

Fate of soil-applied black carbon: downward migration, leaching and soil respiration

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Abstract

Black carbon (BC) is an important pool of the global C cycle, because it cycles much more slowly than others and may even be managed for C sequestration. Using stable isotope techniques, we investigated the fate of BC applied to a savanna Oxisol in Colombia at rates of 0, 11.6, 23.2 and 116.1 t BC ha⁻¹, as well as its effect on non-BC soil organic C. During the rainy seasons of 2005 and 2006, soil respiration was measured using soda lime traps, particulate and dissolved organic C (POC and DOC) moving by saturated flow was sampled continuously at 0.15 and 0.3 m, and soil was sampled to 2.0 m. Black C was found below the application depth of 0–0.1 m in the 0.15–0.3 m depth interval, with migration rates of 52.4 ± 14.5, 51.8 ± 18.5 and 378.7 ± 196.9 kg C ha⁻¹ yr⁻¹ (± SE) where 11.6, 23.2 and 116.1 t BC ha⁻¹, respectively, had been applied. Over 2 years after application, 2.2% of BC applied at 23.2 t BC ha⁻¹ was lost by respiration, and an even smaller fraction of 1% was mobilized by percolating water. Carbon from BC moved to a greater extent as DOC than POC. The largest flux of BC from the field (20–53% of applied BC) was not accounted for by our measurements and is assumed to have occurred by surface runoff during intense rain events. Black C caused a 189% increase in aboveground biomass production measured 5 months after application (2.4–4.5 t additional dry biomass ha⁻¹ where BC was applied), and this resulted in greater amounts of non-BC being respired, leached and found in soil for the duration of the experiment. These increases can be quantitatively explained by estimates of greater belowground net primary productivity with BC addition.

Keywords: biochar, black carbon, carbon leaching, carbon sequestration, dissolved organic carbon, Oxisol, particulate organic carbon, soil carbon cycling, soil respiration

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Introduction

Black carbon (BC) is an important C pool globally. Despite relatively low global production rates of 0.05–0.27 Pg yr⁻¹ (Forbes *et al.*, 2006) compared with terrestrial net primary productivity of about 60 Pg yr⁻¹ (Denman *et al.*, 2007), biomass-derived BC has been found to comprise about 30% of organic C in 76% of 57 soils from six orders worldwide (Skjemstad *et al.*, 1996, 1999a,b; Skjemstad & Taylor, 1999). Therefore, BC cycles at a much slower rate than the non-BC fraction of soil organic C mainly due to its high content of aromatic, graphitic, or elemental refractory C (Glaser *et al.*, 1998).

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Indeed, BC in deep-sea sediments has been found to be 2400–13 900 years older than associated non-BC (Masiello & Druffel, 1998). Black C has also been observed to represent the oldest C fraction in soils (Pessenda *et al.*, 2001). Understanding the stability of BC in soil is crucial in order to balance the global C budget (Czimczik & Masiello, 2007). Managing BC for actively increasing the long-term C sink of atmospheric CO₂ in the form of BC from biochar in soil has been proposed by Lehmann *et al.* (2006) and also relies on accurate information about its stability.

However, very little is known about the stability of BC under field conditions. Most studies are conducted by using laboratory incubations (Baldock & Smernik, 2002; Cheng *et al.*, 2008b; Liang *et al.*, 2008; Kuzyakov *et al.*, 2009). The few published field observations using repeated soil sampling show generally rapid disappearance rates (Bird *et al.*, 1999; Hammes *et al.*, 2008; Nguyen

et al., 2008) which may be explained by the fact that a full mass balance was not possible and some BC loss may have occurred by mass transport rather than mineralization.

Despite the observed long-term stability of BC, significant initial mineralization is likely to occur. Rapid oxidation over several months of incubation was reported for experimentally produced BC (Cheng *et al.*, 2006, 2008a). BC generated in the laboratory is likely to contain a range of compounds exhibiting varying stability (Lehmann, 2007). During the first 10 years after BC deposition following forest fires in Kenya, the O/C ratio significantly increased on BC surfaces (Nguyen *et al.*, 2008), and 100-year-old BC particles in Kenya (Nguyen *et al.*, 2008) and dissolved BC-derived molecules in the United States (Hockaday *et al.*, 2007) were found to be significantly altered, bearing abundant carboxyl groups. The dynamics of BC mineralization during the first years after deposition to field soil have not been studied up to now.

Several studies have argued that BC might stimulate the rates of loss of non-BC soil C (Pietikäinen *et al.*, 2000; Wardle *et al.*, 2008), and proposed mechanisms for this include priming of decomposition by labile C (glucose) (Hamer *et al.*, 2004), and the sorption by BC of compounds which inhibit microbial growth, such as phenols (Gundale & DeLuca, 2007). No data have been reported that test these processes under field conditions in mineral soil.

In addition to mineralization to CO₂, BC may be transported in the landscape (Rumpel *et al.*, 2006a,b; Hockaday *et al.*, 2007; Guggenberger *et al.*, 2008) both laterally and vertically through soil. While BC has been identified in dissolved organic C (DOC) (Guggenberger *et al.*, 2008) and particulate organic C (POC) (Mitra *et al.*, 2002) of natural river water, the magnitude of leaching with percolating soil water has not been quantified. Similarly unclear is whether BC moves primarily in dissolved or particulate form. Several authors have identified surface-deposited BC in subsoils (e.g. Brodowski *et al.*, 2007; Leifeld *et al.*, 2007). Yet while the BC was found to be associated with coarse silt and sand (Brodowski *et al.*, 2007), actual mechanisms for its movement have not been established. Black C, alone or associated with mineral fractions, could move through soil by facilitated transport in macropores. Particles with a median size of 2–5 µm moved from topsoil through a sandy loam in the field (Laubel *et al.*, 1999), and natural colloids of up to 200 µm were mobilized through a coarse disturbed soil (Totsche *et al.*, 2007), also in the field. Black C found in soil has very similar size distributions, with most of the particles typically being smaller than 50 µm (Skjemstad *et al.*, 1996).

This work was undertaken to assess the fate of biomass-derived BC after addition to surface soil in the field over 2 years. Our hypotheses were: (i) CO₂ evolution will initially increase due to rapid mineralization of the labile fraction of BC; (ii) longer-term mineralization of BC over 2 years will be low due to its high stability; (iii) BC will move rapidly into the subsoil; and (iv) BC will mainly travel in dissolved form through a poorly aggregated clay Oxisol.

Materials and methods

Site characteristics

Experimental plots were established at Matazol farm in the Llanos Orientales nonflooded savanna region of Colombia (04°10'15.2"N, 07°36'12.9"W). The soil in the experimental plots is an isohyperthermic kaolinitic Typic Haplustox sandy clay loam (Soil Survey Staff, 1994), which developed from alluvial sediments originating in the Andes (Rippstein *et al.*, 2001). Long-term average annual rainfall measured approximately 200 km northeast of the plot is 2200 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. Based on stable C isotope signatures, present-day native C₄ vegetation dominated the area for a very extensive period, perhaps since the Late Glaciation Period (Behling & Hooghiemstra, 1998). Trees are found almost exclusively along waterways, except in areas where fire control has been practiced in modern times. This C₄ vegetation results in δ¹³C values for soil of –10.9 to –13.5‰ up to a depth of 2 m as measured in this experiment.

Field experiment

The BC applied to the plots was produced in a controlled manner, in order to provide sufficient amounts for a replicated experiment that included high application rates, and yielded the most uniform BC material that could be obtained under local conditions. Black C material 1 was produced in December 2004 from prunings of old mango (*Mangifera indica* L.) trees, with a resulting δ¹³C value of –29‰ (Table 1). A mound of tightly packed logs (approximately 2 m high, 5 m diameter) was formed, covered with dry grass and soil, and ignited through a tunnel at the base. The temperature in simple kilns may range between 400 and 600 °C and carbonization times typically last 48 h (Emrich, 1985). Black C was then ground by hand using a metallic disk pestle, to pass through a 0.9 mm sieve, and mixed well. Black C generated under natural fires

Table 1 Properties of BC applied to a Colombian savanna Oxisol

	BC material	
	1	2
pH (H ₂ O)	10.14	10.07
pH (KCl)	8.92	8.74
Total C (%)	71.7	63.5
$\delta^{13}\text{C}$ (‰)	-28.86	-28.20
Total N (%)	0.26	0.32
C/N	280	197
H/C	0.022	0.027
O/C	0.22	0.23
Ash (%)	8.8	12.0
Ca (mg g ⁻¹)*	2.93	6.44
Mg ($\mu\text{g g}^{-1}$)*	291	185
P ($\mu\text{g g}^{-1}$)*	259	116
K (mg g ⁻¹)*	3.30	2.61
CEC (mmol _c kg ⁻¹)	235	248

Values are averages of two analytical replicates. BC material 2 was used in the experiment to assess CO₂ losses during the first year after BC application.

*Available nutrient contents.

BC, black carbon.

(Masiello, 2004) or produced using modern technology for deliberate application as biochar (Lehmann, 2007) can have varying properties. Depending on the charred biomass type and charring conditions, chemical properties including decomposability may differ significantly (Baldock & Smernik, 2002; Antal & Grønli, 2003). The results shown here have to be viewed in the context of the BC material used (Table 1).

At the onset of the dry season in December 2004, BC was incorporated to soil under native savanna vegetation which to our knowledge had never been tilled or cropped. The fields were selected on a flat plain with no visible inclination and the slope was estimated to have been at most 2%. The site was mowed, and disked to break up the soil. A randomized complete block design was applied, with plots measuring 4 × 5 m, using three replications. Black C application rates were 0, 11.6, 23.2 and 116.1 t BC ha⁻¹ ($n = 3$). These rates correspond approximately to a 50% increase, doubling and fivefold increase in soil C in the top 0.1 m, respectively. Skjemstad *et al.* (1999a) reported a maximum, conservative estimate of BC content in Australian soils of 28 t BC ha⁻¹ (at our soil's density and application depth), and the rate of 116.1 t BC ha⁻¹ brought the soil in the range of soil organic C (SOC) stocks found in BC-rich Amazonian *Terra preta* soils (147–506 t C ha⁻¹ m⁻¹) (Glaser *et al.*, 2003). Black C was applied to each plot uniformly using rakes, and incorporated to 0.1 m with two disk harrow passes. The control plots were also disked.

Soil sampling

On 13–16 December 2006, i.e. two rainy seasons after application, soil was sampled in all plots, in depth increments of 0–0.15, 0.15–0.3, 0.3–0.6, 0.6–1.2 and 1.2–2 m. Sampling was carried out manually to 0.6 m with a ~50 mm diameter corer, and using a tractor-driven hydraulic version of the same corer to 2 m. Composite samples were taken in each plot, from five random sampling locations to 0.6 m and three of these locations to 2 m, and hand mixed in buckets before a ~500 g subsample was taken for analysis. These subsamples were air-dried, crushed and passed through an aluminum sieve with 2 mm circular holes.

Soil was analyzed for particle size distribution by the hydrometer technique (Bouyoucos, 1927), after dispersion with sodium hexametaphosphate. In July 2006, additional samples were taken for physical property analysis, using aluminum cores. In each plot, a small pit was dug to 0.3 m, and subsamples were taken from two opposite sides of pits from the surface, 0.15 and 0.3 m depths. Two cores (50 mm diameter, 50 mm high) were taken at each depth and from each side of the pits. For depths of 0.6, 1.2 and 2 m, we assumed no effect of BC application on physical properties and two soil pits located 5–10 m away from the experiment were used. In each of these pits, cores were taken from two profiles on the side closest to the experiment. This yielded a total of four samples for each sampling depth.

Bulk density was determined by oven drying at 105 °C for 24 h for samples from all plots and depths (84 samples). Samples to 0.3 m depth from the control and 23.2 t BC ha⁻¹ treatments were used to determine saturated hydraulic conductivity with a constant head permeameter. Abnormally high saturated hydraulic conductivity data for one of the control plots, at 0.3 m, was removed before statistical analysis due to the observation of high termite activity in that plot and depth.

Carbon leaching measurement

In May 2005, free-draining lysimeters for measuring POC and DOC in water moving by saturated flow were installed in the unamended control and the plots receiving 23.2 t BC ha⁻¹. These were inserted from soil pits at depths of 0.15 and 0.3 m, in 'galleries' dug from the face of the pits and into the experimental plots. The lysimeters consisted of 0.15 m diameter Pyrex[®] (Corning Inc., Corning, NY, USA), glass funnels filled with quartz sand after washing with dilute HCl and NaOH, held by a glass wool plug. The C content of the sand after washing was 0.04% by weight. Two funnels were placed at each depth in each plot. Funnel pairs were

fitted with plasticizer-free Tygon[®] (St-Gobain Performance Plastics, Akron, OH, USA) (Formula 2075) hose and the hoses joined with copper 'T' fitting, itself draining into one amber glass bottle (washed as described above). This yielded a total of 24 funnels and 12 collection bottles (1 per depth per plot). Field collection bottles were checked at least weekly, and emptied when water had been collected. After each emptying of bottles, a solution of HgCl₂ was added as a biocide to achieve a final concentration of 30 µM in a 1-L sample. Water sampling was carried out between May 2005 and January 2006 (year 1), and March and December 2006 (year 2). At each collection time, the height of water in the bottles was recorded and converted into volume using a curve created with the bottles. Upon collection, water samples were stored in borosilicate glass vials with Teflon[®]-lined caps and refrigerated at 4 °C until analyzed. Samples were not refrigerated for 3–5 days while being shipped to the United States.

Depending on sample availability, 40–60 mL of each water sample was vacuum filtered using glazed ceramic Buchner funnels through binder-free glass filters (Whatman[®], Whatman plc, Kent, ME, USA, GF/F; 13 mm diameter, 0.7 µm pore size), which were then dried at 60 °C for 24–36 h, cut up, and placed in tin cups for C and N analysis by dry combustion. Filtered water samples were freeze-dried in progressively smaller glass vials, and the solids weighed and prepared for C and N analysis by dry combustion. In the present study, we used 0.7 µm to separate DOC from POC. However, we recognize that this separation is operational and that some colloids may have sizes of <0.7 µm.

For the calculation of total C leaching, the flux in each lysimeter was multiplied by the C concentration in the sample. On two dates no samples were available for analysis for the control due to sample loss. For one of these dates the value was calculated as the average of the two adjacent dates, since these were very similar. In the other case, the date was dropped completely since no assumption of similarity could be made.

Soil respiration measurement

Static-chamber soda lime traps (after Edwards, 1982) were used in order to determine the amount and isotopic composition of soil-respired CO₂. Plastic rings obtained from cutting 20-L buckets (0.273 m diameter) were buried into the soil to a depth of 0.1 m and measurements started in the second year after BC application on April 6 2006. To discern the short-term response of respiration during the first year after BC addition, a second set of rings was installed on 11 May 2006 on an adjacent area, and identically treated using BC material 2 which was produced similarly to material

1, except a soil trench was used instead of a mound (Table 1). In both sets of plots, two rings were inserted at random locations away from the edges inside each replicate plot of the 23.2 t BC ha⁻¹ and control treatments, for a total of 24. The soil inside the rings was kept free of vegetation. Initially, 30 g of four to eight mesh soda lime with indicator were exposed in each chamber, based on recommendations from Edwards (1982). After 5 weekly trials, the amount of soda lime was reduced to 10 g, since CO₂ absorption did not exceed 10% of the saturation value for this amount of soda lime (as specified by the manufacturer). The highest mass of CO₂ absorbed in a single trial represented 11% of the mass of soda lime used. Before field exposure, soda lime was dried in wide-mouth (44 mm) glass jars for 24 h at 105 °C, capped tightly, cooled and then weighed on a scale with 1 mg resolution. Uncapped jars ('traps') were placed on elevated pieces of wire mesh, on the soil inside each ring. Chamber tops were formed from the rest of the 20 L plastic buckets, sealed using a thick, tight rubber band covering the junction. Control traps were placed in the plots, in chambers of the same internal volume as the treatment chambers. However, they consisted of two bucket bottoms sealed together, i.e. no soil was exposed. Initially, one control trap was used in each plot (total 12 control traps), but after observing low variability among control traps, their number was reduced to six for the entire experiment. Sampling frequency was initially weekly, but was reduced to biweekly halfway into the rainy season.

The soda lime was left in the field for 24 h, removed and dried again for 24 h as above. Final mass was obtained and the difference between initial and final mass multiplied by 1.69 to correct for chemical water generation during the process of CO₂ absorption (Grogan, 1998). Control traps account for CO₂ absorbed during drying, manipulation, from the initial atmosphere inside the chamber and any additional CO₂ contributed by leaks in chamber seals. Absorbed CO₂ mass for the controls were averaged, and this average value subtracted from absorbed CO₂ mass in each treatment jar. The maximum standard error observed among control traps was 17% for the duration of the experiment. Trapped CO₂ mass was further corrected for time of exposure, which differed from 24 h by a maximum of 74 min over the duration of measurements.

The amount of CO₂ trapped depended in part on the diameter of the jars used to expose the soda lime. On four occasions it was necessary to use jars of different mouth size. To correct for this difference, a relationship was established between mouth size and CO₂ trapped by exposing jars of various sizes (30–44 mm mouth diameter) to ambient air for approximately 60 h. This trial was repeated four times and conversion factors averaged.

Exposed soda lime jars were sealed with Teflon[®] tape and stored in sealed drums with silica gel to absorb humidity. Samples were later composited into periods defined by peaks in amount of CO₂ absorbed over time (Fig. 4). All samples for dates within individual peak absorption periods were combined, mixed, and a subsample ground for 90 s by hand using a mortar and pestle. For the first and last sampling dates, subsamples were combined but replicates and controls were analyzed separately, to provide more detailed data as well as information on variability. Approximately 0.2 g of ground composited soda lime was placed into acid-washed glass tubes, which were then sealed and evacuated. Three milliliters of phosphoric acid (40%) were added, and the tubes were set on an orbital shaker for 1 h. The headspace gas was then sampled using a syringe and transferred to evacuated single-use tubes.

Plant biomass sampling

Plant biomass was sampled on 19 October 2006, where all aboveground vegetation inside two 1-m² quadrats was sampled in three replicated plots of the control and 23.2 t BC ha⁻¹, on the new set of plots used for first year soda lime measurements. Vegetation was separated into grasses, forbs and legumes, and fresh and dry mass was determined after drying at 65 °C for 72 h.

Analytical procedures

Air-dried BC and soil were ground using a ball grinder (Oscillating Mill MM400 by Retsch, Newtown, PA, USA). Carbon and N contents and isotope ratios were determined by combustion on an isotope ratio mass spectrometer (IRMS; Europa Hydra 20/20 by Europa Scientific, Crewe, UK) for solid samples, and gas on a GC-C-IRMS (Europa Geo 20/20-Orchid by Europa Scientific). The H content of BC was measured by combustion on an oxygen analyzer (PDZ Europa 20-20, Heckatech HT by Europa Scientific). Ash content was measured according to ASTM (2007). To measure pH, BC was mixed with either water or 1 N KCl in a 1:10 mass:volume ratio, stirred three times over 1 h and the pH was read with a gel epoxy electrode (Symphony by VWR, West Chester, PA, USA). Cation exchange capacity (CEC) of BC was determined by double extraction with 1 N ammonium acetate at pH 7, flushing with isopropyl alcohol followed by double 2 N KCl extraction. The ammonium content of the KCl extract was determined colorimetrically using a Technicon[®] flow analyzer (Technicon Corporation) and Nessler's reagent (Naude, 1927). Available nutrients were extracted using 2.5 g BC and 25 mL Mehlich III solution (Mehlich, 1984), followed by shaking for 5 min

and filtering. Nutrients (K, Ca, Mg, P) were analyzed by ICP atomic emission spectrometry (IRIS Intrepid by Thermo Elemental, Franklin, MA, USA).

Calculations and statistical analyses

The amount of C contributed by BC and soil in samples was calculated as follows:

$$\delta^{13}\text{C}_{A+B}(A+B) = \delta^{13}\text{C}_A A + \delta^{13}\text{C}_B B, \quad (1)$$

where $\delta^{13}\text{C}_A$ is the $\delta^{13}\text{C}$ of corresponding control soil within field replicate, $\delta^{13}\text{C}_B$ the $\delta^{13}\text{C}$ of BC, $\delta^{13}\text{C}_{A+B}$ the $\delta^{13}\text{C}$ of field sample, A the amount of C derived from C₄ sources (soil-C), B the amount of C from BC, $A+B$ is the total amount of C in field sample.

When no corresponding control was available for a specific sample, the average $\delta^{13}\text{C}$ of controls for that date was used. When no controls were available for a specific date, the average $\delta^{13}\text{C}$ of controls at the closest date was used. It is recognized that end members may not necessarily contribute C with isotopic values that are identical to the bulk $\delta^{13}\text{C}$. For example, the easily mineralizable or leachable fraction of BC may have a different $\delta^{13}\text{C}$ than the total BC. This could be due to the fact that lignin is typically depleted in ¹³C compared with other plant compounds (Benner *et al.*, 1987) and greater BC yields from lignin than from cellulose or hemicellulose (Yang *et al.*, 2007). However, C isotope ratios have not been found to change with increasing charring temperature of C₃ plants (Krull *et al.*, 2003) suggesting that labile and stable BC fractions have similar $\delta^{13}\text{C}$ values compared with the large differences between the C₃-derived BC and the C₄ vegetation.

Statistical analyses were conducted using the general linear model procedure of SAS (SAS Institute Inc., (2003) SAS version 9.1 for Windows, Cary NC), and means separated using the *t*-test at $\alpha = 0.05$.

Results

Soil

The highest rate of BC application (116.1 t BC ha⁻¹) reduced soil bulk density at the surface and 0.15 m depths ($P < 0.05$) (Fig. 1). Also, BC application significantly increased saturated hydraulic conductivity at the surface from 2.7 to 13.4 cm h⁻¹ in the control and 23.2 t BC ha⁻¹ application rate, respectively (data not shown).

Soil C contents were greater in plots receiving greater amounts of BC (Fig. 2), although only the highest BC application rate resulted in a significant difference from the control ($P < 0.05$) at 0–0.15 m depth. For the 0.15–0.3 m depth increment, both the 23.2 and 116.1 t BC ha⁻¹ rates had significantly more total C than

the control ($P < 0.05$, $n = 3$). Black C was found mostly in the surface layer which comprised the application depth with the highest application rate producing a significantly greater BC stock than others ($P < 0.05$, $n = 3$). Small amounts of applied BC were also found in the 0.15–0.3 m depth increment, with the high application rate (116.1 t ha⁻¹) always resulting in significantly greater ($P < 0.05$) BC stocks than the control (Fig. 2). When controlling for bulk density, the non-BC stock was greater in the high BC application rate than the control at both the 0–0.15 and 0.15–0.3 m depths, after 2 years (Fig. 2). The concentration of non-BC was greater with all BC application rates ($P < 0.05$) at 0–0.15 m (6.48, 8.01, 7.81 and 10.25 mg soil C g soil⁻¹ for 0, 11.6, 23.2 and 116.1 t BC ha⁻¹ applied, respectively). Only the highest rate significantly increased non-BC content at 0.15–0.3 m, from 4.60 to 6.46 mg soil C g soil⁻¹ ($P < 0.05$).

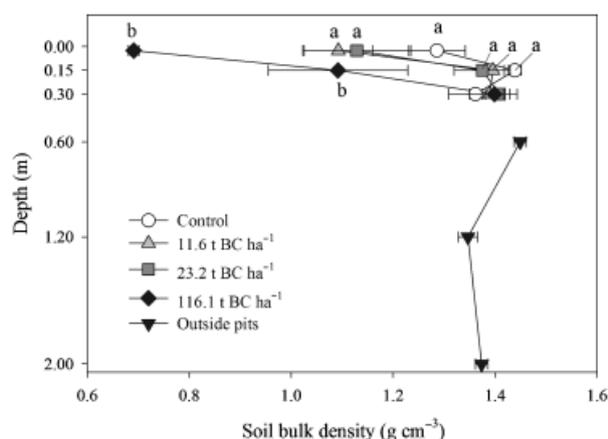


Fig. 1 Bulk density of a Colombian savanna Oxisol, 18 months after BC incorporation to 0.1 m (\pm SE, $n = 6$ to 0.3 m depth, and $n = 4$ below 0.3 m). Significant differences ($P < 0.05$) within a single depth are represented by different letters.

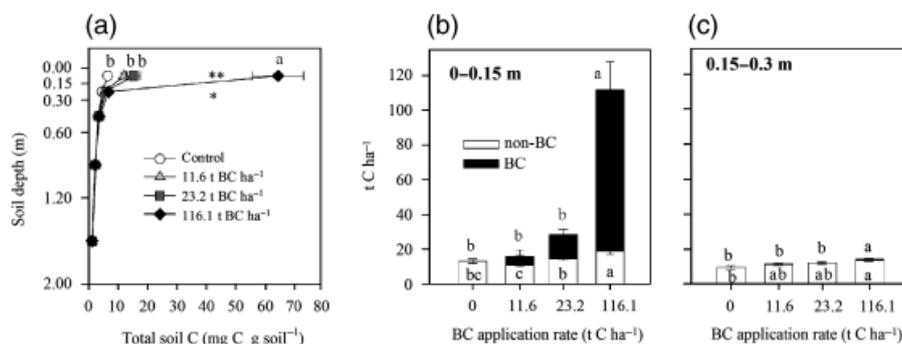


Fig. 2 Total soil C concentration (a) and C stocks from soil and BC (b and c), two rainy seasons after BC application to a Colombian savanna Oxisol under natural vegetation (\pm SE, $n = 3$). Significant differences within a single depth are represented by different lower-case letters (significant differences in total C at 0.3 m not shown), and significant main effects are indicated by ** $P < 0.01$ and * $P < 0.05$. Letters showing differences in BC content in (b) and (c) are placed above bars. Points in (a) are placed at the center of the depth increment they represent.

Plant biomass

Total aboveground plant biomass measured 5 months after biochar application increased by 189% when 23.2 t BC ha⁻¹ was applied. Grasses, forbs and legumes on BC amended plots had 93, 292 and 1916% greater biomass, respectively, than on plots without BC application ($P < 0.05$). The proportions of forbs and legumes were also greater when BC was applied (Table 2).

Biomass was not measured in year 2, however, it was observed in the second-year plot that vegetation composition had greater similarity to that which predominates in the region and which covered the plots before establishment. Grasses dominated and forbs were not as prominent, with or without BC application, than when sampling was carried out at 5 months.

Carbon leaching

The concentration of POC in water was greater at both 0.15 and 0.3 m ($P < 0.0001$ and < 0.005 , respectively) in fields with 23.2 t BC ha⁻¹ than those without BC additions. Results were similar for the total flux of POC

Table 2 Amount and proportion of above-ground biomass of spontaneous vegetation sampled on a control and BC-amended (23.2 t C ha⁻¹) Colombian savanna Oxisol

	Dry matter (t ha ⁻¹)		Proportion of total (%)	
	-BC	+ BC	-BC	+ BC
Grasses	1.13	2.19	69	46
Forbs	0.47	1.86	29	39
Legumes	0.04	0.71	2	15
Total	1.64	4.75	100	100

BC, black carbon.

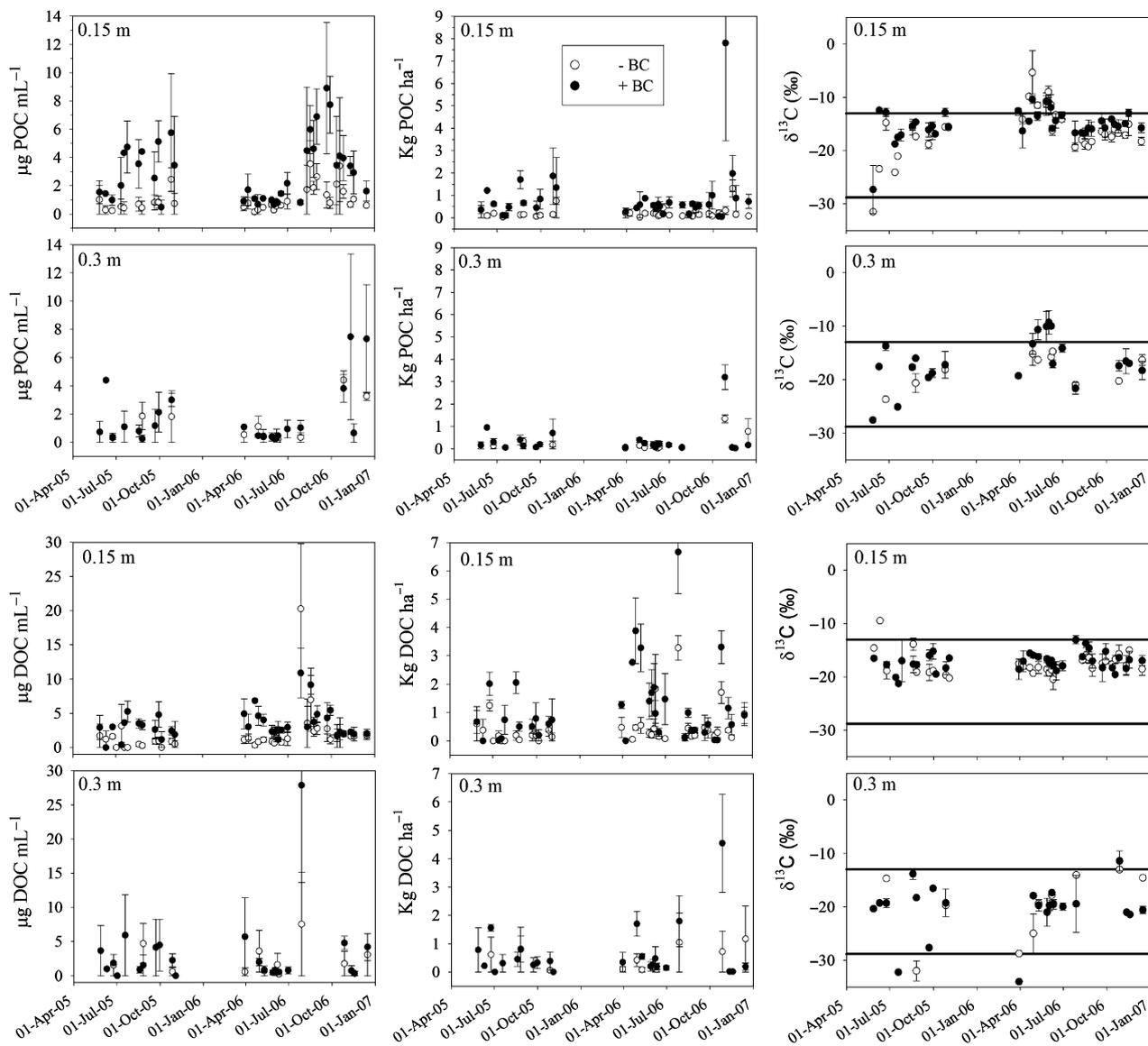


Fig. 3 Concentration (left), total amount (center) and $\delta^{13}\text{C}$ values (right) of POC (top) and DOC (bottom) leached over two years in free-draining lysimeters placed at 0.15 and 0.3 m depth, either with (+ BC, 23.2 t C ha^{-1}) or without BC addition (-BC) to a Colombian savanna *Oxisol* under natural vegetation (\pm SE, $n = 1, 2$ or 3 depending on whether samples were collected for all replicates in the field, and whether samples were lost during transportation or storage). In the $\delta^{13}\text{C}$ panels, the upper reference line corresponds to the $\delta^{13}\text{C}$ value of the soil and the lower line to the $\delta^{13}\text{C}$ value of BC.

leached ($P < 0.005$ at both depths) (Fig. 3). Cumulatively, 317% and 267% more POC was leached at 0.15 and 0.3 m, respectively, when BC was applied (only $23.2 \text{ t BC ha}^{-1}$ was investigated for leaching in comparison with the control). At 0.15 m, both the volume-weighted average POC concentration and total flux of POC leached were greater with BC addition, while at 0.3 m the volume-weighted concentration of POC was not significantly affected by BC additions. Greater water flux therefore explains the increase in total POC leached only at 0.3 m (Table 3). Volume-weighted $\delta^{13}\text{C}$ values for POC were not significantly different between treat-

ments at 0.15 m. However, at 0.3 m, BC additions resulted in significantly higher volume-weighted $\delta^{13}\text{C}$ values. Calculated amounts of BC-derived POC leached were low (Table 3), corresponding to $< 1\%$ of applied BC after 2 years. Black C application led to greater amounts of non-BC-derived POC leached ($P < 0.05$), corresponding to increases by 308% and 254% at 0.15 and 0.3 m, respectively over control plots.

Similar trends were observed for DOC, with cumulatively 158% and 199% more DOC and 131% and 122% more non-BC-derived DOC leached 0.15 and 0.3 m, respectively, when BC was applied as compared with

Table 3 Total amounts and volume-weighted average concentrations of C leached over 2 years as POC and DOC, at 0.15 and 0.3 m depths on a Colombian savanna Oxisol

Depth (m)	Volume-weighted averages		Total amounts					BC-induced increase in non-BC leaching (kg C ha ⁻¹ yr ⁻¹)*
	Total C conc. (µg C mL ⁻¹)	δ ¹³ C (‰)	C leached (kg C ha ⁻¹)	Proportion from soil (%)	Proportion from BC (%)	Prop. of applied BC (%)	BC leaching rate (kg C ha ⁻¹ yr ⁻¹)*	
0.15								
POC								
-BC	0.91b	-15.87a	7.3b	100a	0b	0	0b	0b
+BC	2.50a	-13.91a	30.2a	98.1b	1.9a	0.003	0.32a	12.2a
DOC								
-BC	2.21b	-17.57a	16.8b	100a	0b	0	0b	0b
+BC	5.73a	-16.69a	43.2a	89.4b	10.6a	0.020	2.49a	11.9a
0.3								
POC								
-BC	2.04a	-16.86a	2.2b	100a	0b	0	0b	0b
+BC	1.39a	-14.95b	8.0a	96.6b	3.4a	0.001	0.15a	3.0a
DOC								
-BC	5.02a	-18.39a	5.2b	100a	0b	0	0b	0b
+BC	2.68b	-17.91a	15.5a	74.3b	25.7a	0.017	2.16a	3.4a

Different letters represent significant differences ($P < 0.05$) between control (-BC) and BC-amended (+BC) soil.

*Sampling was carried out over two rainy seasons and one dry season. To generate this estimate, a second dry season was assumed to last the same number of days as the season sampled.

BC, Black carbon; DOC, dissolved organic C; POC, particulate organic C.

nonamended plots. However, both volume-weighted concentrations and total amounts of DOC (in both treatments) were generally substantially greater than for POC. Also, this trend was much stronger when BC had not been applied and the relative increase of POC leaching was greater than that of DOC after BC addition. Thus, the ratio of total DOC-to-total POC was 1.43 and 2.31 at 0.15 m with and without BC addition, respectively. At 0.3 m, these ratios were 1.93 and 2.37, respectively. The amount of C in DOC originating from BC was 680% greater at 0.15 m and 1342% greater at 0.3 m than that in POC, while absolute amounts of BC-induced increases in leached non-BC were similar in DOC and POC at both depths (Table 3).

Soil respiration

The amount of C respired followed similar trends over time in both treatments but was consistently greater ($P < 0.05$) when BC was added, during both the first and second year after BC application (Fig. 4; only 23.2 t BC ha⁻¹ was investigated in comparison with the control). Yet overall respiration rates were greater in the first than the second year. Cumulatively, 41% and 18% more C was respired when BC was applied, as compared

with the nonamended control, in the first and second year, respectively (Table 4).

A small percentage of respired C originated from applied BC ($P < 0.05$) (Table 4). For the two dates where replicate samples of CO₂ were analyzed, no significant difference ($P > 0.05$) in δ¹³C was found between the control and BC-amended soil. However, BC addition resulted in a 25% increase in non-BC respired ($P < 0.05$). This increase was greater in the first year after application (40%) than the second (6%).

Overall, the most important fate of C originating from BC directly measured here was respiration (Table 5). The proportion which was mobilized by water was two (DOC) to three (POC) orders of magnitude lower. Increases in non-BC losses were also greatest for respiration, and again between two and three orders of magnitude greater than for DOC and POC, respectively.

Discussion

Vertical movement of total C and BC in soil

After 2 years, only a small proportion of soil-applied BC had moved below the 0.1 m application depth into the 0.15–0.3 m sampling depth. Leifeld *et al.* (2007) observed

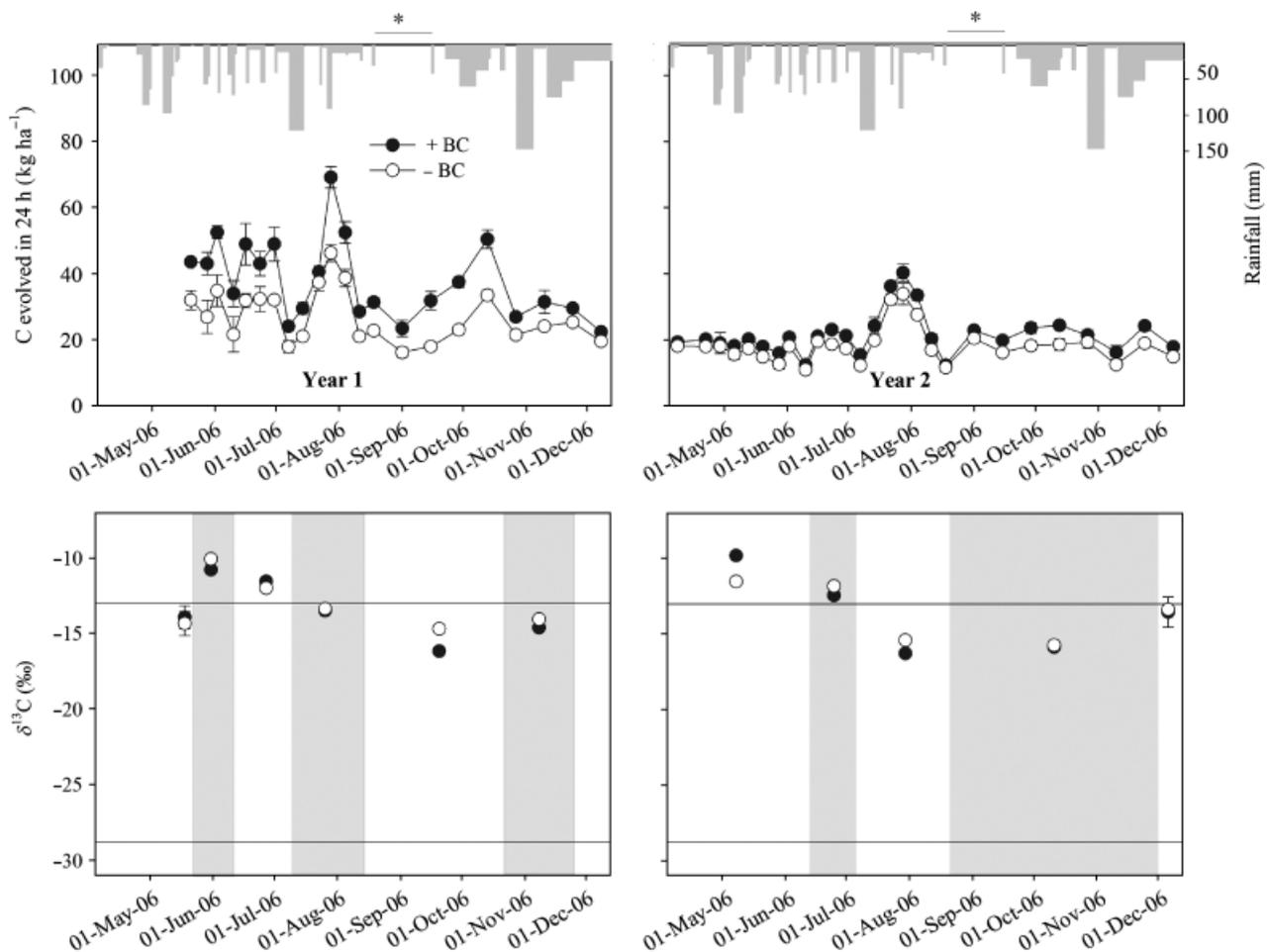


Fig. 4 Amount of C respired and $\delta^{13}\text{C}$ from a Colombian savanna Oxisol, measured using soda lime traps (\pm SE, $n = 6$ for amounts of C). Years 1 and 2 were sampled from different plots. Average rainfall collected over irregular time periods is shown with bars and given per day. For $\delta^{13}\text{C}$, all samples within chosen intervals (shaded and white areas) were composited, and replicates were analyzed separately only on the first date of year 1 and the last date of year 2 (\pm SE, $n = 3$). The upper reference line corresponds to the $\delta^{13}\text{C}$ value of the soil and the lower line to the value for BC. *Missing rainfall data.

BC migration rates of 630–1160 mm yr⁻¹, where 21–69% of BC migrated below the incorporation depth of 0.3 m, down to a maximum of 1.40 m over a maximum of 95 years in peat soils with very low bulk density. In our sandy Oxisol, BC traveled from 0.1 to 0.3 m with water as both POC and DOC at the first collection date after BC application and the onset of the rainy season. For the 23.2 t BC ha⁻¹ application rate, 4.25 kg BC ha⁻¹ (0.02% of applied amount) over 2 years moved below 0.3 m depth as POC and DOC (from Table 3), while 103.4 kg BC ha⁻¹ (0.45% of applied amount) was found in soil between 0.15 and 0.3 m (Fig. 2). Black C was thus retained by the mineral subsoil.

We suspect that bioturbation could have been additionally involved in BC movement below 0.15 m. Surface-applied lime was incorporated into an acidic Australian soil by earthworms to a depth of 0.15 m

(Chan *et al.*, 2004), and earthworm burrows were observed in our plots in cores from the 0.6–1.2 m depth increment, where the inside of the burrow was much darker in color than the surrounding soil. Termites were also observed to be active on experimental plots.

At 0–0.15 m, BC stocks after 2 years were 53%, 41% and 20% less than applied amounts of 11.6, 23.2 and 116.1 t BC ha⁻¹, respectively, and leaching below 0.15 m accounts for a movement of 0.02% of applied BC at the 23.2 t ha⁻¹ rate. Given that respiration accounted for a 2.2% loss, and that much smaller proportions were found in the soil between 0.15 and 0.3 m or leached below 0.3 m, a large proportion of applied BC may have been lost by surface runoff. This represents the largest BC flux in this study. Shortly after application, biochar might have been hydrophobic (Knicker *et al.*, 2007), which could have facilitated runoff during intense rain

Table 4 Total C respired over 2 years from a Colombian savanna Oxisol, measured using soda lime traps during the rainy season only

Total amounts							Volume-weighted average
	Total respired C (t ha ⁻¹)	Respired BC (kg ha ⁻¹)	Prop. of C as BC (%)	Prop. of applied BC respired (%)	BC respiration rate (kg ha ⁻¹ yr ⁻¹)*	BC-induced increase in non-BC respiration (t ha ⁻¹ yr ⁻¹)*	δ ¹³ C (‰)
-BC	9.97b	0b	0b	0b	0b	0b	-13.76a
+BC	13.03a	513.8a	3.94a	2.21a	377.0a	1.82a	-14.08a

Years 1 and 2 were sampled from different plots. Different letters represent significant differences ($P < 0.05$) between control (-BC) and BC-amended (+BC). Data were extrapolated from 24 h soda lime assays, with assay dates taken as center points of time intervals between assays.

*To generate these estimates, the respired amounts for the day with lowest measured respiration in each rainy season were used to estimate respiration for the duration of the dry season. Respired BC was estimated using the average proportion of BC respired for each year. The dry season was taken to last the same number of days in 2006 as in 2005 and was defined as ending on the first day when free-draining water was collected in March.

BC, Black carbon.

Table 5 Fate of soil-applied BC, 2 years after application to soil (including dry seasons). Losses of BC by surface runoff were not measured and are excluded

Flux type	Total flux over 2 years (kg C ha ⁻¹)	Proportion of total flux (%)	Rate (kg ha ⁻¹ yr ⁻¹)	Proportion of applied BC (%)	BC-induced increase in non-BC flux (kg ha ⁻¹ yr ⁻¹)	Net effect on C stocks (t C ha ⁻¹)*
Respired as CO ₂	751.9	98.8	377.0	3.241	1818.0	+ 22.80
<i>Leached below 0.15 m</i>						
As POC	0.586	0.08	0.32	0.003	12.18	
As DOC	4.580	0.60	2.49	0.020	11.90	
Total	5.166	0.68	2.81	0.023	24.08	+ 24.55
<i>Leached below 0.3 m</i>						
As POC	0.276	0.04	0.15	0.001	3.03	
As DOC	3.978	0.32	2.16	0.017	3.44	
Total	4.254	0.52	2.31	0.018	6.47	+ 2.56
Total	761.32	100.00		3.282		
Net for respiration and leaching to 0.3 m						+ 22.79

*For each line, the BC-induced 'loss' of non-BC was added to the amount of BC lost, and this was subtracted from the C added as BC (23.2 t ha⁻¹) and additional non-BC as found in soil samples (Fig. 2). For respiration the depth increment used was 0–0.3 m.

BC, Black carbon.

events. On steep slopes in Laos, surface-deposited BC was preferentially eroded in comparison with other types of soil organic matter due to its lack of association with minerals shortly after deposition, its light nature and the fact that it did not significantly degrade during transport (Rumpel *et al.*, 2006a). Guggenberger *et al.* (2008) also found a larger proportion of BC from vegetation fire exported by stream water than non-BC in a tundra catchment. A total export of 1 kg BC ha⁻¹ yr⁻¹ was observed, where 0.22 to 34.4 t BC ha⁻¹ was stored in catchment soil and uniformly distributed to a depth of 1 m. In contrast to runoff, transfer of BC between plots

likely did not occur in our study, since the δ¹³C of surface soil in control plots did not change according to the direction of runoff on the field.

Lower bulk density, improved saturated hydraulic conductivity and water infiltration at the surface (Fig. 1) resulted in greater water flux at both depths when BC was added. Consequently, at 0.15 m the increase in total amounts of leached C after BC additions was proportionally greater than the increase in the volume-weighted concentration of POC as well as DOC (Table 3). At 0.3 m, volume-weighted C concentrations were lower when BC was applied, but total C leached was

still greater with BC addition for both POC and DOC. This implies that greater water flux was solely responsible for the increase in total C leached at 0.3 m. DOC concentrations found at 0.15 m (mean = 2.6 mg L⁻¹) in our study are in the range of those found at 0.1 m below an Oxisol in a Brazilian Amazon forest (mean = approximately 7 mg L⁻¹) (Johnson *et al.*, 2006).

The proportion of BC in DOC was much greater than BC in POC (Table 3). This suggests that BC preferentially travels as colloidal particles <0.7 µm, or as by-products of BC decomposition and/or weathering. On the other hand, leaching of non-BC as a result of BC additions increased 3.5–4.1 times for POC, but only 2.3–3.1 times for DOC (Table 3). The reason may lie in the adsorptivity of BC. Black C sorbs a wide range of organic compounds found in soils such as phenols (Gundale & DeLuca, 2007), pesticides (Yu *et al.*, 2006), glucose and DOC from birch leaf extract (Pietikäinen *et al.*, 2000).

Black C effect on C cycling

The increase in respired C was mostly not related to BC, but rather to non-BC respiration (Table 4). Still, soil respiration accounted for an overwhelmingly greater proportion of BC flux than movement with water (Table 5). Black C may preferentially harbor microorganisms in its highly porous structure (Pietikäinen *et al.*, 2000), and these are active as demonstrated by greater basal respiration with BC than with pumice (Pietikäinen *et al.*, 2000) and by greater substrate-induced respiration by BC addition to forest humus (Wardle *et al.*, 2008), in laboratory incubation studies. However, Steiner *et al.* (2004) found no difference in basal or substrate-induced respiration in the laboratory, when BC was added to either a control or synthetically fertilized Oxisol. Our results show that despite greater soil C:N ratios with BC additions (26.1 vs. 14.8 with and without BC, respectively), soil respiration increased. Possible reasons are (i) a greater amount of biomass production and hence mineralization of plant litter; (ii) possibly a larger microbial population in soils that received BC; or (iii) greater root respiration. The latter was partly captured here despite rings being kept free of vegetation, since they were only inserted to 0.1 m. The increase in non-BC respired with BC application was greater in the first year than the second year, and this may indicate that BC's stimulatory effect on soil and/or plant respiration tapers off during the first years after application.

Black C application resulted in greater amounts of non-BC in soil. This follows from greater plant biomass production. A literature review by Lehmann & Rondon (2006) found that plant biomass increased by up to

230% with BC application in 24 experiments using 10 different crops, when compared with optimally managed controls not receiving BC. Greater plant productivity and consequently greater root and leaf turnover and microbial activity likely led to greater POC and DOC leaching with BC application, and explain the observed increase in non-BC cycling and non-BC soil stocks. Induced increases were greatest, in absolute terms, for respired C and this is in agreement with the explanation that greater non-BC fluxes with BC occurred through increased plant biomass, with associated increases in both heterotrophic and autotrophic respiration. Trujillo *et al.* (2006) estimated belowground net primary productivity to 0.5 m of mature savanna vegetation at 12.5 t ha⁻¹ yr⁻¹ (5.0 t C ha⁻¹ yr⁻¹ with 41% C in roots) on the same farm where this work was carried out, using the compartment-flow model. The calculated additional C input through root turnover after BC application would represent 29 t C ha⁻¹ over 2 years, assuming that our measured increases in aboveground biomass (Table 2) translate into similar increases belowground. This amount is greater than the sum of the additional non-BC respired (1.82 t C ha⁻¹), leached below 0.3 m (0.007 t C ha⁻¹), and of additional non-BC in soil accrued to 0.3 m (3.98 t ha⁻¹) over 2 years. Thus, greater biomass production alone can explain the observed increases in non-BC fluxes, and BC-induced increased fluxes of native soil organic C is unlikely the cause.

Wardle *et al.* (2008) observed that the addition of BC to litterbags containing boreal forest humus resulted in greater humus-C loss than expected from the loss of the components taken separately. Hamer *et al.* (2004) also found that BC enhanced the degradation of glucose in laboratory incubation studies. Our findings show the opposite, where applying BC to soil leads to greater non-BC content. The effect of BC on plant biomass and available substrates is not accounted for in data by Wardle *et al.* (2008), since the litter bags necessarily exclude BC-stimulated plant C input. Physical export of C might also have been attributed to C mineralization, since mineral surfaces are expected to retain leached C and this would not be the case in the organic layer of the forest floor (Lehmann & Sohi, 2008). In addition, the experiment by Hamer *et al.* (2004) did not include plants. Our results represent the net effect of BC on the soil and plants.

Black C stability and implications for biochar soil management and C sequestration

The considerable proportion of BC which may have been lost by surface erosion with water could accumulate in depressions, travel mostly as sediment in waterways, potentially to the deep ocean where BC

remains stable for thousands of years (Masiello & Druffel, 1998).

DOC and POC leached are likely to be adsorbed in subsoils, and thus become even more stable than topsoil C. DOC concentrations in temperate and arctic forests decreased sharply as soil solution moved through mineral soil (Qualls & Haines, 1992; Guggenberger & Zech, 1994). Experimental evidence suggests that organic molecules such as plant-derived carbohydrates and lignins (Guggenberger & Zech, 1994) are mainly retained abiotically by the soil matrix (Qualls & Haines, 1992), and subsequently degraded *in situ* by microorganisms. Sorption of organic C to soil minerals is enhanced by the presence of Al and Fe oxides (Kaiser *et al.*, 1996) which are abundant in Oxisols. Indeed, organic C below 0.6 m in a temperate grassland soil was >2000 years old, and had a residence time eight times greater than C found at the surface (Fontaine *et al.*, 2007). The small amounts of leached BC observed here are also expected to sorb to the mineral matrix in the subsoil.

Over 2 years, we calculated that <3% of applied BC had been respired, of which 75% occurred during the first year. As time passes and labile BC fractions are mineralized, respiration of BC is likely to decrease even further. Using a first-order decay model with two pools, the mean residence time (MRT) of the BC obtained from isotope recovery calculated to 600 years ($r^2 = 0.928$; $n = 12$). When normalized to the same mean annual temperature of 10 °C (from 26 °C using a Q_{10} of 3.4 from Cheng *et al.*, 2008b) the resulting MRT of 3264 years is in the same order of magnitude as that from laboratory incubation studies of similar duration using soils from charcoal storage sites (1335 years, Cheng *et al.*, 2008b), Amazonian Dark Earths (4035 years, calculated from Liang *et al.*, 2008), or fresh ryegrass BC (2000 years, Kuzyakov *et al.*, 2009). Modeling to long-term equilibrium yielded slightly longer MRT of 1300 and 2600 years for BC from savanna fires in Australia at a similar mean annual temperature of 27 °C (Lehmann *et al.*, 2008). In addition to the degree of aging and the environmental conditions, however, also the production conditions have to be considered when comparing BC decomposition rates, for which little information is available to date.

Conclusions

Less than 3% of the applied BC was lost by CO₂ evolution, with a calculated MRT of 600 years at 26 °C mean annual temperature (3264 years at 10 °C). Since 75% of the BC losses by mineralization occurred over the course of the first year, we expect that such losses will decrease even further with time as the labile BC fraction is mineralized. These low respiration losses

suggest high stability of BC in soils, which confirms the role that BC plays as a C sink in the global C cycle. When linked to sustainable and renewable feedstock production, it also affirms the validity of exploring purposeful application of BC to soils as a sink enhancement of stable SOC. We did not find evidence for an enhanced loss of existing SOC due to addition of BC, but rather greater amounts of non-BC in soil, leachate and respired C explainable by greater plant productivity. In addition to higher plant productivity, greater POC and DOC leaching could also be explained by a greater water flux through soil due to influences of BC on soil structure. Black C additions therefore had effects on both soil and plant C dynamics.

The suspected physical export of BC was significantly greater than mineralization, with most of the BC likely being moved by surface erosion. This potentially large translocation of BC in the landscape must be recognized and losses of BC from soil cannot be interpreted solely as mineralization. We cannot provide information about whether the leached or eroded BC is mineralized to a greater or lesser extent during transport or after accumulation. Since erosion fluxes were estimated to be a significant portion of the total loss, the fate and the effects of BC moving laterally in the landscape warrant further investigation.

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