

Modeling black carbon degradation and movement in soil

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Received: 3 September 2010 / Accepted: 16 March 2011 / Published online: 27 April 2011
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Abstract Black carbon (BC), the residue from burning with insufficient oxygen supply, is assumed to be very stable in the environment. Here we present a simple model for BC movement and decomposition in soils based on the assumption that BC consists of two fractions with different turnover time, and that BC can move in the environment as well as decompose. Decomposition rate was calibrated against laboratory data, whilst a recent field experiment was used to calibrate losses from downward movement through the soil profile. Losses by erosion are still poorly quantified, but mass balance indicates that they may be one of the most important fluxes. The model was able to acceptably predict CO₂ production from BC as well as BC left in the soil at the end of the experiment, although BC in the subsoil was underestimated. The model was sensitive to erosion rate (varied ±50%), moisture and temperature response

function on a 100-year time scale. The model was not sensitive to the decomposition rate of the stable pool on a 100 year time scale, but it was very sensitive to that on a millennial time scale. Implications and directions for future research are discussed.

Keywords Black carbon · Decomposition · Simulation model · Dissolved black carbon · Biochar

Introduction

Fire occurs in most terrestrial ecosystems (Bowman et al 2009), and has been studied as a major disturbance factor (Bond and Keeley 2005). Fire consumes vegetation carbon and produces CO₂ and other greenhouse gases, but a fraction of the vegetation carbon is transformed into black carbon (BC) during incomplete combustion and most of this BC is initially left on the soil surface (Forbes et al. 2006; Kuhlbusch and Crutzen 1995; Kuhlbusch, 1998; Schmidt and Noack 2000). Although the production of BC is small as a percentage of total vegetation carbon consumed by fire (<10%, Forbes et al. (2006)), it is still important in the global carbon cycle since it degrades slowly in the environment. Its formation is often credited as a CO₂ sink by transferring fast-cycling carbon from the atmosphere–biosphere system into much slower cycling carbon forms that may persist for millennia (Masiello 2004; Preston and Schmidt 2006).

Responsible Editor: Eric Paterson.

Electronic supplementary material The online version of this article (doi:10.1007/s11104-011-0773-3) contains supplementary material, which is available to authorized users.

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Soils rich in BC are usually fertile, and charcoal material added to the soil in the Amazon has dramatically improved fertility in the so-called “Terra Preta” soils compared to adjacent soils (Glaser et al. 2002; Lehmann et al. 2003; Major et al. 2005). The use of charred material as a soil amendment (“biochar”) has been suggested also in modern times (Lehmann et al. 2006; Lehmann and Joseph 2009). It is thought that biochar amendment may also be a way to sequester carbon in the soil (Gaunt and Cowie 2009; Lehmann et al. 2006), but little effort has gone into mathematically describing its long term stability and fate. Better predictions of stability would also improve assessments of the greenhouse gas mitigation effect of biochar application.

Simulation models can be used to investigate possible effects of perturbations on a complicated system. Increasingly, models are used to predict the effect of environmental change (e.g. Betts et al. 1997; Cox et al. 2000; Jones et al. 2005). When models are used to predict biotic feedback to climate change, the largest uncertainty is in the soil carbon pool (Friedlingstein et al. 2006). Models of soil carbon dynamics usually assume that soil organic matter can be conceptually assigned to pools with different turnover time (Jenkinson et al. 1987; Parton et al. 1987). A large part of the pool with the slowest turnover time is probably BC, but this cannot easily be verified within model structures.

Some attempts have been made at modeling BC decomposition or including BC in carbon turnover models (Lehmann et al. 2008a; Zimmerman 2010), sometimes as an inert pool (Skjemstad et al. 2004). If BC decomposition was included, it is typically described as one pool with exponential decay. However, whilst incubation experiments and chronosequence studies indicate that BC is degraded to some extent (Hamer et al. 2004; Kuzyakov et al. 2009; Nguyen et al. 2009; Nguyen and Lehmann 2009; Zimmerman 2010), incubations with aged BC (Cheng et al. 2008; Liang et al. 2008), budget analyses (Lehmann et al. 2008a) and ^{14}C dating of BC found in soils indicate that at least part of it lasts for millennia in some systems (Passenda et al. 2001; Gouveia et al. 2002; Gavin et al. 2003; Schmidt et al. 2002). This suggests that there are different chemical fractions within BC that turn over at different rates. Using a model with only one pool may therefore not be adequate, and multi-pool

models have been suggested (Lehmann et al. 2009) but have not yet been developed. Hammes et al. (2008) discussed the possibility of using a two- or multi-pool model, but concluded that not enough data were available to parameterize it. However, many experiments on BC turnover have been conducted in recent years, making at least parameterization of the pool with the fastest turnover time possible (Hamer et al. 2004; Kuzyakov et al. 2009; Nguyen et al. 2009; 2010; Nguyen and Lehmann 2009; Whitman 2010; Zimmerman 2010).

Nguyen et al. (2009) found that BC in a chronosequence after fire could be adequately described as a two-pool model where one pool disappeared within decades whilst the other did not degrade. However, the stable pool probably does degrade over very long time-scales, and in fact it should have a very low rate of decomposition. This suggests that BC decomposition dynamics can be described with a two-pool model. It is also known that BC can move in the landscape through losses by horizontal and vertical movement, with soil texture, physiography, and climate (and the presence of permafrost) adding to this complexity (Guggenberger et al. 2008; Hockaday et al. 2007; Leifeld et al. 2007; Major et al. 2010a; Rumpel et al. 2006, 2009). To predict BC content left in the soil at a certain time, both decomposition and movement need to be taken into account.

Here we developed a model for BC degradation and movement in soil based on recent evidence from incubation and field studies. We used similar theory as used in most soil organic matter models, but we aimed to keep the model as simple as possible, and base it on experimental evidence as much as possible. The model was calibrated and tested using laboratory data and a data set where field applied BC was monitored in the soil profile. The model was used to assess the importance of BC decomposition versus movement in the landscape. We also ran two longer simulations and assessed the sensitivities of uncertain parameters.

Materials and methods

Field data and modeling setup

For calibration of BC movement in soils, we used data from an experiment where a known quantity

of BC (23.2 kg C/ha) with a distinct isotopic signature was incorporated into the soil at the beginning of the dry season and monitored as it moved and was decomposed (Major et al. 2010a). The experiment was carried out in the Colombian Llanos region ($04^{\circ}10'15.2''N$, $72^{\circ}36'12.9''$) over a 2 year period. The soil at the site was a sandy clay loam (64% sand, 21% clay, pH 3.9, 0.65% C and 0.044% N in top soil). Long-term average annual rainfall measured approximately 200 km northeast of the plot is 2,200 mm, and 95% of precipitation falls between April and December. A marked dry season occurs between January and March, and average annual temperature is 26°C. Downwards movement of water and BC at 0.15 and 0.3 m depth was measured during the rainy season in both years. The amount of added BC left in the soil profile was measured towards the end of the experiment. Soil respiration was only measured during the second year of the experiment, but a similar experimental plot was established adjacent to the first one, for monitoring soil respiration with BC in the first year after application. Those measurements are used as first year respiration here. The data were used both to calibrate water movement and to run a simple test of the decomposition model. In the field study leached BC was separated into particulate organic matter ($> 0.7 \mu m$) and dissolved organic matter ($< 0.7 \mu m$), but as we could not find any difference between them in how they behaved in the soil, they are

analyzed together here. The BC model was implemented in Microsoft Excel, and all curve fitting was done in Excel or SigmaPlot. The model was initially implemented with daily time steps. An implementation of the model is available as online supplementary material. A list of calibrated parameters can be found in Table 1.

We used the DayCent model (Del Grosso et al. 2001; Parton et al. 1998) to calculate soil water content, temperature and water fluxes. These were used as inputs to the BC model developed. Necessary climate input (temperature and rainfall) were measured at a site with a distance of 3.6 km during the rainy season. During the dry season climate data measured 200 km away, but at similar altitude, were used after being adapted using a linear relationship between the two measurements obtained where the two data sets overlap. Soil profile data (bulk density, water retention, texture organic matter content, saturated hydraulic conductivity and pH) were measured at the site (Major et al. 2010a). The option “warm season grasses” in DayCent was chosen as plant type to simulate the growth of the native savanna grasses that were allowed to regrow after plot establishment at the site. Simulated plant productivity was also tuned to match observed levels of biomass and growing season length, and water flux rates predicted by the model were checked to make sure they were comparable to those observed in the field.

Table 1 Parameters for the model of BC degradation and movement in soil

Symbol	Value used	Unit	Interpretation	Reference/motivation
k1	0.0038	d^{-1}	Maximum decomposition rate for labile pool	Whitman (2010)
f	0.122	—	Fraction of new BC in labile pool	Whitman (Whitman 2010)
k2	1.37E-06	d^{-1}	Maximum decomposition rate for stable pool	Own estimate
a	1.452	—	Parameter for temperature response	Calculated from Nguyen et al. (2010)
b	-2.4599	—	Parameter for temperature response	Calculated from Nguyen et al. (2010)
c	4	—	Parameter for moisture response	From the DayCent model
d	-6	—	Parameter for moisture response	From the DayCent model
C1	8e-7	m^{-1}	Constant in BC transport equation in topsoil	Fitted to data set from Major et al. (2010a)
C2	0.01	m^{-1}	Constant in BC transport equation in subsoil	Fitted to data set from Major et al. (2010a)
fr	0.9	—	Fraction of BC available for erosion	Nguyen et al. (2009)
r	0.03	d^{-1}	Rate of erosion	Total runoff within range found by Rumpel et al. (2009), reaching stable state as Nguyen et al. (2009) and fit final BC to data in Major et al. (2010a)

BC model and calibration

We assume that the dynamics of BC in the soil can be described as shown in Fig. 1. BC can decompose as well as leach to a deeper soil layer and eventually out of the profile, or it can be lost by runoff (erosion) on the surface. Decomposition is described by a two pool model:

$$BC(t) = BC0 \times (f^* e^{-tk1} + (1-f)^* e^{-tk2}) \quad (1)$$

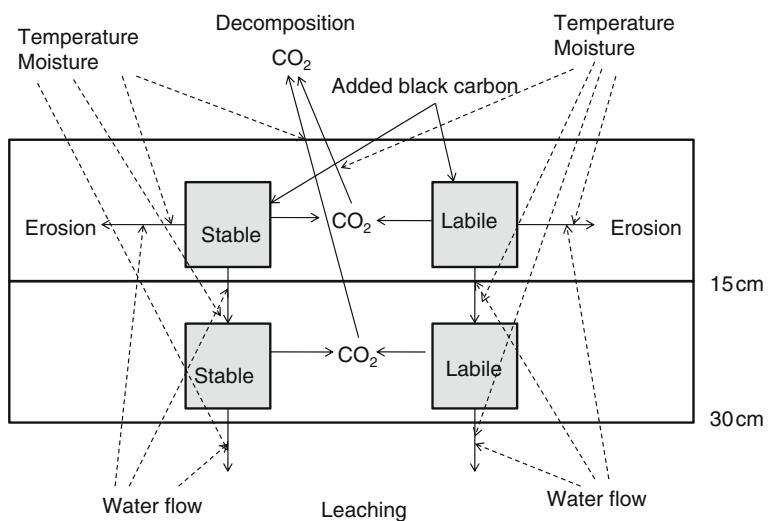
Where $BC(t)$ is the amount of BC left at time t , $BC0$ is the amount of BC at time 0, f is the fraction of $BC0$ that is labile (with the fastest turnover rate) and $k1$ and $k2$ are constants for decomposition rate of the labile and stable (with the slowest turnover rate) pools respectively. Climatic conditions are assumed to influence decomposition rates by modifying the k -values as explained below.

The labile fraction (f) and decomposition rate of the labile pool ($k1$) for different types of BC were based on data from an experiment where BC was incubated for 3 years under near optimal conditions generating maximum decomposition rates (Whitman 2010). This experiment included multiple plant materials which were pyrolysed at various temperatures. Since the BC in the experiment of Major et al. (2010a) was produced from prunings of mango tree pyrolysed at 400–600°C, we calculated constants from the data of Whitman (2010) from materials produced at 500°C, using averaged data from two

woody plant materials (pine and oak) as well as data from herbaceous material (corn stalks). It was assumed that within the time frame of this experiment, only the decomposition of the labile pool could be detected. The stable pool was therefore assumed to be constant, and Eq. 1 was fitted to the data, assuming $k2=0$. As there was large variability in the data set, the fit was fair ($r^2=0.37$; $N=20$; $P<0.012$). Decomposition rates of the stable fraction cannot be accurately calibrated using any available data. However, the range of possible values can be somewhat constrained. ^{14}C dating has found ages from 64 to 12,220 years for BC found in the soil (Gavin et al. 2003). Indicating that the turnover time of BC is long. However, it is not possible to quantify turnover time further from these data, as initial amount of BC is not known. Lehmann et al. (2008a) calculated turnover times based on BC stocks and assumptions on fire frequency and BC formation and obtain a range of 718–9,259 year. However, this calculation assumed a one-pool turnover model. Nguyen et al. (2009) could not measure any significant change in the stable pool over 100 years, suggesting that the turnover time must be significantly longer than 100 years. It can be concluded from this that the turnover time of the stable pool is probably in the order of thousands of years. Here we use a turnover time of 2,000 years as a base scenario, but we also explore sensitivity to varying this parameter.

Nguyen et al. (2010) measured decomposition rates for BC at different temperatures. The results show that the actual decomposition rate can be

Fig. 1 Flow diagram of the suggested model of BC decomposition and transport in soils. Boxes show pools and arrows show fluxes. Dashed lines show fluxes which are affected by temperature and moisture modifiers and water flow



expressed as the product of a maximum decomposition rate and a modifier:

$$Mt = \alpha^* \ln(T) - b \quad (2)$$

Where Mt is the modifier, T is temperature and a and b are empirical constants, values are given in Table 1. The parameters were adapted assuming the standard decomposition as in Whitman (2010), and the temperature modifier function from Nguyen et al. (2010). We used the labile fractions and $k1$ for BC as found above, assumed that the decomposition measured over this short time period was only from the labile pool, and calculated the parameters (Fig. 2). The same temperature sensitivity was used for the stable pool, but the effect of changing that assumption was investigated in a sensitivity test (see below).

The only data we could find on the effect of moisture on BC degradation was by Nguyen and Lehmann (2009) where saturated and non-saturated water conditions were compared. The results showed little effect of water regime in most cases. We found no data on the effect of water content below field capacity on decomposition rates of BC. We therefore use the moisture modifier (Mw) from the DayCent model where decomposition rate increases from close to 0 at dry conditions to a maximum at high water content:

$$Mw = \frac{1}{1 + c * e^{(-d * \text{relative water content})}} \quad (3)$$

where c and d are constants.

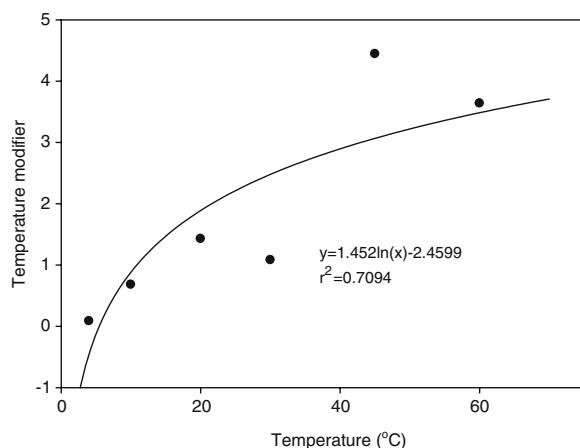


Fig. 2 Calibration of temperature modifier based on data from Nguyen et al. (2010)

We assumed that transported BC represented a constant fraction of BC remaining in the soil on each day when downwards water flow occurred, and that BC transport was also modified by temperature and moisture content in a similar way as decomposition:

$$BCt = C * BC * Mt * Mw \quad (\text{when } Wf > 0) \quad (4)$$

where BCt is the transport of BC out of the soil layer, BC is the amount of BC present in the soil layer, C is an empirical constant, Wf is the water flow out of the soil layer and Mt and Mw are the temperature and moisture modifiers, respectively. Climate modifiers were included as a weak correlation between carbon dioxide evolution and BC flux was observed (Fig. 3). As there was (surprisingly) no correlation between volume of water and amount of BC leached over any given time period (Fig. 4), water flow volume is not included in the equation. However, we assumed that no BC downward movement could take place without some water movement. The transport of each fraction (stable and labile) was assumed to be proportional to the fraction of each present. The empirical constants were calibrated so that the total downward movement over the 2-year period was similar in the measured and simulated results. This model is calibrated for a region with flat topography, and should not be applied on strongly sloping land.

We had no direct data on BC lost by runoff/erosion although this may be the most important flux (Major et al. 2010a; Rumpel et al. 2009). BC is also less dense than other soil components, so it

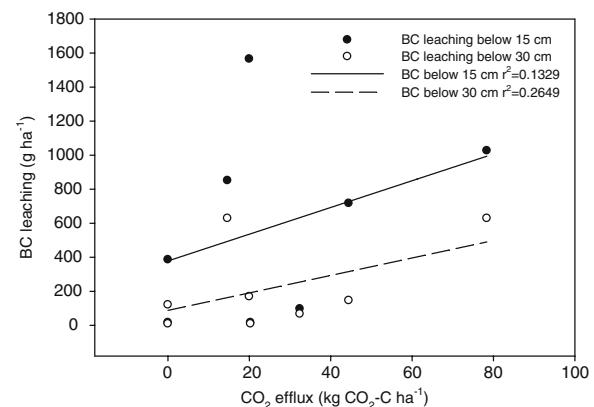


Figure 3 Observed BC movement downwards in the soil profile as a function of CO_2 fluxes measured over the same time period. Correlations are shown on graph. Data from Major et al. (2010a)

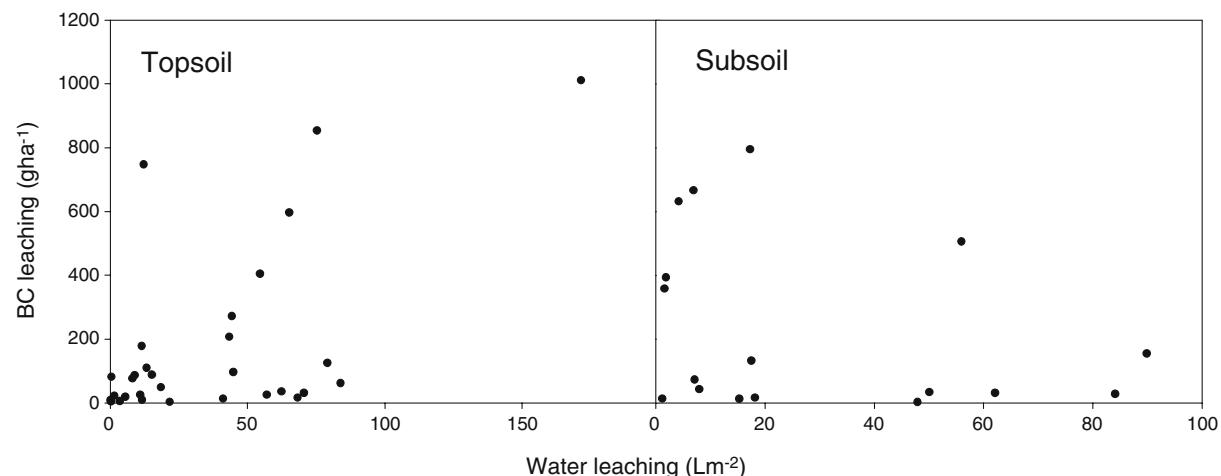


Fig. 4 Downward transport of BC out of the topsoil (*left*) and out of the subsoil (*right*) as a function of water flow by downward movement over the same time period. Data from Major et al. (2010a)

may be expected to move and float more easily. Guggenberger et al. (2008) found that a larger fraction of BC than other soil organic matter was eroded. There is therefore reason to believe that models developed for erosion of other soil components are not valid for BC. Furthermore, most models of soil erosion in the literature are very detailed and require a large number of calibrated parameters (e.g. Nearing et al. 2005; Neitsch et al. 2005). We can therefore not apply them directly. It is, however, reasonable to assume that the quantity of BC lost depends on the quantity still left, i.e. as an exponential decay function. Nguyen et al. (2009) found that large pieces of BC reached a stable level after about 20 years. We believe the larger pieces are most prone to erosion. We therefore assume that a fraction of BC will not erode, and obtain a function for loss by erosion similar to decomposition:

$$BC(t) = BC_0 \times (fr * e^{-tr} + (1 - fr)) \text{ (when } er > 0\text{)} \quad (5)$$

where $BC(t)$ is the amount of BC left at time t , BC_0 is the amount of BC at time 0, fr is the fraction of BC_0 that can erode, r is the erosion rate and er is water runoff flow. Similar to downward movement, we assume that erosion of BC can only take place when there is water runoff. Erosion rate is modified with climatic factors in a similar way as decomposition. Nguyen et al. (2009) found that the stable fraction was about 10%. We had no direct measurement of r (erosion rate), but Rumpel et al. (2009)

found that 7–55% of surface deposited BC after slash-and-burn with no incorporation can be subject to horizontal transport when slope was less than 1%, and Nguyen et al. (2009) found that it took about 20 years to reach a stable level of larger pieces of BC. We also tried to fit the model to predict close to the measured amount of BC at the end of the experiment of Major et al. (2010a).

Long term simulation and sensitivity

A longer simulation of 100 years was carried out for the site, based on data from the two year field study (Major et al. 2010a) repeated in monthly time-steps. Water flow was averaged over the number of days when water flow occurred. The predicted longer term decomposition and transport of BC was assessed. Since some parameters in the model are not based on firm data, individual sensitivity tests were carried out. This applies to the decomposition rate for the stable pool and the moisture and temperature modifier equations, as well as erosion rate. The high and low ends of the range of the stable pool turnover times were tested (500 and 5,000 years). For the moisture modifier, the DayCent model has a second set of parameters ($c=30$, $d=-8.5$), which were tried in addition to the standard parameter as in Table 1 ($c=4$, $d=-6$). For the temperature modifier, a simulation was carried out with the modifier scaled to reach unity at 30°C, the temperature at which the standard decomposition rate

was calibrated (Whitman 2010). Erosion rates (r) were increased and decreased by 50%.

To assess model behavior in the very long term, a long simulation of 2,000 years was also carried out, using monthly time steps as above. Also on this time scale, sensitivities to erosion rate and the turnover time of the stable pool were assessed, using the same variations as above. The effect of making the stable pool more sensitive to temperature was also assessed, using the assumptions of Knorr et al. (2005). Activation energy of the pool was assumed to depend on turnover rate as an empirical formula from Knorr et al. (2005), where temperature sensitivity increase with pool stability. The temperature sensitivity of the stable pool was modified assuming Arrhenius kinetics as in Knorr et al. (2005) so that the turnover rate at 15°C did not change.

Results

The model could predict the overall pattern of BC decomposition and downward movement after calibration, but not short term variation. CO₂ production was predicted to fluctuate, presumably with climatic factors, decline during the measurement period and be somewhat lower during the dry season (Fig. 5). However, substantial CO₂ efflux was predicted also in the dry season. The levels of CO₂ production predicted by the model were somewhat higher than

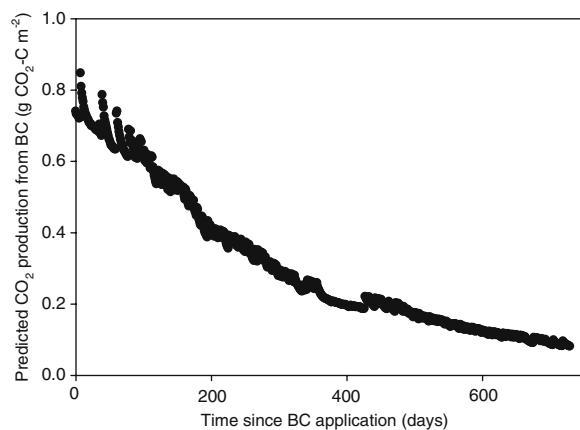


Fig. 5 Model output of CO₂ efflux from the added BC during the 2-year experiment as a function of time after BC application. The dry season is approximately from day 324 to day 452 on the figure (November 20th to March 28th)

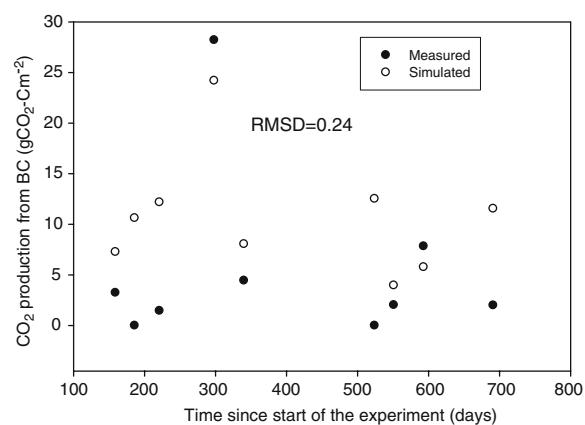


Fig. 6 Comparison of observed and simulated CO₂ efflux from the added BC as a function of time after BC application. Field data was collected from a “false time series”, where data for first and second year after BC application were collected during the same year and therefore both years are simulated with climate data from Major et al. (2010a)

the measured values (Major et al. 2010a), and could not track short term variation (Fig. 6). The model could not predict temporal variation in BC downward movement, but the total BC amounts were calibrated to match observed values. The observed data also show more BC transport out of than into the subsoil during the first rainy season. This means that some BC may have moved to the subsoil before the rainy season, further supporting the idea that some movement took place during the first dry season. Most of the BC remained in the topsoil during the experimental period, since amounts of BC applied reasonably corresponded with observed values at the end of the experiment (Fig. 7). The model underestimated the amount of BC in the subsoil at the end of the experiment (Fig. 7).

The 100-year simulation showed an exponential decrease in the amount of BC in the topsoil, and a rise followed by decline in the subsoil (Fig. 8). Sensitivities are expressed as average difference over the 100 year simulation. Changing the decomposition rate of the stable pool had very little effect at this time scale (Fig. 8), less than a 1% difference from the standard on average over the 100 years. Changing the parameters of the moisture modifier had quite a large effect on BC left in the soil (58%), as had changing the temperature modifier (40%) (Fig. 8). Also erosion rate was important (Fig. 8), and increasing the erosion rate

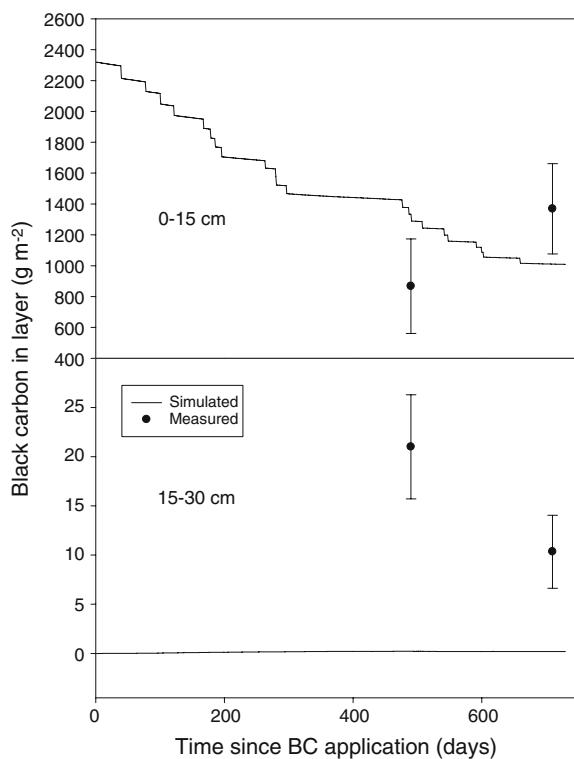


Fig. 7 Predicted and measured BC content in both topsoil and subsoil as a function of time after BC application. Data from Major et al. (2010a)

decreased BC content by 13% on average, while decreasing the erosion rate increased BC content in the soil by 37% on average. However, these were all important mostly on short to medium time scales. Towards the end of the 100 year simulation, neither erosion rate nor the modifiers had much effect on BC left in the soil (Fig. 8).

On a 2,000-year time scale, the time when the labile pool was depleted and erosion stopped can easily be identified, early in the simulation (Fig. 9). On this time scale the model was very sensitive to the decomposition rate of the stable pool (turnover rate of 500 years resulted in 62% less BC on average, and turnover rate of 5,000 years resulted in 174% greater BC). The model was sensitive to decreased erosion rate (156% increase), but not to increased erosion rate (5% decrease) (Fig. 9). The reason for this is that only a fraction can erode, and whether this fraction is depleted before or after the labile pool is depleted by decomposition is critical. The model was also

somewhat sensitive to the temperature sensitivity of the stable pool (27% decrease in BC content on average) (Fig. 9).

The model predicted that the largest flux of BC (75%) was runoff/erosion, with decomposition being second (20%), while losses by downward movement were very small in comparison (0.5%). Erosion was proportionally somewhat more important in the short term than the long term, but remained the most important process on all time-scales (Table 2). Downward movement became proportionally more important on longer time-scales than shorter time scales (0.03% of the total BC loss from the site after 2 years and 0.54% of the total BC loss from the site after 2,000 years), but was still unimportant with respect to total BC loss from the site on all time-scales (Table 2). A large proportion (47%) of total decomposition over 2,000 years was predicted to occur during the first 2 years.

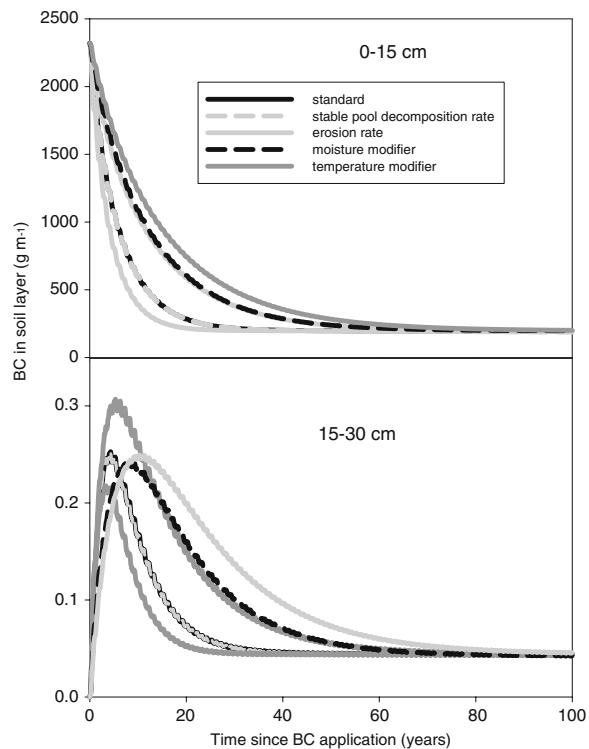


Fig. 8 Results from a 100-year simulation using different values for the turnover rate of the stable BC pool (varying between 500 and 5,000 years, standard 2,000 years) and erosion rate increased and decreased by 50%, as well as changed moisture and temperature modifiers. Standard values for all parameters are given in Table 1

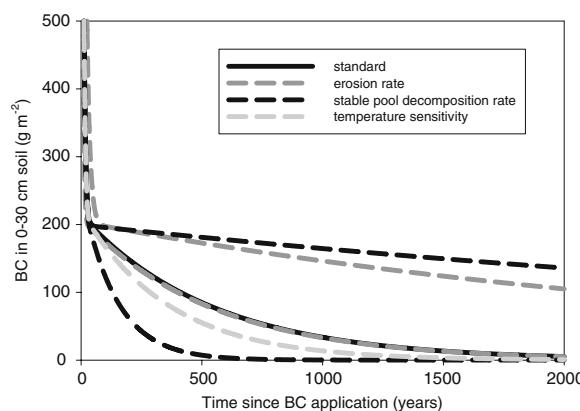


Fig. 9 Results from a 2000-year simulation with the same changes in stable pool turnover rate and erosion rate as in Fig. 8 as well temperature sensitivity of the stable pool increased according to Knorr et al. (2005). Standard values for all parameters are given in Table 1

Discussion

Our model could predict observed patterns of BC dynamics at the experimental site to a reasonable degree. In accordance with measurements (Major et al. 2010a), the model predicts that decomposition is much more important as a mechanism for carbon loss from the system than downward transport with water. Downward movement accounted for a slightly larger portion of total carbon loss in the long term simulations. This is a consequence of the assumption chosen here where erosion and decomposition are both assumed to have a stable fraction, but downward movement is not. Even though current data are weak in this regard, this is a reasonable scenario, as significant amounts of BC are typically found in subsoils while actual rates of downward movement are low (Dai et al. 2005; Rodionov et al. 2006; Leifeld et al. 2007; Major et al. 2010a). However, losses from downward movement are unimportant in terms of mass balance, and a model could ignore them without impacting the accuracy of the estimate of amount of BC remaining at the end of the simulation. The

model predicted, in agreement with the experimental observation that the majority of the BC remained at or near the surface for a long time. This implies that applied BC may be consumed by subsequent vegetation fires. This pathway of BC loss must also be quantified. Experimental evidence indicates that recent fire history often does not affect BC content in the topsoil to a significant extent, indicating that fires may consume as well as produce BC (Dai et al. 2005; Knicker et al. 2006).

One of the main findings from the work of Major et al. (2010a) was that there was a large flux of BC out of the system that was not accounted for. Major et al. (2010a) speculate that most of this loss can be attributed to surface erosion, the only unmeasured flux. Our simulation also indicates that decomposition and to some extent downward movement and erosion, can occur during the dry season, when no measurements were made by Major et al. (2010a). This is based on the temperature and moisture content in the soil and water flux between layers as predicted by DayCent. The conclusion that decomposition happens also in the dry season will therefore depend on the moisture modifier, which is an uncertain and sensitive parameter. Furthermore, we also needed to assume large erosion losses to achieve predictions of BC left in the soil at the end of the experiment that are close to the measured values. This means that erosion, the most poorly quantified BC flux in our model, is probably the most important pathway for loss of BC from the system. This highlights the need for better quantification of the size of this flux, how erosion occurs temporally and the fate of eroded BC. BC erosion rate may also depend on soil texture. We have not included this in our model, as we only have data from one site, and therefore cannot parameterize it. Future work should focus on measuring BC erosion on different soil types. Since surface erosion is potentially such an important loss factor, large-scale deployment of biochar technology will require the development of best management practices to minimize such losses.

Table 2 Fluxes of BC during a 2-year (short term), a 100-year (medium term) and a 2000-year (long term) simulation in percent of the total at the beginning

	Decomposition	Downward movement	Runoff	Total
Short term	9.78	0.02	49.06	58.86
Medium term	11.68	0.13	76.09	87.89
Long term	20.65	0.52	74.83	96.00

Many of the shortcomings of the model can be alleviated by experiments where a known quantity of BC is followed over time in the field, similar to the experiment of Major et al. (2010a), but where BC erosion is also measured directly. The experiment should ideally be repeated under different conditions of soil types and climates, to obtain a better understanding of how the magnitude of fluxes depends on environmental conditions.

Downward movement in this heavy textured soil was not an important bulk flux of BC, but may still be needed to explain that BC is found in subsoils (Dai et al. 2005; Leifeld et al. 2007; Major et al. 2010a). However, more BC was observed in the sub-soil at the end of the experiment than the model and the data on downward movement from the field predict (Major et al. 2010a). Therefore it seems that an additional mechanism for vertical transport may be relevant, apart from movement with water. We can only speculate what this mechanism may be, i.e. termites or other soil fauna or pedoturbation (Czimczik and Masiello 2007; Lehmann et al. 2009). More work is needed to determine the mechanisms of BC movement in the soil profile. Downward movement may be more important quantitatively in soils with lighter texture.

The model is not fully tested here, because the field data set was also partly used to calibrate the model. Only CO₂ production measured in the field can be interpreted as an independent test, since decomposition rate was calibrated using other data from the laboratory. However, we were not been able to find any other acceptable field data set on the fate of soil-applied BC over time, which would be needed for proper independent tests of the model.

The model was not sensitive to the turnover rate of the stable pool on a 100-year time scale. It follows that on time scales up to a century, the model should be quite reliable, even when this parameter is very uncertain. This means that the model could potentially be used in future models for IPCC climate impact assessments, which usually consider a century time scale (IPCC 2007). On a millennial time scale, the model was sensitive to the turnover rate of the stable pool, as expected. On that time scale, erosion will have stopped if we assume that a fraction of BC is resistant to erosion. Therefore decomposition was the only important loss function for BC on that time scale.

The model was quite sensitive to the moisture modifier, as expected. This underlines the need to

conduct more experiments to measure the effect of moisture on BC decomposition. This can probably best be achieved in laboratory incubations, where the effect of moisture can be studied in isolation from other factors. Although the extent of BC decomposition during the dry season may change with better quantification of the moisture modifier, it is likely that significant decomposition occurs during the dry season. Assuming some vertical transport during the dry season can explain why there was more transport of BC out of than into the lower layer during the first measurement season. However, as mentioned above, there must be factors other than only water flow involved in vertical transport, which may also explain this finding.

The data set used to parameterize maximum decomposition rates (Whitman 2010) measured a lower decomposition rate than the data set used to parameterize temperature sensitivity (Nguyen et al. 2010). The temperature modifier therefore reaches 1 (unity) at a low temperature, and actual decomposition rates will be increased above the one measured by Whitman (2010) during the simulation of the field experiment of Major et al. (2010a). This means that actual decomposition rates that the model predicts will be similar to the high values observed by Nguyen et al. (2010). Comparison with soil respiration rates in the experiment by Major et al. (2010a) indicates that simulated values are somewhat higher than observed values. The model is also quite sensitive to this. Decomposition rates and temperature sensitivities still require further study, in particular to identify the important difference between apparently similar experiments. A possible explanation is that the experiment by Nguyen et al. (2010) lasted for a shorter time period than that by Whitman (2010). Measured turnover times tend to be shorter with a shorter the experimental period if we assume that BC actually consists of a large number of chemical fractions that all decompose with different turnover times (Lehmann et al. 2009).

There was large variability in the data-set of Whitman (2010) that was used to parameterize the labile pool parameters. The variability stems only in part from uncertain estimates, but is largely a result of different feedstocks and pyrolysis conditions generating BC materials with inherently different k values (Zimmerman 2010). Our model does not explicitly capture BC materials with different k values, for which still too few data are available.

Since we had no data on the climate sensitivity of the most stable pool, we assumed that this sensitivity was equivalent to that of the labile pool. This assumption is also made in most soil organic matter models, where the climate sensitivity of different fractions of soil organic matter is taken to be the same. The validity of this assumption is, however, hotly debated (Davidson and Janssens 2006; Fang et al. 2005; Knorr et al. 2005; Reichstein et al. 2005; Waldrop and Firestone 2004). Nguyen et al. (2010) found that for BC, there was evidence for steeper response to temperature in the more resistant BC types. We found that the model was sensitive to changing the assumption on temperature sensitivity on time scales of millennia, when the turnover of the stable pool becomes important. However, on time scales of up to a century this will be unimportant because the turnover of the stable pool is low.

Soil organic matter models usually assume that soil texture influences decomposition rate or carbon retention in the soil in some way (Coleman and Jenkinson 1999; Parton et al. 1988). The degree to which stability of BC is conferred by physical stabilization is not yet clear. Using polytungstate for density fractionation, Glaser et al. (2000) found most of the BC in Terra preta soils in the light fraction, whereas Liang et al. (2008) reported 72–90% of the organic carbon in Terra preta soils to reside in the organo-mineral fraction using sodium iodine. Several studies also report BC to be embedded within micro-aggregates (Glaser et al. 2000; Lehmann et al. 2008b) suggesting stabilization mechanism through aggregation. Also Brodowski (2004) found greater BC decomposition in incubations conducted in sand than soil. However, Glaser and Amelung (2003) found that BC content in soil did not correlate with soil properties as other soil organic matter fractions do. It is possible that stabilization is more important for the labile than the stable pool. However, we do not have sufficient data to parameterize any relationship between soil texture and BC decomposition rates, so we assume that texture does not influence BC stability in our model until further refinements are possible.

As decomposition is a microbial process, it would be expected that microbes would appear in models of decomposition and soil organic matter turnover. Most soil organic matter turnover models do not include microbes explicitly, although a model pool is often assumed to correspond to microbial biomass (Jenkinson

et al. 1987; Parton et al. 1987). It is also mostly assumed that microbial diversity is large enough for an appropriate microbial community to develop, so that microbial community structure is controlled by substrate availability and abiotic factors. Schimel and Weintraub (2003) modeled decomposition using Michaelis-Menton kinetics, and concluded that in soils Michaelis-Menton kinetics and exponential decay functions produce similar results. Nocentini et al. (2010) found a modest effect of different microbial inoculums on decomposition rates of BC, indicating that explicitly including microbes may improve the model only slightly. However priming, an increased decomposition rate as a response to added fresh organic matter has been shown in many experiments, both in the laboratory and in the field (Fontaine et al. 2004; Fontaine et al. 2007; Hoosbeek and Scarascia-Mugnozza, 2009; Paterson et al. 2008). Priming has also been shown to play a role in BC degradation (Hamer et al. 2004; Kuzyakov et al. 2009; Nocentini et al. 2010). Including priming in soil organic matter models, may improve them, particularly their predictions of the effect of supplying fresh organic matter, which may not always increase organic matter content (Fontaine et al. 2004; Fontaine et al. 2007; Hoosbeek and Scarascia-Mugnozza, 2009). Including priming into our model for BC decomposition may also improve it. However, at present there is limited data to quantify the priming effect and how it depends on substrate supply. Including priming should however, be a priority both for future modeling of BC degradation and soil organic matter turnover.

The model does not recognize any BC decomposition product left in the soil (Lehmann et al. 2009). These may form another stable pool that may change decomposition rates in the longer term. This is potentially a weakness of the model, but with the data sets that are available at present no further calibration of microbial metabolites is possible. It does, however, highlight the need for quantitative data on how BC transforms during degradation in soils.

Here we also ran the BC model independently from possible effects on other forms of soil carbon (Wardle et al. 2008; Lehmann and Sohi 2008) or plant productivity (Lehmann and Rondon 2006; Major et al. 2005; 2010a and b; Rondon et al. 2007). This was desirable as a starting point for simplicity and using available data, but future modeling efforts will need to address this aspect.

Conclusions

The model developed here should be seen as a first attempt, and it can be modified and developed further as more data become available. Particularly, erosion needs to be better quantified as mass balance indicates that it is the most important loss factor. This can be achieved in field experiments where all fluxes of BC, including erosion, are measured over time. We have shown that a two-pool model can adequately describe BC dynamics. We found the decomposition of the labile pool to be the process best constrained by experimental data. The data we used provide only a first approximation of the accuracy of the decomposition rate of the stable pool. However, we have shown that this parameter is not important for time scales up to a century. New BC additions can be integrated into current soil organic matter models e.g. the Century or RothC models by allocating the BC entering various pools based on turnover rates. However, erosion losses may be more important for BC than other types of soil carbon and the models may therefore need to be modified to take erosion into account. Also different BC qualities are not explicitly captured and should be included in future iterations of the model, as soon as empirical data are available that allow its parameterization.

Acknowledgements The lead author was funded by NASA-USDA award No. 2008-35615-18961. We thank three anonymous referees for their constructive comments.

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