the parameters of the model of Fig 4 obtained for the four different soils. This information is somehow imbedded in Fig 12, but as total stocks and fluxes, and not with the values of the parameters used to obtain these numbers. We added a table to give the values of the parameters (Table 4).

## • Figures. Figure captions are very poor. Please provide enough information in the caption to better interpret the figures.

This problem corresponded to a poor framing of the figures, which cut some of the legend given within the figures. It was corrected in the new version.

## **Response to Referee #2**

The referee comments are given in quotation marks. As a preamble, we emphasize that most of the answers to the referee's questions can be found in the original manuscript. We agree, however, with the referee that several explanations were unclear and we have improved the manuscript in this regard.

### Response to the general comments

"This study used the measurements of carbon stock and 14C of soil carbon at different soil layers to constrain the carbon fluxes into and out of the Bh layer and its carbon turnover rate. Even for a single –pool model of soil carbon in Bh layer at non-steady state, there are three unknowns: influx, efflux and turnover rate, with only two observations for each site (total amount of carbon and carbon age). Theoretically, the optimization problem is under-determined, there will be infinite number of solutions. However only a unique solution was found in this study. Therefore I must have missed additional data constraint used in the optimization by the authors."

Response: In a first step (§ 3.1.2) we used the single-pool model to determine two particular solutions for which there are only two unknowns, the conditions for obtaining the stationary state (input = output) and the minimum formation time (output = 0). This first step showed that the output fluxes from older Bhs were too low compared to the measures reported by previous studies and that it is therefore necessary to consider two Bh pools. In the second step (§ 3.2.2) we clearly stated that " there is an infinity of solutions for modelling the Bh formation" (line 225 of initial manuscript) and that "We therefore carried out a sensitivity analysis to determine how the main parameters (size of the fast pool of the Bh, C flux input and output C rates for the Bh pools) affected the profile genesis time and to understand the relationships between these parameters" (lines 226-228 of initial manuscript). This analysis and data from literature allowed to exclude unrealistic values and to constrain C fluxes and mineralization rates, as explained on lines 245 to 251 of old manuscript. To better explain the data constraint we modified the manuscript on lines 263-266 and lines 316-326 of the new version of the manuscript.

"In general I found that the manuscript provides quite a lot of details and reasoning for the approach taken in this study. However the key message was somehow buried by detail as presented. Significant modifications should be made to distil wealth of information to highlight the key message. That is what are the magnitudes of carbon influx and efflux from the Bh soil layer and its turnover rate."

Response: The magnitude of carbon influx and efflux to the Bh pools are given on Fig. 12. We did not specify the turn-over rates because the slow pool of the Bh is not in a steady state. However, we agree with the referee that it would be informative to give instantaneous turnover times at present day, so we added these values on lines 318-319.

"Estimates of carbon influxes by previous studies varied by one order of magnitude, and result from this study suggests that a lower estimate of the carbon influx is more likely."

Response: It is indeed our conclusion, which is even more important for us that several authors of the present study were also authors of the previous study which gave a higher estimate.

"After presenting the modelling results of the one-pool model for the Bh layer, the section was unfortunately ended with one sentence "These observations are not consistent with very low A to Bh rates, suggesting that a single Bh C pool is incorrect and that two pools of Bh C are required to adequately represent Bh C dynamics". I find that quite disappointing."

Response: The ending sentence cited by the referee was preceded by another sentence (lines 201-203 of old manuscript, ), which, based on data from the literature, explained that the Bh output flow should be at least 2 mgC L-1, which is not consistent with the 1-pool model. We think we need to

demonstrate to the reader that the one pool model was not suitable. For more clarity, we changed the text in the new version (lines 257-259).

"The authors went on to model the formation of the whole profiles with soil carbon Bh being represented using a two-pool model. My question is then how the results in Section 3.1 were used in Section 3.2, ie how the fluxes and turnover rates of the two-pool model for the Bh soil layers are estimated? This is quite unclear to me. In presenting optimization problem, you need to state clearly: observations, optimizing model parameters, the model and optimization method including cost function. This has not been done adequately in this manuscript. Therefore I recommend major revisions."

Response: Section 3.1 was necessary to show, from a simplified system, the conditions for obtaining the stationary state and the minimum formation time. These notions seem indispensable to us to understand the sensitivity study given in § 3.2.2. As explained above, to improve the presentation of the problem, we better explained at the end of section 3.1 why the one pool model is incorrect (lines 257-259) and, agreeing with the referee that observations, optimizing model parameters and cost functions were not clearly presented, we amended the text accordingly: lines 263 to 266 for the topsoil modelling, lines 316-326 for the Bh modelling.

### "Some additional comments.

The results are quite specific to the sites you studied. What are more broad implications? L56 and L58. In L56, you stated that data from 11 test areas were used to constrain a model of C fluxes, but you actually only presented results of four profiles (see L58). Inconsistent!""

Response: We agree with the referee (as well with referee #1) that this is unclear. For more clarity, we explained now on lines 61-65 that four podzol profiles were selected from a database of 80 podzol profiles (from 11 test areas) which have been studied in detail and of which 11 have been dated. This database will be the subject of a further publication dedicated to the podzolic system genesis. These profiles were selected as representative both from the point of view of the profile characteristics and the 14C apparent age of the Bh organic matter stock (lines 73-74).

"Section 2.3 Would it be simpler to assume that soil carbon pools at different layers were at steady state before 1950 and solve the model analytically at 1950, then integrate the model forward after 1950 to match both the observed carbon pool and age using optimization?"

Response: As stated in section 3.1.2, there is no evidence that a steady state has been reached, especially in the case of the two youngest profiles. Considering the possible C influx values in the Bh, which are very small with regard to the C stock, no correction for the bomb carbon was needed. This is not true for the topsoil horizons, which show Fa values greater than 1: a correction for bomb carbon was therefore necessary to calculate the steady state conditions and the Fa values to be used for the carbon transferred for topsoil to the Bh pools.

# Modelling the genesis of equatorial podzols: age and implications <u>onfor</u> carbon fluxes

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**Abstract.** Amazonian podzols store huge amounts of carbon and play a key role in transferring organic matter to the Amazon river. In order to better understand their C dynamics, we modelled the formation of representative Amazonian podzol profiles by constraining both total carbon and radiocarbon. We determined the relationships between total carbon

- 15 and radiocarbon in organic C pools numerically by setting constant C and <sup>14</sup>C inputs over time. The model was an effective tool for determining the order of magnitude of the carbon fluxes and the time of genesis of the main carbon-containing horizons, i.e. the topsoil and deep Bh. We performed retro calculations to take in account the bomb carbon in the young topsoil horizons (calculated apparent <sup>14</sup>C age from 62 to 109 y). We modelled four profiles representative of Amazonian podzols, two profiles with an old Bh (calculated apparent <sup>14</sup>C age 6.8 10<sup>3</sup> and 8.4 10<sup>3</sup> y) and two profiles with
- 20 a very old Bh (<u>calculated apparent</u> <sup>14</sup>C age 23.2 10<sup>3</sup> and 25.1 10<sup>3</sup> y). The calculated fluxes from the topsoil to the perched water-table indicates that the most waterlogged zones of the podzolized areas are the main source of dissolved organic matter found in the river network. It was necessary to consider two Bh carbon pools to accurately represent the carbon fluxes leaving the Bh as observed in previous studies. We found that the genesis time of the studied soils was necessarily longer than 15 10<sup>3</sup> and 130 10<sup>3</sup> y for the two younger and the two older Bhs, respectively, and that the genesis time

calculated considering the more likely settings runs to around  $15 \ 10^3 - 25 \ 10^3$  and  $150 \ 10^3 - 250 \ 10^3$  y, respectively.

#### 1 Introduction

Podzols are soils characterized by the formation of a sandy, bleached horizon (E horizon) overlying a dark horizon with illuviated organic matter as well as Fe- and Al-compounds (spodic or Bh horizon). In wet tropical areas podzols can be very deep, with E horizons thicker than 10 m and Bh horizons thicker than 4 m (Chauvel et al., 1987; Dubroeucq and Volkoff, 1998; Montes et al., 2011). This means that they can store huge quantities of organic matter: Montes et al. (2011)estimated the C stocks in Amazonian podzols to be around 13.6 In wet tropical areas podzols can be very deep, with E horizons thicker than 10 m and Bh horizons thicker than 4 m (Chauvel et al., 1987; Dubroeucq and Volkoff, 1998; Montes et al., 2011). This means that they can store huge quantities of organic matter: Montes et al., (2011)estimated the C stocks in Amazonian podzols to be around 13.6 In wet tropical areas podzols can be very deep, with E horizons thicker than 10 m and Bh horizons thicker than 4 m (Chauvel et al., 1987; Dubroeucq and Volkoff, 1998; Montes et al., 2011). This means that they can store huge quantities of organic matter: Montes et al. (2011)estimated the C stocks in Amazonian podzols to be around 13.6 Pg C.

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Figure 1. Schematic of the main C fluxes in a podzol.

- 40 This C constitutes a non-negligible portion of the C stored in the Amazonian basin. Indeed, the carbon stored in the aboveground live biomass of intact Amazonian rainforests is estimated to be 93 ± 23Pg23 Pg C (Malhi et al., 2006). Such large amounts of carbon may play a central role in the global carbon balance (Raymond, 2005), which raises the question of the magnitude of the carbon fluxes during podzol genesis and in response to drier periods that might occur in the future due to climate change. A schematic of the main carbon fluxes in Amazonian podzols (Leenheer, 1980; Lucas et al., 2012; Montes et al., 2011) is presented in Fig. 1. It should be noted that the organic matter (OM) released by the topsoil
- horizons can be transferred downwards to the Bh horizons, but may also be rapidly transferred laterally to the river network via a perched water-table on top of the Bh that circulates in the E horizon. The OM stored in the upper part of the Bh can also be remobilized and be transferred to the river network by the perched water-table. Some of these fluxes have been estimated in a small number of case studies or extrapolated from studies of the chemistry of large rivers (Tardy
- 50 et al., 2009), but most of them remain unknown. Studies measuring carbon budgets at the profile scale or during soil profile genesis in temperate, boreal or tropical podzols are rare (Schaetzl and Rothstein, 2016; Van Hees et al., 2008). Schwartz (1988) studied giant podzol profiles in the Congo that began to form 40 10<sup>3</sup> y ago but where carbon accumulation in Bh was discontinuous because of a drier climate between 30 and 12 ky BP. The <sup>14</sup>C age of organic C from the Bh horizon of podzol profiles situated in the Manaus region (Brazil) was found to range from 1960 to 2810 y
- and it was concluded that the podzols developed in less than 3 10<sup>3</sup> y (Horbe et al., 2004). As pointed out by Sierra et al. (2013), in order to corroborate this conclusion it is necessary to produce a model that accounts for C additions and losses over time. Montes et al. (2011) roughly estimated the C flux to the Bh horizon to be 16.8 gC m<sup>-2</sup> y<sup>-1</sup>. Sierra et al. (2013) used a compartment model that was constrained by <sup>14</sup>C dating to estimate the carbon fluxes in a Colombian shallow podzol (Bh upper limit at 0.9-\_m). They showed that the C fluxes from topsoil horizons to the Bh horizon were smaller (2.1 gC m<sup>-2</sup> y<sup>-1</sup>) than the fluxes estimated in Montes et al. (2011). However, they did not account for the age and genesis

time of the Bh horizon.

In order to better understand the fluxes of C in Amazonian podzols and in particular to determine the rate of carbon accumulation in Bh horizons during podzol genesis, the size of the C fluxes to rivers via both the perched and the deep water-tables and the vulnerability of the podzol C stocks to potential changes in the moisture regime due to global climate change, data collected from 11 test areas in the high Rio Negro Basin were used to constrain a model of C fluxes (Fig 1). The high Rio Negro basin was chosen because it is a region that has the highest occurrence of podzol in the Amazon (Montes et al., 2011) (Fig. 2). Four representative profiles were selected from a database of 80 podzol profiles to constrain the simulations of C fluxes.four representative podzol profiles from the high Rio Negro Basin were used to constrain a model of C fluxes. The high Rio Negro basin was chosen because it is a region that has the highest occurrence of podzol in the Amazon (Montes et al., 2011) (Fig. 2). The four representative profiles were selected from a database of 80 podzol profiles issued from 11 test areas which have been studied in detail and of which 11 have been dated; this database will be the subject of a further publication. The four profiles were used to constrain the simulations of C fluxes. We used a system dynamics modelling software package (Vensim) to simulate the formation of representative Amazonian podzol profiles by constraining both total carbon and radiocarbon with the data collected.



Figure 2. Location of the studied profiles. Grey areas in the detailed map indicate hydromorphic podzol areas. Orange spots identify test areas.

#### 2 Methods

#### 80 2.1 Podzol profiles and carbon analysis

Four podzol profiles were selected from our database as representative both from the point of view of the profile characteristics and the <sup>14</sup>C age of the Bh organic matter (Table 1 and Fig. 3). The MAR9 profile was developed on the Icá sedimentary formation, has a water-logged A horizon, a thin eluvial (E) horizon, a sandy-clay loam Bh with young organic matter (OM) and a low C content; the DPQT profile was developed on a late quaternary continental sediment

85 younger than the Içá formation, has an E horizon of intermediate thickness, a sandy Bh with young OM and a low C content; the UAU4 profile was developed on the Icá sedimentary formation, has an thick E horizon, a sandy Bh with old OM and the C content is high; the P7C profile was developed on crystalline basement rock, has a thick, water-logged O horizon, a E horizon of intermediate thickness, a silt-loam Bh with old OM and a high C content. It should be noted that in the cases of the DPQT and the UAU4 profiles, the lower limit of the Bh was not reached because of the auger hole

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Table 1. The main characteristics of the podzol profiles used in the study. C stock and ages are given  $\pm$  maximum absolute error.  $F_{a_1}$  and  $F_{a_2B_1}$ : measured Fraction Modern of topsoil and Bh organic matter, respectively. Apparent <sup>14</sup>C age of OM

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#### Figure 3. Sketch of the studied profiles.

Soil samples were analysed for C content with a TOC-LCPN SSM-5000A, Total Organic Carbon Analyzer (Shimadzu). Radiocarbon measurements and conventional age calibration were carried out at the Poznań Radiocarbon Laboratory, Poland. The conventional We assumed that the proportion of bomb carbon in the Bh organic matter was negligible and calculated a conventional, uncalibrated age from the radiocarbon pMC (percent Modern Carbon) value. As the Bh organic matter is an open system mixing organic carbon of different ages, this age calibration was performed using the program OxCal ver, 4.2 against the INTCAL13 calibration curve.is an apparent age. Samples from the topsoil had a pMC (percent Modern Carbon) higher than 100%, which indicates that a significant part of the carbon in the topsoil is post-bomb. We calibrated the age and therefore should not be neglected. Assuming that the topsoil horizons reached a steady state before 1950, we retrocalculated the pre-1950 pMC value of these samples using a dedicated model described in section 2.2.

110 The data given in Table 1 were calculated by linear extrapolation of values measured on samples taken at different depths: between 11 and 28 samples per profile were used for the C stocks calculation and between 6 and 8 samples per profiles were used for radiocarbon measurements.

#### 2.2 Model design

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We used an approach comparable to previous studies which dealt with carbon budgets and radiocarbon data (e.g. Baisden

et al., 2002; Menichetti et al., 2016; Sierra et al., 2013, 2014; Tipping et al., 2012). The model structure, based on the

schematic shown in Fig. 1, and the names of compartments and rate constants are given in Fig. 4. As the turn-over time

of the OM in the topsoil horizons is short relative to the average OM turn-over time in the Bh, only one topsoil carbon pool was used, whereas two pools (fast and slow) were used to describe organic carbon dynamics in the Bh horizon. The C can leave the topsoil pool by mineralization, transfer to the Bh pools or to the river by the perched water-table; it can leave the Bh pools by mineralization, transfer to the river by the perched water-table or via the deep water-table. We chose to neglect the flux of C from the fast Bh pool to the slow Bh pool in order to facilitate the numerical resolution of the system comprising equations describing both the carbon and radiocarbon contents.



The equations describing changes in the carbon content of the different pools are presented below (see Fig. 4 to see the fluxes with which each rate constant is associated);

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$$\frac{dC_t}{dt} = C_I - (k_t + \alpha_{t-fBh} + \alpha_{t-sBh} + \alpha_{t-r})C_t$$
$$\frac{dC_{fBh}}{dt} = \alpha_{t-fBh}\frac{C_{ft}}{C_{ft}} - (k_{fBh} + \alpha_{fBh-r} + \alpha_{fBh-d})C_t - (k_{fBh} + \alpha_{fBh-r} + \alpha_{fBh-d})C_{fBh}$$

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(1)

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 $\frac{dC_{sBh}}{dt} = \alpha_{t-sBh} \frac{C_{sT}}{C_t} C_t - (k_{sBh} + \alpha_{sBh-r} + \alpha_{sBh-d}) C_{sBh}$ (3)

(2)

135 where  $C_l$  is the C input from litter and roots into the topsoil C pool;  $C_l$  the amount of C stored in the topsoil C pool;  $C_{fBh}$ and  $C_{sBh}$  the amount of C stored in the fast and the slow Bh C pools, respectively;  $k_t$ ,  $k_{fBh}$  and  $k_{sBh}$  the C mineralization rate constants in the topsoil, the fast Bh and the slow Bh CpoolsC pools, respectively;  $\alpha_{t-fBh}$  and  $\alpha_{t-sBh}$  the transfer rates from the topsoil pool to the fast and the slow Bh C pools, respectively;  $\alpha_{t-r-}$ ,  $\alpha_{fBh-r}$  and  $\alpha_{sBh-r}$  the transfert rates from respectively the topsoil, the fast Bh and the slow Bh pools to the river by the perched water-table;  $\alpha_{fBh-d}$  and  $\alpha_{sBh-d}$  the transfer rates from the fast Bh and the slow Bh pools to the deep water-table, respectively.

The equations describing changes in the radiocarbon content of the different pools are the following:

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$$\frac{dF_{at}c_{t}}{dt} = C_{l}F_{a\nu} - \left(k_{t} + \alpha_{t-fBh} + \alpha_{t-sBh} + \alpha_{t-r}\right)F_{at}C_{t} - \lambda F_{at}C_{t}$$

$$\tag{4}$$

$$\frac{dF_{afBh}C_{fBh}}{dt} = \alpha_{t-fBh}F_{at}C_t - \left(k_{fBh} + \alpha_{fBh-r} + \alpha_{fBh-d}\right)F_{afBh}C_{fBh} - \lambda F_{afBh}C_{fBh}$$
(5)

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$$\frac{dF_{a\,sBh}C_{sBh}}{dt} = \alpha_{t-sBh}F_{a\,t}C_t - (k_{sBh} + \alpha_{sBh-r} + \alpha_{sBh-d})F_{a\,sBh}C_{sBh} - \lambda F_{a\,sBh}C_{sBh}$$
(6)

where  $\lambda$  is the <sup>14</sup>C radioactive decay constant,  $F_{av}$  the radiocarbon fraction in the organic matter entering the topsoil C pool and  $F_{ai}$  the radiocarbon fraction in each pool *i*, the radiocarbon fractions being expressed as absolute fraction modern, i.e. the <sup>14</sup>C/<sup>12</sup>C ratio of the sample normalized for <sup>13</sup>C fractionation to the oxalic acid standard <sup>14</sup>C/<sup>12</sup>C normalized for <sup>13</sup>C fractionation and for radio decay at the year of measurement (Stuiver and Polach, 1977).



#### Figure 5. Evolution of the 14C pool in a topsoil that reached a steady state before 1955.

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With regard to the apparent age calibration of the topsoil organic matter enriched in post-bomb carbon, we considered a single pool that reached a steady state before 19501955 (Fig. 5), which allowed the retrocalculation of the radiocarbon fraction  $F_{at}$  in <u>19501955</u> based on the following equation:

$$C_t F_{at_{i+1}} = C_t F_{at_i} - \lambda C_t F_{at_i} + (F_{av_i} - F_{at_i}) C_l \qquad \Leftrightarrow \qquad F_{at_i} = \frac{C_t F_{at_{i+1}} - C_t F_{av_i}}{C_t - \lambda C_t + C_l} \tag{7}$$

where  $F_{at_i}$  and  $F_{at_{i+1}}$  are the radiocarbon fraction of the topsoil C pool in year i and i+1, respectively, and  $F_{av_i}$  the radiocarbon fraction in the organic matter entering the topsoil C pool in year i. Starting from the  $F_{a t_{2015}}$  value (value at the year of measurement), the  $F_{a t 1955}$  value (pre-bomb value) is calculated by successive iterations, giving an expression as a function of  $C_{l}$ , which is then computed by approximation to satisfy the steady state condition. We used the tropospheric D<sup>14</sup>CO<sub>2</sub> record from 1955 to 2011 at Wellington (NIWA, 2016) to estimate the annual value of  $F_{av}$ .

An underlying assumption of this work is that soil formation processes remained constant over time. An alternative assumption might be, for example, that all the Bh organic matter had accumulated in very short time, after which the Bh was no longer subjected to external exchanges. This scenario could also produce a profile ages close to the observed 14C profile ages. Such a case, however, is unlikely. The climate of the high Rio Negro region is likely to have remained humid and forested since the Pliocene, although less humid episodes may have occurred during the Holocene glacial

170 episodes (Colinvaux and De Oliveira, 2001; Van der Hammen and Hooghiemstra, 2000). It is also possible that the rate at which soil formation proceeded decelerated over time. This will be commented on below.

#### 2.3 Model running and tuning

We used the Vensim ® Pro (Ventana Systems inc.) dynamic modelling software to simulate the C dynamics. After 175 setting the initial values for C pools, the model was run in the optimize mode, leaving the model to adjust the rate constants in order to minimise the difference between simulated and measured C pool values and ages. However, frequently the model did not converge when run in this way. We found that it was because of the great difference between the convergence times between the topsoil C pool and the slow Bh C pool. The long times required to model the genesis of the Bh horizons resulted in numerical errors when modelling the topsoil behavior, because of the values of 180 exponential exponents exceeded the maximum values that the computer could handle (see for example eq. 12 below). To

- circumvent this technical problem, we optimized the model separately for the topsoils and for the Bh horizons and we found that at the time scale of the formation of Bh, the topsoil C pool and the topsoil C fluxes to river and Bh horizons could be considered constant.
- Although the model structure in Fig. 4 contains two C pools in the Bh horizon, we calculated the numerical solutions of 185 equations considering both carbon budget and radiocarbon age for a single pool Bh in order to determine whether the model could be simplified. Furthermore, this approach allowed us to better assess the weight of the different rate constants in the long-term behaviour of a given pool. The calculation in the simplified configuration is shown in Fig. 6.



#### Figure 6. Simplified design for one pool.

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In this configuration, the carbon content of the pool is given by:

 $\frac{dC_{Bh}}{dt} = \alpha_{t-Bh}C_t - \frac{\beta_{PBh}C_{PBh}}{\beta_{Bh}C_{Bh}}$ (8)

where  $C_t$  is the amount of C stored in the topsoil pool,  $\alpha_{t-sBh}$  the transfer rates from the topsoil pool to the Bh pool,  $C_{Bh}$ 195 the amount of C stored in the Bh pool and  $\beta_{Bh}$  the transfer rate of C leaving the Bh pool. The solution of this equation with the initial condition  $C_{Bh} = C_{0 Bh}$  when t = 0 is:

$$C_{Bh} = \frac{a_{t-Bh}C_t}{\beta_{Bh}} + \left(C_{0\ Bh} - \frac{a_{t-Bh}C_t}{\beta_{Bh}}\right)e^{-\beta_{Bh}t} \tag{9}$$

The equation related to radiocarbon content is the following:

$$200 \qquad \frac{dF_{a Bh}C_{Bh}}{dt} = \alpha_{t-Bh}C_t F_{a t} - (\beta_{Bh} + \lambda)F_{a Bh}C_{Bh}$$

where  $F_{a Bh}$  is the radiocarbon fraction in the Bh.

Considering that the C input from the topsoil to the Bh and its radiocarbon fraction are constant with time, it comes from the two previous equations:

(10)

$$\frac{dF_{aBh}}{dt} = \frac{\beta_{Bh} \, a_{t-Bh} c_t \, F_{a\,t} - F_{a\,Bh} \left(\beta_{Bh} \, a_{t-Bh} c_t + \lambda \left(a_{t-Bh} c_t - (a_{t-Bh} c_t - \beta_{Bh} c_{0\,Bh}) \, e^{-\beta_{Bh} t}\right)\right)}{a_{t-Bh} c_t - (a_{t-Bh} c_t - \beta_{Bh} c_{0\,Bh}) \, e^{-\beta_{Bh} t}} \tag{11}$$

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The analytical solution of this equation with the initial condition  $F_{a Bh} = F_{at}$  when t = 0 is:

$$F_{a\,Bh} = \frac{\beta_{Bh}F_{a\,t} \ e^{-\lambda t} \left(\beta_{Bh}c_{0\,Bh} + a_{t-Bh}c_{t} \left(e^{(\beta_{Bh}+\lambda)t} - 1\right) + \lambda \ c_{0\,Bh}\right)}{(\beta_{Bh}+\lambda)(\beta_{Bh}c_{0\,Bh} + a_{t-Bh}c_{t} \left(e^{\beta_{Bh}t} - 1\right))}$$
(12)

#### 3 Results and discussion

#### 3.1 Modelling the formation of a single pool Bh

210 This section presents conceptual results on the basis of the simplified diagram given on Fig. 6 and in which the flux leaving the Bh is described by a single rate  $\beta_{Bh}$ . This single rate represents loss from the pool both through the mineralization of organic carbon, through lateral flow in the perched water-table to the river and through percolation of dissolved organic carbon (DOC) to the deep water-table.

#### 3.1.1 Obtaining the carbon stock

215 Unsurprisingly, the greater the difference between input and output C fluxes, the faster a given  $C_{Bh}$  stock is reached. With a constant input flux and a constant output rate, the output flux progressively increases with time because  $C_{Bh}$  increases, until the input and output fluxes become equal, after which the  $C_{Bh}$  reaches a steady state.



Figure 7. Single-pool modelling of  $C_{Bh}$  of the P7C profile;  $C_{0 Bh}$  set to 0.

When the model is constrained only by the measured values of C stocks, a number of solutions are possible (Fig 7). The example given in Fig. 7 is based on data from the P7C profile (Table 1). Curves 1 and 2 describe the evolution of C<sub>Bh</sub> with time when the β<sub>Bh</sub> rate is constrained to reach a steady state for the currently observed C stock (158 465 gC m<sup>-2</sup>).
The input flux was set at 2.1-g m<sup>-2</sup> y<sup>-1</sup> and 16.8-g m<sup>-2</sup> y<sup>-1</sup> for curves 1 and 2, respectively, values proposed by Montes et al. (2011) and Sierra et al. (2013), respectively. The resulting constrained values of α<sub>t-Bh</sub> and β<sub>Bh</sub> rates are given in the figure. The times required to reach 99% of the steady state values are <u>43 10<sup>3</sup> and 345 10<sup>3</sup> and 43 10<sup>3</sup>-</u>y for curve 1 and 2, respectively. We used here and thereafter an arbitrary 99% threshold because, as shown on Fig. 8, this value gives a result sufficiently close to the horizontal asymptote to give a reasonable evaluation of the time necessary to reach a steady state.

The currently observed C stock can be reached in a shorter time, however, if for a given input flux the value of  $\beta_{Bh}$  is reduced below the value needed to obtain the currently observed C stock at a steady state. An example is given by the curve 3: the input flux is set at 2.1-g m<sup>-2</sup> y<sup>-1</sup>, as for curve 1, but the  $\beta_{Bh}$  rate is reduced by one order of magnitude. In such a case, it would require 78 10<sup>3</sup> y to obtain the currently observed C stock. A value of  $\beta_{Bh}$  set to 0 gives the minimum time required to obtain the carbon stock (50 10<sup>3</sup> y if the input flux is set to 2.1-g m<sup>-2</sup> y<sup>-1</sup>).

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#### 3.1.2 Obtaining both carbon stock and <sup>14</sup>C age



Figure δ. Single-pool modelling of both CBh and Bh <sup>14</sup>C age of the P7C profile. Corresponding values of C input fluxes and β<sub>Bh</sub> rates are given in Table 2

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When the model was constrained by both carbon stock and <sup>14</sup>C age, then a unique solution for reaching the steady state was obtained. This is shown for the P7C profile in Fig. 8 (solid lines), where <u>99% of the measured</u> values of  $C_{Bh}$  and <u>apparent</u> <sup>14</sup>C age (158465 gC m<sup>-2</sup> and 25096 y, respectively), which represent more than <u>99% of the measured</u> values, were obtained in approximately 590 10<sup>3</sup> y; carbon input flux to the Bh and  $\beta_{Bh}$  rate were constrained to very low values, 0.95-g m<sup>2</sup> y<sup>1</sup> and 5.9 10<sup>-6</sup> y<sup>-1</sup>, respectively. Note that for higher values of the  $\beta_{Bh}$  rate, there was no solution because the <sup>14</sup>C age could never be reached.

The simulation of the minimum time required for the observed carbon stock and <sup>14</sup>C age to be reached is also shown in Fig. 8 (dashed lines). This simulation was obtained by adjusting the input fluxrate with an output flux close to 0-(, but different from zero for numerical reasons. We used  $\beta_{Bh} = 10^{-10}$ ; after checking that the difference between the minimum time obtained using  $\beta_{Bh} = 10^{-10}$  and  $\beta_{Bh} = 10^{-20}$  was negligible (lower than 0.0005%).

The minimum time required for the C stock and <sup>14</sup>C age to be reached and the time required to reach 99% of the C stock and <sup>14</sup>C age at a steady state are given, along with the associated C input fluxes and  $\beta_{Bh}$  rates, in Table 2 for each of the studied profiles. Under each of the conditions, the time required is an exponential function of the <u>apparent</u> <sup>14</sup>C age of the Bh (Fig. 9).

#### Table 2. Results of simulation for a single pool Bh-: minimum genesis time and time to steady state ...

	MAR9	DPQT	UAU4	P7C
Bh <u>apparent</u> <sup>14</sup> C age (y)	6,751	8,442	23,193	25,096
Corresponding F <sub>a Bh</sub> value	<u>0.4315</u>	<u>0.3496</u>	0.0557	<u>0.0440</u>
<u>C<sub>l</sub> (gC m<sup>-2</sup>)</u>	17,722	8,056	<u>7,519</u>	74,129
<u><i>F<sub>at</sub></i> value of the C input</u>	<u>0.9923</u>	<u>0.9866</u>	<u>0.9919</u>	<u>0.9865</u>
Minimum time required for obtaining C stock and ${}^{14}C$ age ( $\beta$ Bh	$= 10^{-10}$ )			
Time (y)	15,929	21,011	143,000	180,100
Input C flux (gC m <sup>-2</sup> y <sup>-4</sup> )	<del>5.52</del>	<del>3.68</del>	<del>0.84</del>	<del>0.95</del>
$\beta - \alpha_{\perp Bh}$ rate (y <sup>-1</sup> )	1.97 10-4	3.14 10-4	1.00 10-4	1.19 10-5
Current output corresponding to B Bh Input C flux (gC m <sup>-2</sup>	3.49	2.53	0.75	0.88

Tableau mis en forme

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Time (y)	48,000	66,700	489,000	650,000
$\underline{\alpha_{1 Bh}}$ rate (y <sup>1</sup> )	<u>9.63 10-5</u>	4.51 10-4	1.06 10-4	1,24 10-
Input C flux (gC m <sup>-2</sup> y <sup>-1</sup> )	5.36	3.63	0.80	0.92
$\beta_{Bh}$ rate (y <sup>-1</sup> )	9.56 10 <sup>-405</sup>	<u>6.83</u> 10-	7.41 10-406	5.81 10 <sup>-10</sup>



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Figure 9. Relationship between the <sup>14</sup>C age of the Bh and the time needed to form the Bh (single pool modelling).

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Taking into account the maximum absolute error propagation does not significantly change the simulation results: the maximum absolute error on the genesis times is lower than  $1_{\frac{1}{2}}0\%$ , 0.9%,  $3_{\frac{1}{2}}5\%$  and  $2_{\frac{1}{2}}9\%$  for Mar9MAR9, DPQT, UAU4 and P7C, respectively. Since such percentages do not alter the orders of magnitude and trends discussed below, the error propagation will not be considered in the following.

The time taken for the Bh horizon of a given profile to form is likely between the two values shown in Table 2 and Fig. 9. The minimum time required for obtaining C stock and <sup>14</sup>C age is an absolute minimum which assumes that the C output from the Bh was zero, which is not likely. On the other hand, there is no evidence that a steady state has been reached, especially in the case of the two youngest profiles (MAR9 and DPQT). Consequently, the time taken for the formation of 270 the Bh horizons is very likely comprised between 15 103 and 65 103 y for the two youngest profiles and between 140 103 and 600 103 y for the two oldest-, durations compatible with rough estimates given in Du Gardin (2015). These results also show that the input C fluxes to the Bh and correspondingly the output C fluxes are 3 to 5 times higher for younger than for older profiles and that the older profiles would have an output rate of one order of magnitude lower than the younger profiles. It is not immediately clear why such large differences would exist. Previous studies have shown (1) that 275 a part of the accumulated Bh OM is remobilized and exported towards the river network (Bardy et al., 2011); (2) that the water percolating from the Bh to deeper horizons OM contains significant amounts of DOC, even in older profiles (around 2-mg L<sup>-1</sup>, Lucas et al., 2012). These observations are not consistent with the obtained very low  $\beta_{Bh}$  rates, suggestingwhich give input and output C fluxes lower than 1 gC m<sup>2</sup> y<sup>-1</sup> for profiles UAU4 and P7C. This suggests that a single Bh C pool is incorrect and that two pools of Bh C are required to adequately represent Bh C dynamics.

#### 280 **3.2 Modelling the formation of the whole profile with a two-pools Bh**

horizons of the studied profiles are given in Table 3.

#### 3.2.1 Topsoil horizons

As explained in section 2.3., the topsoil horizons were simulated<u>modelled</u> separately because the time needed to reach a steady state is very much shorter for the topsoil horizons than for the Bh horizons. The steady state condition was given by  $\beta_L = C_L C_L^{-1}$ . Observations data were  $C_L F_{a,v}, F_{a,t}$  and  $k_L$  The  $k_L$  mineralization rate was set to 2.57 10<sup>-3</sup> y<sup>-1</sup>, following preliminary mineralization experiments (unpublished data). Optimizing parameter was  $\beta_L$  and a multiple cost function was minimizing the differences between modelled and observed value for  $C_L$  and  $F_{a,L}$ . The model outputs for the topsoil

	MAR 9	DPQT	UAU4	P7C
$C_t$ (g m <sup>-2</sup> )	17 722	8 056	7 519	74 129
Apparent <sup>14</sup> C age (y)	62	108	65	109
<u><i>F<sub>at</sub></i> value</u>	<u>0.9923</u>	<u>0.9866</u>	<u>0.9919</u>	<u>0.9865</u>
$C_I (g m^{-2} y^{-2})$	286	74	116	676
Time to steady state (y)	399	696	420	705
$\beta_{I}(y^{-1})$	1.61 10-2	9.23 10-3	1.54 10-2	9.12 10-3

Table 3. Modelling the topsoil horizons. Ct: topsoil C stock; CI: C input flux from roots and litter; Time to steady state: time required to reach 99% of the steady state values for Ct and 14C age;  $\beta_i$ : sum of the output rates ( $\beta_i = k_i + \alpha_{ir} + \alpha_i - f_{Bh} + \alpha_i$ ).

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The results suggest that the topsoil OM in the four profiles needed only between 400 and 700 y to reach a steady state, if the present day topsoils are indeed in a steady-state. The total C flux through the topsoil ( $C_i$ ) is high for the MAR9 profile (286-g m<sup>-2</sup> y<sup>-1</sup>) and very high for the P7C profile (676-g m<sup>-2</sup> y<sup>-1</sup>), in accordance with their high topsoil C stock (17722 and 74129-g m<sup>-2</sup>, respectively) and the very young age of their organic matter. Note that the topsoil OM ages are younger than ages reported by Trumbore (2000) for boreal, temperate or tropical forests. Differences between modelled fluxes through the topsoil are consistent with the field observations: the lowest fluxes (UAU4 and DPQT) correspond to welldrained topsoil horizons, with a relatively thin type Mor A horizons, when the highest fluxes (P7C) corresponds to a podzol having a thick O horizon in a very hydromorphic area. The MAR9 profile is intermediate. It should be noted that the flux through the P7C topsoil would correspond to more than  $\frac{34 \text{ of } 1.5 \text{ times higher than}}{1.5 \text{ times higher than}}$  the commonly accepted value

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for the C annually recycled by <u>the aboveground</u> litter in equatorial forests (around <u>850 g425 gC</u> m<sup>-2</sup> y<sup>-1</sup> – (Wanner, <u>1970</u>(Wanner, <u>1970</u>; Cornu et al., <u>1997</u>; Proctor, 2013).

, indicating a strong contribution of the belowground litter (root litter).

#### 3.2.2 Bh horizons

The partitioning of the C flux leaving the topsoil between the river (rate  $\alpha_{t-r}$ ), the fast pool of the Bh (rate  $\alpha_{t-rBh}$ ) and the slow pool of the Bh (rate  $\alpha_{t-rBh}$ ) is unknown. This is also the case for the partitioning of the C flux from the Bh pools between the river (rates  $\alpha_{fBh-r}$  and  $\alpha_{sBh-r}$ ) and the deep horizons (rates  $\alpha_{fBh-d}$  and  $\alpha_{sBh-d}$ ). Consequently, the system is not sufficiently constrained with the <sup>14</sup>C age of the bulk Bh and there is an infinity of solutions for modelling the Bh formation.





310 We therefore carried out a sensitivity analysis to determine how the main parameters (size of the fast pool of the Bh, C flux input and output C rates for the Bh pools) affected the profile genesis time and to understand the relationships between these parameters.

Figure 10. Effect of the fast Bh pool size on the whole Bh genesis time and the <sup>14</sup>C age of the fast Bh. Left graph: absolute values; right graph: values expressed in %.

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Sensitivity to the size of the fast Bh pool<sup>-2</sup> Fig. 10 shows simulation results with an output C flux from Bh set to be 2-g m<sup>-2</sup> y<sup>-1</sup> at end of the genesis time and with values for  $C_{fBh}$  ranging from 2.5 10<sup>3</sup> to 40 10<sup>3</sup>-g m<sup>-2</sup>, through 5 10<sup>3</sup>, 10 10<sup>3</sup> and 20 10<sup>3</sup>. In most configurations, the presence of a fast pool in the Bh extends the time taken for the whole Bh genesis relative to a single-pool Bh. This lengthening of the genesis time increases as a function of the <sup>14</sup>C age of the whole Bh and as a function of the size of the fast Bh pool ( $C_{fBh}$ ). A size of the fast Bh pool set to 5% of the whole Bh stock would give a low estimate of the Bh genesis time.

Sensitivity to the *C* fluxes leaving the *Bh* pools; the genesis time of the profile lengthens with increasing *C* flux from the bulk Bh. The lengthening of the genesis depends, however, on how the C fluxes leaving the Bh C pools vary and on the source of the variation (Fig. 11). In the situation where there is a progressive increase of the Bh output beginning from 0, and this increase is due to the fast Bh pool, the lengthening of the genesis time is fast at first and then slows. An example

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is given in Fig. 11 for the UAU4 profile for two values of  $C_{\beta Bh}$ . When the increase is due to the slow Bh pool, the lengthening of the genesis time is slow at first and then becomes very high. An example is given in Fig. 11 for the MAR9 and P7C profiles, respectively.

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Figure 11. Effect of constraining the ouput C fluxfluxes from the Bh on the genesis time. UAU4: effect of the fast Bh output flux. MAR9 and P7C: effect of the slow Bh output flux.

The conclusion of this sensitivity study is that, when the size of the fast Bh pool or the C output fluxes from the Bh pools begin to grow from zero, the genesis time of the profiles increases rapidly by a factor of 5 to 20% for the two youngest profiles and 15 to more than 60% for the two oldest profiles.

- Modelling the formation of the whole profiles: we modelled the formationobservation data were C<sub>Bh</sub> (sum of the four profiles using the most likely settings issued from these preliminary results C<sub>Bh</sub> and from the literature.C<sub>abb</sub>, F<sub>a t</sub>, F<sub>a bb</sub> (F<sub>a</sub> value of the bulk Bh), a<sub>t(Bb</sub>, k<sub>Bb</sub>, a<sub>tBb</sub>, a<sub>tBb</sub>, a<sub>sbb</sub>, a<sub>tBb</sub>, d<sub>sbb</sub>, d<sub></sub>
- The The size of the present-day observed fast Bh (C<sub>(Bh</sub>)) was arbitrarily set toat 5% of the total Bh. As the k<sub>µµh</sub> mineralization rate had to be set to a value below 1.5 10<sup>-4</sup> y<sup>-1</sup> for solutions to be possible, a value of 5 10<sup>-5</sup> y<sup>-1</sup> was chosen. The C (see above). The present day output flux from slow Bh to the riverdeep horizons was constrained to a value between 0.458 and 0.2 g05 gC m<sup>-2</sup> y<sup>-1</sup>; for the fast and the slow Bh pool, respectively, in order to have a sufficient flux to deep horizon without zeroing the flux from the slow Bh to the river to account for the export to river of very humified OM, as observed by Bardy et al. (2011), Results are shown in Fig. 11. The output flux from the whole Bh to deeper

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-	Mis en forme : Couleur de police : Noir
1	Mis en forme : Anglais (Royaume-Uni)

horizons was constrained to be between 0,5 and 1 g m<sup>-2</sup> y<sup>-1</sup>, to account for observations from Montes et al. (2011). Results are shown in Fig. 12As the  $k_{fBh}$  and the  $k_{sBh}$  mineralization rate had to be set below 1 10<sup>-4</sup> and 1 10<sup>-6</sup> y<sup>-1</sup>, respectively, for solutions to be possible, values of 5 10<sup>-5</sup> and 5 10<sup>-7</sup> y<sup>-1</sup>, respectively, were chosen. Optimizing parameters were  $\alpha_{1:sBh}$ ,  $\beta_{fBh}$  and  $\beta_{sBh}$  and a multiple cost function was minimizing the differences between modelled and observed value for  $C_{Bh}$  and  $F_{a,Bh}$ . Results are shown in Fig. 12 and corresponding parameters in Table 4. The resulting present day instantaneous turnover times of C in the whole Bh are 12940, 16115, 67383 and 98215 gC for profiles MAR9, DPQT, UAU4 and P7C, respectively.





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#### Table 4. Parameters used for the modelling shown in Fig. 12.

Rates (y-1) MAR9 DPOT UAU4 P7C  $\beta_{1}$ 1.61 10-2 9.19 10-3 1.54 10-2 9.12 10-3 <u>k</u>1 2.57 10-3 2.57 10-3 2.57 10-3 2.57 10-3 <u>a</u>t-fBh 5.64 10-5 1.24 10-4 1.35 10-5 <u>a</u> t-sBh 1.85 10-4 2.90 10-4 8.61 10-5 1.01 10-5 <u>*a*</u> <sub>t-r</sub> 1.33 10-2 6.20 10-3 1.26 10-2 6.53 10<sup>-3</sup>  $\beta_{fBh}$ 3.59 10-4 3.76 10-4 1.86 10-4 1.26 10-4 5.00 10-5 <u>k <sub>fBh</sub></u> 5.00 10-5 5.00 10-5 5 00 10-5 2.79 10-5 1.01 10-4 3.01 10-6 <u>a. fBh-r</u> 1.08 10-4 7.32 10-5  $2.09\,10^{-4}$  $2.18 \ 10^{-4}$  $1.08 \ 10^{-4}$ <u>a. fBh-d</u> 1.57 10-6  $2.00\ 10^{-6}$ <u>β</u>sBh 2.00 10-6 1.20 10-6 5.00 10-5.00 10-5.00 10-5.00 10-7 <u>k <sub>sBh</sub></u> 6.35 10-8.86 10-1.83 10-7.62 10-7 <u>a.</u> sBh-r 9.46 10-9.90 10-4.88 10-3.32 10-7 <u>a sBh-d</u>

Mis en forme : Anglais (États-Unis)

Mis en forme : Légende, Paragraphes solidaires

#### 365 3.3 Age, carbon fluxes and carbon turnover

Considering that the forest aboveground litter production is around 850 g425 gC m<sup>-2</sup> y<sup>-1</sup>, the proportion of the litter aboveground\_OM produced by the forest transferred to the river network is 28, 6, 1156, 12, 22 and 57114% for profiles MAR9, DPQT, UAU4 and P7C, respectively. This large range of The high values for MAR9 and P7C profiles indicates a significant contribution of belowground litter and indicates how waterlogging of the podzol surface horizons affects the transfer of carbon from atmosphere to dissolved organic carbon.

With regard to the Bh horizons, it should be noted that the total C flux leaving these horizons can be distributed in any manner between mineralization, transfer to depth and transfer to the river. However, at least two pools are required for the total C flux leaving the Bh to be sufficiently large to match the measured values. Obtaining the measured old ages requires a long genesis time (around 195 103 y for UAU4 and 274 103 y for P7C) and very small input and output carbon

- fluxes. Because younger profiles, such as MAR9 and DPQT, can form with higher fluxes, it is likely that the flux rates 375 changed during the development of the profile, reducing progressively with time. Higher flux rates during the earlier periods of profile development, however, would lengthen the profile genesis time (Fig. 11), so that the genesis time estimated here for the slow Bh (around 17 103, 22 103, 195 103 and 274 103 for MAR9, DPQT, UAU4 and P7C, respectively) can be considered as a good estimate of the minimum time required to form the presently observed soils.
- 380 This is especially true for the DPQT and UAU4 profile as their Bh C stock value is a low estimate (cf. §2.1). SuchAnother source of overestimation of the genesis time is that, to simplify the calculations, we have not considered changes in atmospheric <sup>14</sup>C content over the past 50,000 years when it was shown that for most of this period conventional ages have to be corrected by more than 10% (Reimer et al., 2009). The estimated ages are very old when compared to temperate mature podzol that developed in 1 103-6 103 y (Sauer et al., 2007; Scharpenseel, 1993).

#### 385 4 Conclusion

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Modelling the carbon fluxes by constraining both total carbon and radiocarbon was an effective tool for determining the order of magnitude of the carbon fluxes and the time of genesis of the different carbon-containing horizons. Here modelling the upper horizons separately was necessary because of numerical constrains due to the great differences in carbon turnover time between topsoil horizons and Bh. Steady-state values obtained for the topsoil horizon could subsequently be introduced in Bh modelling. The approach we used can be applied to a wide range of situations, if necessary with simplifying assumptions to sufficiently reduce the degree of freedom of the system.

The results obtained showed that the organic matter of the podzol topsoil is very young (<sup>14</sup>C age from 62 to 109 y), with an annual C turnover, i.e. the carbon flux passing annually through the horizon, that increases if the topsoil is hydromorphic. This indicates that the most waterlogged zones of the podzolized areas are the main source of dissolved 395 organic matter to the Amazonian hydrographic network.

The model suggests that the Amazonian podzols are accumulating organic C in the Bh horizons at rates ranging from 0.54 and 3.17 gC m<sup>-2</sup> y<sup>-1</sup>, equivalent to 0.005 to 0.032 tC ha<sup>-1</sup> y<sup>-1</sup> of very stable C. Climate models predict changes in precipitation patterns, with greater frequency of dry periods, in the Amazon basin (Meehl and Solomon, 2007), possibly resulting in less frequent waterlogging. The change in precipitation patterns could have a dramatic effect on the C dynamics of these systems with an increase in the mineralisation of topsoil OM and an associated reduction in DOC

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determine the proportion of DOC topsoil origin and of Bh horizon origin. The topsoil horizons reached a steady-state in less than 750 y. The organic matter in the Bh horizons was older (<sup>14</sup>C age around 7 ky for the younger profile and 24 10<sup>3</sup> y for the older). The study showed that it was necessary to represent the Bh C with two C pools in order to replicate a number of carbon fluxes leaving the Bh horizon that have been observed in previous studies. This suggests that the response of the Bh organic C to changes in water regime may be quite complex. The formation of the slow Bh pool required small input and output C fluxes (lower than 3.5 and 0.8–g cm<sup>-2</sup> y<sup>-1</sup> for the two younger and the two older Bhs, respectively). Their genesis time was necessarily longer than 15 10<sup>3</sup> and 130 10<sup>3</sup> y for the two younger and the two older Bhs, respectively. The time needed to reach a steady state is very long (more than 48 10<sup>3</sup> and 450 10<sup>3</sup> y, respectively) so that a steady state was probably not reached. The genesis time calculated by considering the more likely settings runs around 15 10<sup>3</sup> - 25 10<sup>3</sup> and 180 10<sup>3</sup> - 290 10<sup>3</sup> y, respectively; the determination of these ages, which can be considered as low estimates, can help to constrain the dating of the sedimentary formations on which podzols have developed. Finally, a greater frequency of dry periods during the year might also possibly result in an increase in Bh mineralization rates and therefore of CO<sub>2</sub> degassing from the Bh, this question will be the object of a further publication.

transfer to both the deep Bh and the river network. -It may be noted that a 14C dating of the river DOC would help to

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#### 420 5 References

Baisden, W. T., Amundson, R., Brenner, D. L., Cook, A. C., Kendall, C. and Harden, J. W.: A multiisotope C and N modeling analysis of soil organic matter turnover and transport as a function of soil depth in a California annual grassland soil chronosequence, Global Biogeochem. Cycles, 16(4), 82-1-82–26, doi:10.1029/2001GB001823, 2002.
Bardy, M., Derenne, S., Allard, T., Benedetti, M. F. and Fritsch, E.: Podzolisation and exportation of organic matter in

425 black waters of the Rio Negro (upper Amazon basin, Brazil), Biogeochemistry, 106(1), 71–88, doi:10.1007/s10533-010-9564-9, 2011.

Chauvel, A., Lucas, Y. and Boulet, R.: On the genesis of the soil mantle of the region of Manaus, Central Amazonia, Brazil, Experientia, 43(3), 234–241, doi:10.1007/BF01945546, 1987.

Colinvaux, P. A. and De Oliveira, P. E.: Amazon plant diversity and climate through the Cenozoic, Palaeogeogr.
Palaeoclimatol. Palaeoecol., 166(1–2), 51–63, doi:10.1016/S0031-0182(00)00201-7, 2001.

Cornu, C., Luizão, F. J., Rouiller, J. and Lucas, Y.: Comparative study of litter decomposition and mineral element release in two Amazonian forest ecosystems : litter bag experiments., Pedobiologia (Jena)., 41(5), 456–471, 1997.
Dubroeucq, D. and Volkoff, B.: From oxisols to spodosols and histosols: Evolution of the soil mantles in the Rio Negro basin (Amazonia), Catena, 32(3–4), 245–280, doi:10.1016/S0341-8162(98)00045-9, 1998.

435 <u>Du Gardin, B.: Dynamique hydrique et biogéochimique d'un sol à porosité bimodale : Cas des systèmes ferralsols-podzols d'Amazonie, Presses Académiques Francophones., 2015.</u>

Van der Hammen, T. and Hooghiemstra, H.: Neogene and Quaternary History of Vegetation, Climate, and Plant Diversity in Amazonia, Quat. Sci. Rev., 19(8), 725–742, doi:10.1016/S0277-3791(99)00024-4, 2000.

Van Hees, P. A. W., Johansson, E. and Jones, D. L.: Dynamics of simple carbon compounds in two forest soils as

#### Mis en forme : Anglais (Royaume-Uni)

440	revealed by soil solution concentrations and biodegradation kinetics, Plant Soil, 310(1–2), 11–23, doi:10.1007/s11104-008-9623-3, 2008.	
	Horbe, A. M. C., Horbe, M. A. and Suguio, K.: Tropical Spodosols in northeastern Amazonas State, Brazil, Geoderma,	
	119(1-2), 55-68, doi:10.1016/S0016-7061(03)00233-7, 2004.	
	Leenheer, J. A.: Origin and nature of humic substances in the waters in the Amazon river basin., Acta Amaz., 10(10),	
445	513–526, 1980.	
	Lucas, Y., Montes, C. R., Mounier, S., Loustau Cazalet, M., Ishida, D., Achard, R., Garnier, C., Coulomb, B. and Melfi,	
	a. J.: Biogeochemistry of an Amazonian podzol-ferralsol soil system with white kaolin, Biogeosciences, 9(9), 3705-	
	3720, doi:10.5194/bg-9-3705-2012, 2012.	
	Malhi, Y., Wood, D., Baker, T. R., Wright, J., Phillips, O. L., Cochrane, T., Meir, P., Chave, J., Almeida, S., Arroyo, L.,	
450	Higuchi, N., Killeen, T. J., Laurance, S. G., Laurance, W. F., Lewis, S. L., Monteagudo, A., Neill, D. A., Vargas, P. N.,	
	Pitman, N. C. A., Quesada, C. A., Salomão, R., Silva, J. N. M., Lezama, A. T., Terborgh, J., Martínez, R. V. and Vinceti,	
	B.: The regional variation of aboveground live biomass in old-growth Amazonian forests, Glob. Chang. Biol., 12(7),	
	1107-1138, doi:10.1111/j.1365-2486.2006.01120.x, 2006.	
	Meehl, G. and Solomon, S.: Climate Change 2007: The Physical Science Basis, in Cambridge University Press., 2007.	
455	Menichetti, L., Katterer, T. and Leifeld, J.: Parametrization consequences of constraining soil organic matter models by	
	total carbon and radiocarbon using long-term field data, Biogeosciences, 13(10), 3003-3019, doi:10.5194/bg-13-3003-	
	2016, 2016.	
	Montes, C. R., Lucas, Y., Pereira, O. J. R., Achard, R., Grimaldi, M. and Melfi, A a, J.: Deep plant-derived carbon	 Mis en fo
	storage in Amazonian podzols, Biogeosciences, 8(1), 113-120, doi:10.5194/bg-8-113-2011, 2011.	
460	NIWA: Data set. Available on-line, Natl. Inst. Water Atmos. Res. New Zeal. [online] Available from:	
	http://ds.data.jma.go.jp/gmd/wdcgg/pub/data/current/14co2/event/bhd541s00.niwa.as.ot.14co2.nl.ev.dat, 2016.	
	Proctor, J.: NPP Tropical Forest: Gunung Mulu, Malaysia, 1977-1978, R1. Data set., Oak Ridge Natl. Lab. Distrib. Act.	
	Arch. Center, Oak Ridge, Tennessee, U.S.A, doi:10.3334/ORNLDAAC/474, 2013.	
	Raymond, P. a.: Carbon cycle: the age of the Amazon's breath., Nature, 436(7050), 469-470, doi:10.1038/436469a,	
465	2005.	
	Sauer, D., Sponagel, H., Sommer, M., Giani, L., Jahn, R. and Stahr, K.: Podzol: Soil of the year 2007. A review on its	
	genesis, occurrence, and functions, J. Plant Nutr. Soil Sci., 170(5), 581-597, doi:10.1002/jpln.200700135, 2007.	
	Schaetzl, R. J. and Rothstein, D. E.: Temporal variation in the strength of podzolization as indicated by lysimeter data,	
	Geoderma, 282, 26-36, doi:10.1016/j.geoderma.2016.07.005, 2016.	
470	Scharpenseel, H. W.: Major carbon reservoirs of the pedosphere; source - sink relations; potential of D14C and ??13C as	
	supporting methodologies, Water, Air, Soil Pollut., 70(1-4), 431-442, doi:10.1007/BF01105014, 1993.	
	Schwartz, D.: Some podzols on Bateke sands and their origins, People's Republic of Congo, Geoderma, 43(2-3), 229-	
	247, doi:10.1016/0016-7061(88)90045-6, 1988.	
	Sierra, C. a., Jiménez, E. M., Reu, B., Peñuela, M. C., Thuille, A. and Quesada, C. A.: Low vertical transfer rates of	
475	carbon inferred from radiocarbon analysis in an Amazon Podzol, Biogeosciences, 10(6), 3455-3464, doi:10.5194/bg-10-	
	3455-2013, 2013.	
	Sierra, C. A., Müller, M. and Trumbore, S. E.: Modeling radiocarbon dynamics in soils: SoilR version 1.1, Geosci.	
	Model Dev., 7(5), 1919-1931, doi:10.5194/gmd-7-1919-2014, 2014.	
	Stuiver, M. and Polach, H. A.: Radiocarbon discussion reporting of 14C data, Forensic Sci. Int., 19(3), 355–363 [online]	 Mis en fo

Mis en forme : Anglais (Royaume-Uni)

480	Available from: https://journals.uair.arizona.edu/index.php/radiocarbon/article/viewFile/493/498 (Accessed 26 March
	2014), 1977.
	Tardy, Y., Roquin, C., Bustillo, V., Moreira, M., Martinelli, L. A. and Victoria, R.: Carbon and Water Cycles Amazon
	River Basin Applied Biogeochemistry, Environment, 2009.
	Tipping, E., Chamberlain, P. M., Fröberg, M., Hanson, P. J. and Jardine, P. M.: Simulation of carbon cycling, including
485	dissolved organic carbon transport, in forest soil locally enriched with 14C, Biogeochemistry, 108(1-3), 91-107,
	doi:10.1007/s10533-011-9575-1, 2012.
	Trumbore, S.: Age of Soil Organic Matter and Soil Respiration: Radiocarbon Constraints on Belowground C Dynamics
	Ecol. Appl., 10(2), 399-411, doi:10.1890/1051-0761(2000)010[0399:AOSOMA]2.0.CO;2, 2000.
	Wanner, H.: Soil Respiration, Litter Fall and Productivity of Tropical Rain Forest, J. Ecol., 58(2), 543,
490	doi:10.2307/2258289, 1970.