REGULAR ARTICLE

Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol

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Abstract The application of biochar (biomass-derived black carbon) to soil has been shown to improve crop yields, but the reasons for this are often not clearly demonstrated. Here, we studied the effect of a single application of 0, 8 and 20 t ha^{-1} of biochar to a Colombian savanna Oxisol for 4 years (2003–2006),

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Present Address: D. Molina Centro de Investigaciones en Palma de Aceite, cra 42 # 33-07, Villavicencio, Colombia under a maize-soybean rotation. Soil sampling to 30 cm was carried out after maize harvest in all years but 2005, maize tissue samples were collected and crop biomass was measured at harvest. Maize grain yield did not significantly increase in the first year, but increases in the 20 t ha⁻¹ plots over the control were 28, 30 and 140% for 2004, 2005 and 2006, respectively. The availability of nutrients such as Ca and Mg was greater with biochar, and crop tissue analyses showed that Ca and Mg were limiting in this system. Soil pH increased, and exchangeable acidity showed a decreasing trend with biochar application. We attribute the greater crop yield and nutrient uptake primarily to the 77–320% greater available Ca and Mg in soil where biochar was applied.

Keywords Biochar · Colombia · Crop yield · Exchangeable acidity · Maize · Oxisol · Tropical savannas

Introduction

Soil fertility in high-rainfall, low-altitude regions of the tropics can be low due to rapid organic matter mineralization (Jenkinson and Ayanaba 1977), and the presence of highly weathered secondary minerals (van Wambeke 1992). However, fertility can be successfully improved using both inorganic and organic fertilizers. The major drawbacks of inorganic fertilizers are their low accessibility to resource-poor farmers (Garrity 2004) and their low efficiency in highly weathered soils (Baligar and Bennett 1986). While organic fertilizers are able to improve nutrient use efficiency, under tropical conditions they mineralize rapidly in soil and benefits through increases in organic matter last only for a few growing seasons (Bol et al. 2000; Diels et al. 2004; Tiessen et al. 1994). In contrast, biomass-derived black carbon (C), or biochar, is much more stable. While biochar must eventually mineralize in soil (Goldberg 1985; Schmidt and Noack 2000), a fraction remains in a very stable form with a ¹⁴C age greater than that of the oldest soil organic matter (SOM) fractions (Krull et al. 2006; Pessenda et al. 2001; Skjemstad et al. 1996).

Soil nutrient availability in highly weathered tropical soils has repeatedly been increased by those biochar materials studied in prior experiments (Glaser et al. 2002; Lehmann et al. 2002, 2003; Rondon et al. 2007; Steiner et al. 2008). Nutrients applied with certain biochar materials can be responsible for short-term increases in crop growth (Lehmann et al. 2003). However, it has been hypothesized that the long-term effect of biochar on nutrient availability is due to an increase in surface oxidation and cation exchange capacity (CEC) (Liang et al. 2006), which intensifies over time (Cheng et al. 2006, 2008) and can lead to greater nutrient retention in "aged" as opposed to "fresh" biochar. This mechanism has not been demonstrated under field settings over multiple years. If biochar additions can be credibly linked to greater nutrient retention of highly weathered soil, biochar management may provide a significant opportunity for sustainable improvements of soil fertility due to its high stability.

Therefore, our objective for this study was to investigate the long-term effects of biochar on soil fertility and crop yield. Our hypothesis was that biochar-amended soil provides more sites for the retention of base cations in acid tropical soils, thus retaining more of these in available form and resulting in greater crop yields and nutrient uptake.

Materials and methods

Field trial

The field experiment was located at Matazul farm in the Llanos Orientales, non-flooded savannas of Colombia (N 04° 10' 15.2'', W $072 \circ 36'$ 12.9'') (Fig. 1). The soil is an isohyperthermic kaolinitic

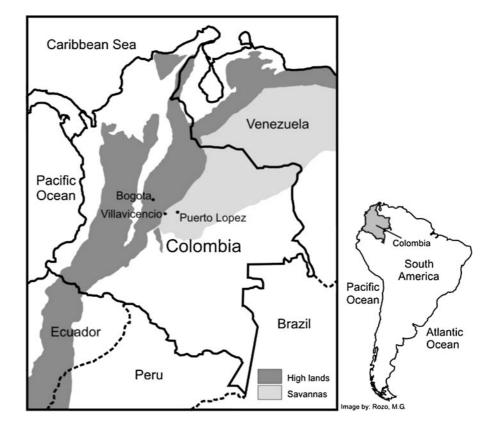


Fig. 1 Location of field experiment, approximately 40 km east of Puerto Lopez

Typic Haplustox (Soil Survey Staff 1994), which developed from alluvial sediments originating in the Andes (Rippstein et al. 2001), containing 20 mg g^{-1} organic C, 1.3 mg g^{-1} total N, 6 mg k g^{-1} available P, 40-44% clay, with a low pH (in KCl) of 3.9 and a potential CEC of 110 mmol_c kg⁻¹ in the upper 10 cm (except for clay content which was measured in the upper 15 cm). Long-term annual rainfall in the region is on average 2,200 mm, as measured at a research station approximately 200 km northeast of the research plot. There is a marked dry season between January and March, and the average annual temperature is 26°C (Rippstein et al. 2001). Average annual rainfall during 2005 and 2006 at the study site was 2,354 and 2,226 mm, respectively. It is possible to grow two cycles of annual crops during the rainy season. Initial vegetation consisted of native savanna grasses (mainly Trachypogon vestitus Andersson and T. plumosus Ness.) (Rippstein et al. 2001), and to our knowledge the experimental plot had never been tilled, cropped or amended prior to this study. This has to be recognized when comparing results to other studies on soils after long-term cultivation (Kimetu et al. 2008). However, fertility in native savanna soils at the experimental site is low with organic C contents of only about 20 mg g^{-1} despite the clayey soil texture, in contrast to often high fertility under other forest and savanna vegetation (Lobe et al. 2001; Zingore et al. 2005; Kimetu et al. 2008). In December 2002, the experimental area was chisel plowed and lime (dolomite) was applied at 2.2 t ha^{-1} , and incorporated to 30 cm using two passes of a chisel plough. Nine days later, biochar (see Table 1) was applied in a randomized complete block design with three replicates. Biochar incorporation was accomplished with one pass of a disc harrow to a depth of 5 cm. Application rates were 0, 8 and 20 t ha^{-1} , for a total of nine experimental plots, each measuring 4 by 5 m. Plots were separated by a 1 m buffer within blocks and a 2 m buffer between blocks. Lime and biochar were applied on only one occasion in 2002. Wood biochar commercially made for cooking using the traditional mound kiln technique (Brown 2009) was ground using a tractor and a roller, to pass through a 5-mm mesh. Details on feedstocks used to make the biochar and production conditions are not available. Beginning in May 2003 and until December 2006, plots were cropped to a maize (Zea mays L.)-soybean (Glycine max (L.) Merr.) rotation. The

Table 1 Properties of wood biochar made commercially forcooking and applied to a Colombian savanna Oxisol in 2002.Values shown are averages of two analytical replicates

		Biochar
рН	(H ₂ O)	9.20
pН	(KCl)	7.17
Total C	(%)	72.9
Total N	(%)	0.76
C/N		120
H/C		0.018
O/C		0.26
Ash	(%)	4.6
Ca ^a	$(\mu g g^{-1})$	330.7
Mg ^a	$(\mu g g^{-1})$	48.9
P ^a	$(\mu g g^{-1})$	29.8
K ^a	$(\mu g g^{-1})$	463.8
Sr ^a	$(\mu g g^{-1})$	2.6
Potential CEC	$(\text{mmol}_{c} \text{ kg}^{-1})$	111.9

^a Available nutrients extracted with Mehlich III (Mehlich 1984) and quantified by inductively coupled atomic emission spectroscopy (ICP-AES)

initial design also included plots seeded to pasture grasses and plots left to savanna vegetation, but only the crop rotation plots were used for the work reported here. No tillage was carried out after biochar incorporation, simulating no-till soil management.

Maize seeds were treated with fungicides (Carboxin and Thiram), and soybean seeds with both fungicides and Rhyzobium inoculum. Both maize and soybean were seeded using hand tools with fertilizer placed in a parallel furrow approximately 10 cm from the seed row. After seeding, side-dressed fertilizer was applied by hand to the soil surface, on crop rows, to all plots. Maize was seeded on 22 May 2003 and 30 April 2004 (variety information unavailable), and hybrid Pioneer® 3041 was seeded on 17 May 2005 and 10 May 2006, all at 62,500 plants ha⁻¹ (6.25 plants m⁻²). Short cycle, indeterminate soybean was seeded on 22 September 2004 (variety information unavailable), and varieties Corpoica Libertad 4 and Corpoica Superior 6 were seeded on 11 October 2005 and 15 September 2006, respectively, all at 400,000 plants ha⁻¹. Dates given are for the last, successful seeding. Re-seeding (up to twice) was necessary due to bird, insect and reptile damage. Initial fertilization took place at first seeding and was not repeated when re-seeding was necessary (Table 2). Weeds, insects and fungal diseases were controlled as necessary using herbicides and pesticides according to local practices. At soybean seeding in 2006, a powdered insecticide was used at a locally recommended dose in seed furrows on some areas of plots.

Soil sampling and analysis

After harvesting maize in 2003, 2004 and 2006, soil was sampled in the control and 20 t ha⁻¹ plots (and 8 t ha^{-1} in 2006 only) in depth increments of 0–0.05, 0.05-0.1, 0.1-0.2 and 0.2-0.3 m. A small pit was dug inside each plot and samples taken along one side of the pit. On 25-26 April 2006, additional samples were taken to 2.0 m using a hand-held core auger for quantification of extractable inorganic N only in treatments receiving 0 and 20 t ha⁻¹ biochar additions. For depth increments 0-0.15 and 0.15-0.3 m, five profiles were sampled on old maize rows and five half-way between rows, in each plot. For increment 0.3–0.6 m, three profiles were sampled on old maize rows and two in between. For increments 0.6-1.2 and 1.2-2.0 m, two profiles were sampled, one at each location. Samples below 0.3 m were also used for determining extractable cations, P, pH and total C and N contents. Soil from each depth increment and profile was collected in buckets and thoroughly mixed manually before a subsample was taken for analysis. During sampling soil subsamples were kept on ice in an insulated box.

Immediately after sampling to 2.0 m, moist subsamples were weighed and set aside for moisture determination after drying at 105°C for 24 h and reweighed. Thirty grams of moist soil were weighed into plastic bottles, and 150 ml of 1 N KCl were added for extraction of inorganic N. Shakers were not available near the field location, and jars were shaken by hand for 5 min (Lehmann et al. 1999). Jars were then kept at 4°C for several days until soil settled, and 20 ml supernatant was transferred to small plastic vials using pipettes (Renck and Lehmann 2004) and kept frozen until analysis. Ammonium and nitrate concentrations of soil extracts were determined colorimetrically on a segmented flow analyzer (Autoanalyzer 3 by Bran+Luebbe, Rochester NY, USA). Data were corrected for N contributed by the extractant and transformed to represent concentrations on a dry soil basis. Leftover soil was air-dried, crushed and passed through an aluminum sieve with 2 mm circular openings. Available nutrients were extracted from 2.5 g of air-dried soil using 25 ml of

Table 2 Fertilizer application rates (kg ha⁻¹). Nitrogen was applied as urea unless otherwise indicated, K as KCl and P as acidified rock phosphate

Year	Crop	Application date	Ν	Р	Κ	Ca	Mg	S	В	Cu	Zn
2002		10 Dec				509	199				
2003	Maize	Total	165	43	86	2.9	16.2	10	0.4	_	4.5
2004	Maize	Total	170	33	84	2.1	15.6	10	0.3	_	4.0
	Soybean	Total	87	39	63	-	19.2	13	0.9	_	4.7
2005	Maize	4 May	30	30	25	1.8	3.0	1.6	0.3	_	1.6
		9 Jun	46	_	62	_	-	_	_	_	_
		21 Jun	80	_	25	_	-	_	_	_	_
		Total	156	30	112	1.8	3.0	1.6	0.3	_	1.6
	Soybean	12 Sep ^a	16	10	110	17.0	4.0	5.0	0.3	0.3	1.7
2006	Maize	27 Apr	31	30	36	-	12.5	15.6	0.3	0.3	1.6
		27 May	58	_	62	_	_	_	_	_	_
		9 Jun	70	_	38	_	_	_	_	_	_
		Total	159	30	138	_	12.5	15.6	0.3	0.3	1.6
	Soybean	7 Sept ^b	16	10	104	_	7.2	12.0	0.2	0.3	1.7

^a Less than 2 kg ha⁻¹ N (82% as KNO₃ and 2% as urea), 0.05 kg ha⁻¹ P and 2 kg ha⁻¹ K total applied as foliar fertilizer on 24 and 28 Oct, and 8 Nov. On these dates trace amounts (<3 g ha⁻¹) of Ca, Mg, S, B, Cu and Zn were also applied

^bLess than 1 kg ha⁻¹ N (82% as KNO₃ and 2% as urea) as foliar fertilizer, plus foliar application of gibberellin on 14 Oct

Mehlich III solution (Mehlich 1984) and horizontal shaking for 5 min. Upon filtering, extracts were analyzed by atomic emission spectrometry (IRIS Intrepid by Thermo Elemental, Franklin MA, USA). Soil pH was determined in a 1:2.5 soil:water or 1 N KCl mixture, agitated three times over the course of 1 h, and measured using a gel electrode (Symphony by VWR, West Chester PA, USA). Exchangeable acidity was determined by extracting 5 g of soil with 25 ml 1 N KCl, shaking lightly, and allowing to rest for 30 min. Samples were then filtered and extraction bottles washed three times with 25 ml of 1 N KCl. Phenolphthalein was added to the extracts, and these were titrated using 0.01 N NaOH. Potential cation exchange capacity (CEC) was determined by extraction with 1 N ammonium acetate at pH 7, flushing three times with isopropyl alcohol followed by extraction with 2 N KCl. The ammonium content of the KCl extract was determined colorimetrically using Nessler's reagent (Naude 1927) on a Technicon[®] flow analyzer. Effective CEC was calculated by summing the amount of charge per unit soil from all cations extracted by Mehlich III except Al, and exchangeable acidity. Wang et al. (2004) found a good correlation between cations extracted using the Mehlich III solution and ammonium acetate at pH 7. Base saturation (BS) was obtained by dividing the total amount of charge per unit soil from Ca, K and Mg by effective CEC. Total C and N contents were determined by combustion on an isotope ratio mass spectrometer (Europa Hydra 20/20 by Europa Scientific, Crewe, UK).

The point of zero net charge (PZNC) of the soil in 2006 was determined on samples of the 0 and 20 t ha⁻¹ biochar application rates, with all replicates combined. The method using K and Cl ions described by Cheng et al. (2008) was used, except quadratic curves were used only to describe the soils' positive charge. Linear and hyperbolic curves were used for negative charge in the control and biochar amended soils, respectively.

Biochar was analyzed similarly to soil, except double extractions were used for potential CEC determination (Cheng et al. 2006) and the ratio of biochar:water or 1 N KCl for pH measurement was 1:10. The H content of biochar was measured after combustion on an automatic gas analyzer (PDZ Europa 20–20, Heckatech HT by Europa Scientific, Crewe, UK). Oxygen content was calculated by difference using the ash, C and H contents.

Crop samples and measurements

Maize leaf tissue samples were taken in 2006 from the flag leaf of ten marked plants per plot at tasseling. Squares of about 50 by 50 mm were cut from one edge towards the midrib, halfway down the leaf. These were kept on ice in the field and frozen until oven drying at 70°C for 72 h. At harvest, maize ears were harvested from 2 linear meters on different rows, avoiding plot edges. Husks were left on the plants. Ears were shelled by hand, and grain and cobs were dried first in the sun and then in an oven at 60°C for 72 h. Grain moisture after drying was determined using a hand-held moisture tester (John Deere, Moline IL, USA), and grain yield is reported on a 15% moisture content basis. In each plot, vegetative biomass with ears removed was harvested at ground level from 1 linear meter, wet weight recorded and subsamples consisting of 2 whole maize plants were weighed and taken to the lab. After oven drying at 70°C to constant weight (about 48 h), dry weights were determined. Vegetative biomass from harvest, dried leaf material from tasseling and subsamples of grain were ground using a laboratory mill (Thomas Wiley, Philadelphia PA, USA) to pass a 1-mm sieve, packaged in sealed plastic bags and stored until analysis by acid block digestion with nitric acid and hydrogen peroxide, followed by determination of total nutrient content by atomic emission spectrometry (IRIS Intrepid by Thermo Elemental, Franklin MA, USA). Samples of vegetative maize tissue from 2006 were not available for analysis.

In 2006, soybean leaf samples were collected at full bloom from the newest mature, trifoliate leaf at the top of plants marked for measuring height. Due to problems with pest damage and insecticide toxicity, soybean growth was heterogeneous. At harvest, all biomass was harvested on 2-4 linear meters of unaffected areas. Biomass was manually separated into seeds and vegetative plant parts, dried, weighed, ground and analyzed as above. Soybean seed, due to its high oil content, was analyzed for total nutrients by dry ashing at 450°C for 7 h, adding hydrogen peroxide and ashing again at 450°C for 2.5 h. The ash was dissolved in a hydrochloric acid matrix and analyzed by atomic emission spectrometry (CIROS by SPECTRO Analytical Instruments, Kleve, Germany).

Statistical analyses

All data was analyzed using PROC GLM of the SAS software package (SAS Institute Inc 2003). Treatment means were separated using the Student T test. Upon inspecting residual plots, it was deemed necessary to log transform data for soil available Ca, K, Mg, Mn, Mo, P, S, and Sr in order to comply with the model's assumption of equal variance.

Results

Crop yield and nutrient uptake

In the first year after biochar application, no significant effect on crop yield was observed (p>0.05). In subsequent years, however, maize yield increased with increasing biochar application rate, and the positive effect of biochar was most prominent in 2006 when absolute yields were the lowest (Fig. 2). Grain yield from soybean was only available in 2006 due to deer grazing in the field in previous years, and no significant differences between treatments were observed (p>0.05, data not shown).

The harvest index (HI) of maize (grain mass divided by total mass) was significantly lower (p> 0.05) in 2006 than in other years, in both the control and 20 t ha⁻¹ biochar amended plots (the average HI for 2003 to 2005 was 0.47 for both treatments, and in

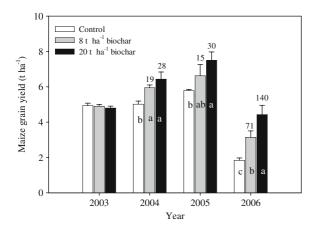


Fig. 2 Maize grain yield on a Colombian savanna Oxisol amended with biochar in late 2002 (\pm SE, n=3). Numbers above bars are percent yield increase compared to the optimally managed control, and different letters indicate significant differences between means (p<0.05) within single years

2006 the HI was 0.37 and 0.42 for the control and 20 t biochar ha⁻¹ application rate, respectively). Interestingly, between 2003 and 2005, no differences in HI were observed in the control plots, while the high biochar application rate produced significantly (p<0.05) increasing HI values in each of these years (0.44 in 2003, 0.47 in 2004 and 0.50 in 2005).

Total nutrient uptake by the maize crop also increased overall with biochar application (Fig. 3), or decreased in the case of Al. Strontium, which is a common contaminant in fertilizers (Senesi et al. 2005), has a similar behavior in soil and plants as Ca (Aberg 1995). In this study, total Sr uptake by plants increased with increasing biochar application. For maize leaf samples taken at tasseling in 2006, concentrations of Ca (1.08 and 1.36 g kg dry matter⁻¹ for 0 and 20 t biochar ha⁻¹, respectively) and Mg $(0.92 \text{ and } 1.03 \text{ g kg dry matter}^{-1})$ were also significantly higher with the high biochar application rate than the control (p < 0.05). For soybean samples, total uptake of K (45.5 and 50.7 kg ha^{-1} respectively), Cu (25.7 and 28.3 g ha⁻¹) and Mn (89.8 and 129.1 g ha⁻¹) in 2006 was significantly greater with biochar application (p < 0.05). Total uptake of Sr was not measured for soybean. Also, the Mn (64.2 and 97.5 mg kg dry matter⁻¹, respectively) content of soybean leaf tissue at flowering was greater when biochar had been applied.

Calcium concentration in maize grain decreased significantly (p < 0.05) after 2004 in all treatments, and Mg concentrations decreased over the duration of the experiment, significantly so (p < 0.05) in the control and high biochar application plots (Fig. 4). With vegetative tissue these decreasing trends were less clear, especially in the case of Mg.

Soil properties

While nitrate accumulation below 60 cm depth was observed (data not shown), no significant differences (p>0.05) were found between biochar-amended and control plots for inorganic N content before seeding maize in 2006. Over most years and depth increments to 0.3 m, biochar application resulted in significantly (p<0.05) greater available Ca (101–320% for significant differences between the control and 20 t ha⁻¹ application rate), Mg (64–217%), Mn (136–342%), Mo (573–860%) and Sr (251–591%), while the availability of Al and Fe showed a decreasing trend

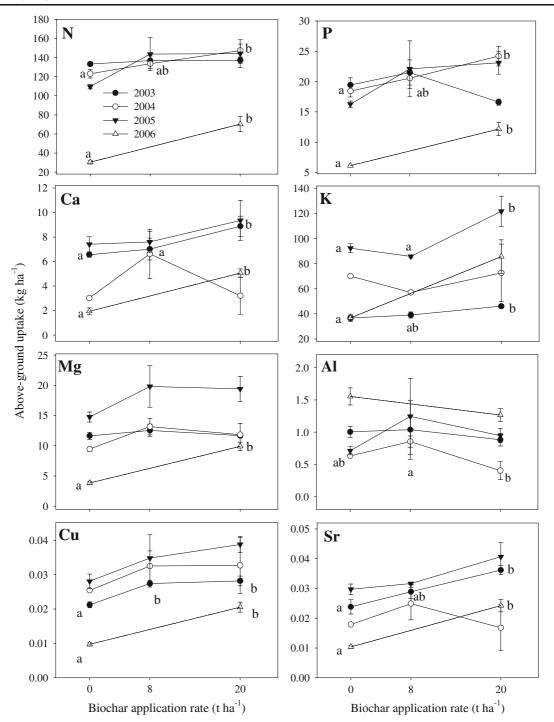


Fig. 3 Total nutrient uptake by maize crops grown during 4 years after biochar application to a Colombian savanna Oxisol (\pm standard error, n=3). Different letters indicate

significant differences between treatment means (p < 0.05) within single years, letters not shown when differences not significant. Note different scales for y-axes

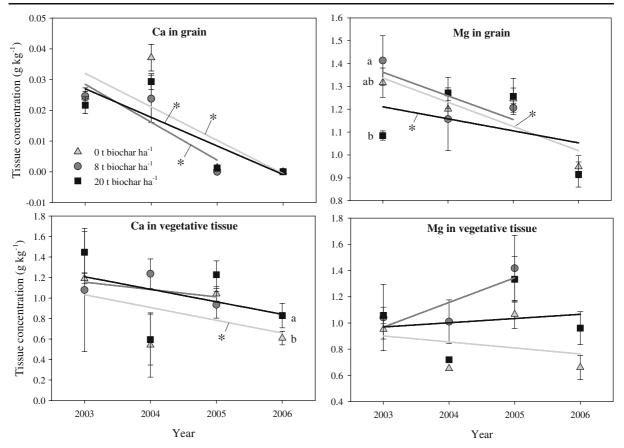


Fig. 4 Maize tissue concentrations of Ca and Mg during 4 years after biochar application to a Colombian savanna Oxisol. Different letters indicate significant differences (p<0.05) between treatments in a single year. * indicates a significant (p<0.05) trend over time

(Table 3). The depth at which amounts of available Ca and Mg increased with biochar became greater with time, with the increase being most important at the surface in 2003, at 5–10 cm in 2004, and at 10–20 cm in 2006. For all biochar application rates, the concentrations of Ca and Mg to 30 cm decreased between 2004 and 2006 by 20–30%, although the trend over time was not statistically significant. The effect of biochar addition on K availability was greatest in 2003, the year after application. Total C and N contents were not significantly different between treatments except in 2004, where the control plots contained more total C and N below the surface.

In 2004 and 2006, soil pH was significantly (p < 0.05) higher when biochar had been applied, at the depths where Ca and Mg availability was also significantly greater (Table 3). No statistically significant differences (p > 0.05) were observed for measurements of potential and effective CEC,

exchangeable acidity and BS (see online supplementary material). Potential CEC as determined from PZNC equations was $18.8 \text{ mmol}_{c} \text{ kg}^{-1}$ for the control and $81.2 \text{ mmol}_{c} \text{ kg}^{-1}$ for biochar-amended soil (see online supplementary material).

Discussion

Yield increases with biochar application have been documented in controlled environments as well as in the field (reviewed by Blackwell et al. 2009; Chan and Xu 2009; Lehmann and Rondon 2006; also Asai et al. 2009). Reported biochar application rates ranged from <1 to over 100 t ha⁻¹, and reported percent yield increases over comparable controls ranged from less than 10% to over 200%. Such high variation likely stems from the large range of biochar application rates, crops and soil types used. However, only a

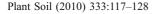


Table 3 Properties of a Colombian savanna Oxisol 1, 2 and 4 years after biochar addition in 2002. Different letters indicate significant differences between treatment means within single years and depths (n=3). Letters not shown when differences not significant

Year	Biochar application rate (t ha ⁻¹)	Depth	pН	Available						Total	
		(m)	KCl	Ca (µg g so	Mg $il^{-1})$	K	Р	Sr	Al	C (mg g	N soil ⁻¹)
2003	0	0-0.05	3.91	128.6b	57.1b	29.9	12.8	0.105b	1,383.1	21.2	1.27
		0.05-0.1	3.94	143.2	54.1	2.1	0.2	0.115	1,392.0	20.9	1.25
		0.1-0.2	3.94	44.5	21.8	<det< td=""><td><det< td=""><td><det< td=""><td>1,420.7</td><td>14.5</td><td>0.85</td></det<></td></det<></td></det<>	<det< td=""><td><det< td=""><td>1,420.7</td><td>14.5</td><td>0.85</td></det<></td></det<>	<det< td=""><td>1,420.7</td><td>14.5</td><td>0.85</td></det<>	1,420.7	14.5	0.85
		0.2-0.3	3.97a	11.1	7.1	<det< td=""><td><det< td=""><td><det< td=""><td>1,424.7</td><td>11.4</td><td>0.67</td></det<></td></det<></td></det<>	<det< td=""><td><det< td=""><td>1,424.7</td><td>11.4</td><td>0.67</td></det<></td></det<>	<det< td=""><td>1,424.7</td><td>11.4</td><td>0.67</td></det<>	1,424.7	11.4	0.67
	20	0-0.05	4.17	288.8a	93.7a	54.9	15.1	0.726a	1,251.3	22.8	1.21
		0.05-0.1	4.06	178.5	63.5	12.7	1.4	0.193	1,299.1	22.6	1.18
		0.1-0.2	3.92	36.0	17.6	<det< td=""><td><det< td=""><td><det< td=""><td>1,345.0</td><td>12.3</td><td>0.76</td></det<></td></det<></td></det<>	<det< td=""><td><det< td=""><td>1,345.0</td><td>12.3</td><td>0.76</td></det<></td></det<>	<det< td=""><td>1,345.0</td><td>12.3</td><td>0.76</td></det<>	1,345.0	12.3	0.76
		0.2-0.3	3.90b	7.3	5.5	<det< td=""><td><det< td=""><td><det< td=""><td>1,390.8</td><td>10.9</td><td>0.65</td></det<></td></det<></td></det<>	<det< td=""><td><det< td=""><td>1,390.8</td><td>10.9</td><td>0.65</td></det<></td></det<>	<det< td=""><td>1,390.8</td><td>10.9</td><td>0.65</td></det<>	1,390.8	10.9	0.65
2004	0	0-0.05	3.80	97.6b	56.6	49.2	7.2	0.076	1,304.1	22.9	1.18
		0.05-0.1	3.85b	113.4b	45.4b	15.1	0.1	0.087b	1,323.8	25.0a	1.11
		0.1-0.2	3.86	99.4	36.7	2.7	<det< td=""><td>0.033</td><td>1,300.5</td><td>22.1a</td><td>1.33a</td></det<>	0.033	1,300.5	22.1a	1.33a
		0.2-0.3	3.94	37.7	20.0	<det< td=""><td><det< td=""><td><det< td=""><td>1,294.7</td><td>18.5a</td><td>0.76a</td></det<></td></det<></td></det<>	<det< td=""><td><det< td=""><td>1,294.7</td><td>18.5a</td><td>0.76a</td></det<></td></det<>	<det< td=""><td>1,294.7</td><td>18.5a</td><td>0.76a</td></det<>	1,294.7	18.5a	0.76a
	20	0-0.05	3.94	196.6a	77.1	43.9	8.3	0.331	1,258.4	23.6	1.14
		0.05-0.1	4.10a	265.8a	91.8a	11.3	<det< td=""><td>0.501a</td><td>1,183.5</td><td>22.1b</td><td>0.95</td></det<>	0.501a	1,183.5	22.1b	0.95
		0.1-0.2	4.09	161.0	65.4	<det< td=""><td><det< td=""><td>0.138</td><td>1,228.9</td><td>17.7b</td><td>0.80b</td></det<></td></det<>	<det< td=""><td>0.138</td><td>1,228.9</td><td>17.7b</td><td>0.80b</td></det<>	0.138	1,228.9	17.7b	0.80b
		0.2-0.3	3.98	68.7	32.6	<det< td=""><td><det< td=""><td><det< td=""><td>1,248.4</td><td>11.1b</td><td>0.49b</td></det<></td></det<></td></det<>	<det< td=""><td><det< td=""><td>1,248.4</td><td>11.1b</td><td>0.49b</td></det<></td></det<>	<det< td=""><td>1,248.4</td><td>11.1b</td><td>0.49b</td></det<>	1,248.4	11.1b	0.49b
2006	0	0-0.05	3.86	116.8	54.7	53.8	48.8	0.137	1,333.9	19.9	1.22
		0.05-0.1	3.89b	120.6	44.6	33.0	10.5	0.133b	1,358.0	20.3	1.21
		0.1-0.2	3.93	30.1c	14.6b	15.4	<det< td=""><td><det< td=""><td>1,107.6</td><td>15.9</td><td>0.95</td></det<></td></det<>	<det< td=""><td>1,107.6</td><td>15.9</td><td>0.95</td></det<>	1,107.6	15.9	0.95
		0.2-0.3	3.99	12.0	8.4	2.7	<det< td=""><td><det< td=""><td>1,317.6</td><td>10.9</td><td>0.64</td></det<></td></det<>	<det< td=""><td>1,317.6</td><td>10.9</td><td>0.64</td></det<>	1,317.6	10.9	0.64
		0.3-0.6	4.13	4.9	7.9	16.2	<det< td=""><td><det< td=""><td>1,275.3</td><td>7.3</td><td>0.44</td></det<></td></det<>	<det< td=""><td>1,275.3</td><td>7.3</td><td>0.44</td></det<>	1,275.3	7.3	0.44
		0.6-1.2	4.27	11.0	10.8	11.3	<det< td=""><td><det< td=""><td>1,146.2</td><td>4.6</td><td>0.35</td></det<></td></det<>	<det< td=""><td>1,146.2</td><td>4.6</td><td>0.35</td></det<>	1,146.2	4.6	0.35
		1.2-2.0	4.17	8.1	10.4	8.5	<det< td=""><td><det< td=""><td>1,134.0</td><td>3.1</td><td>0.31</td></det<></td></det<>	<det< td=""><td>1,134.0</td><td>3.1</td><td>0.31</td></det<>	1,134.0	3.1	0.31
	8	0-0.05	3.87	71.4	37.8	58.3	25.4	0.035	1,358.1	24.3	1.37
		0.05-0.1	3.93ab	130.4	44.6	39.0	6.5	0.179b	1,334.6	21.7	1.24
		0.1-0.2	3.99	86.4b	32.7a	12.7	<det< td=""><td>0.028</td><td>1,334.2</td><td>16.8</td><td>1.02</td></det<>	0.028	1,334.2	16.8	1.02
		0.2-0.3	3.96	23.3	13.1	2.1	<det< td=""><td><det< td=""><td>1,333.5</td><td>12.0</td><td>0.71</td></det<></td></det<>	<det< td=""><td>1,333.5</td><td>12.0</td><td>0.71</td></det<>	1,333.5	12.0	0.71
	20	0-0.05	3.84	133.1	55.3	48.2	27.4	0.223	1,293.3	25.3	1.24
		0.05-0.1	4.03a	213.5	72.1	22.5	9.2	0.468a	1,238.2	20.1	1.51
		0.1-0.2	4.00	126.5a	46.3a	12.0	0.1	0.093	1,271.6	13.9	0.91
		0.2–0.3	3.94	24.5	12.8	1.5	<det< td=""><td><det< td=""><td>1,290.6</td><td>10.5</td><td>0.64</td></det<></td></det<>	<det< td=""><td>1,290.6</td><td>10.5</td><td>0.64</td></det<>	1,290.6	10.5	0.64
		0.3-0.6	4.09	12.6	10.7	19.9	<det< td=""><td><det< td=""><td>1,292.2</td><td>8.2</td><td>0.49</td></det<></td></det<>	<det< td=""><td>1,292.2</td><td>8.2</td><td>0.49</td></det<>	1,292.2	8.2	0.49
		0.6-1.2	4.19	13.4	12.4	10.2	<det< td=""><td><det< td=""><td>1,136.6</td><td>5.0</td><td>0.37</td></det<></td></det<>	<det< td=""><td>1,136.6</td><td>5.0</td><td>0.37</td></det<>	1,136.6	5.0	0.37
		1.2-2.0	4.13	7.6	8.2	16.1	<det< td=""><td><det< td=""><td>1,142.6</td><td>4.0</td><td>0.35</td></det<></td></det<>	<det< td=""><td>1,142.6</td><td>4.0</td><td>0.35</td></det<>	1,142.6	4.0	0.35

< det below detection limit, n/a data not available

handful of reported field experiments took place over more than 1 year. Steiner et al. (2007) reported cumulative yield increases of rice and sorghum on a Brazilian Amazon Oxisol of approximately 75% after four growing seasons over 2 years, when 11 t ha^{-1} biochar was applied at the beginning of the experiment. In a degraded Kenyan Oxisol, Kimetu et al. (2008) found a doubling of cumulative maize yield

after three repeated biochar applications of 7 t ha⁻¹ over 2 years. In both of these studies and as shown in the study reported here, inorganic fertilizers were applied equally in both the biochar-amended and the non-amended control. Here, the percent yield increase with biochar application increased gradually over time up to 3 years after application. A large decrease in overall yields was observed in the fourth year, accompanied by an even greater beneficial effect of biochar. A progressive increase in the beneficial effect of biochar over time was also observed by Steiner et al. (2007). This shows that biochar application to soil can provide increasing benefits over time.

Potassium availability was increased the most by biochar application in the year following its application, and this likely results directly from the considerable amounts of K that were added along with the biochar (Table 1) from which it is readily leached. Similar results for K were obtained by Lehmann et al. (2003) 37 days after wood biochar was added to an Oxisol from the Brazilian Amazon, by Chan et al (2007) 42 days after applying green waste biochar to an Australian Alfisol, and by Rondon et al. (2007) 75 days after wood biochar addition to the same soil as in the present study. However, the greater availability of this nutrient with biochar did not persist beyond the year after application. Steiner et al. (2007) did not observe greater K availability after one cropping season when wood biochar was added to a Brazilian Amazon Oxisol, but the biochar used contained small amounts of K. Several nutrients may be supplied in considerable amounts with biochar, depending on feedstock (Gaskin et al. 2008). However, the application of these nutrients with biochar is unlikely to provide benefits for crop nutrition on the long term.

Biochar had the most significant effect on the availability of Ca and Mg, as well as Sr which was applied with fertilizer. In contrast to K, this increase in availability was not a result of nutrient release, because the amount of available Ca, Mg and Sr applied with biochar (6.6, 1.0 and 0.05 kg ha⁻¹, respectively) in 2002 is negligible, and mineralization of biochar in this environment is very slow (approx. 2% over 2 years) (Major et al. 2010). Calcium and Mg were applied as dolomite in 2002, and in small amounts with fertilizer thereafter. These nutrients are prone to extensive leaching in Oxisols (Cahn et al. 1993; Ernani et al. 2006). Although Ca and Mg stocks declined after 2004, Ca and Mg loss over time was lower with

biochar application. Therefore, biochar helped mitigate the loss of applied Ca and Mg in the rooting zone, as also shown by the fertilizer-applied Sr.

In 2006, the Ca and Mg contents of maize flag leaves at tasseling were significantly greater when biochar was applied. However, all flag leaf Ca and Mg contents observed here are still considered marginal for maize (Bergmann 1986). This, combined with the declining stocks of available Ca and Mg and the decrease in yield and HI in 2006 indicate that the system was Ca and Mg limited, and that the retention of these nutrients by biochar is responsible for the maize yield increases observed. Indeed, in 2006 available Ca and Mg amounts in the soil to a depth of 30 cm were lowest, but the beneficial effects of biochar on Ca and Mg nutrition were the greatest relative to the unamended control. The strong overall decline in maize yields in 2006 is attributed to declining Ca and Mg soil stocks.

CEC increased only slightly after biochar additions that caused a significant increase, however, in pH. Despite the low increase in CEC, Ca and Mg uptake by crops was greater (Fig. 3) and leaching lower with biochar (Major 2009). If biochar indeed improved crop nutrition by Ca and Mg retention, then very low increases in CEC were sufficient.

Apart from direct nutrient additions or nutrient retention with biochar, other authors have attributed increases in crop yields with biochar addition to its effect on soil pH (Rondon et al. 2007; Van Zwieten et al. 2007; Yamato et al. 2006), and to often pH-related increases in nutrient availability and/or reductions in Al³⁺ availability (Lehmann et al. 2003; Rondon et al. 2007; Yamato et al. 2006). Improvements to soil physical properties, such as reduced soil strength of a hard-setting soil (Chan et al. 2007) have also been offered as explanations for yield increases with biochar. The effects of biochar application in the field on soil biota have been poorly studied. However, improved root colonization by mycorrhizal fungi with biochar has been shown (reviewed by Warnock et al. 2007). Here, yield improvements are attributed mainly to pH increase and nutrient retention.

Conclusions

A single biochar application to an infertile, acidic tropical soil improved crop yields up to at least 4 years after application. This indicates that a single biochar application may provide benefits over several cropping seasons, although longer-term studies are still lacking and needed to determine when a steadystate is reached or if and when a decline starts to occur. Biochar could be a valuable tool for the management of agroecosystems in humid tropical regions of the world, where both industrial and subsistence agriculture are practiced. Although biochar may conceivably enhance crop growth through several mechanisms (microbiologically or through improved soil physical properties, for example), improved pH and base cation retention in the rooting zone likely caused improved crop nutrition in the studied acid soil under high rainfall conditions.

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