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Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil

Shelby Rajkovich · Akio Enders · Kelly Hanley · Charles Hyland · Andrew R. Zimmerman · Johannes Lehmann

Abstract The effects of biochar properties on crop growth are little understood. Therefore, biochar was produced from eight feedstocks and pyrolyzed at four temperatures (300°C, 400°C, 500°C, 600°C) using slow pyrolysis. Corn was grown for 46 days in a greenhouse pot trial on a temperate and moderately fertile Alfisol amended with the biochar at application rates of 0.0%, 0.2%, 0.5%, 2.0%, and 7.0% (w/w) (equivalent to 0.0, 2.6, 6.5, 26, and 91 t biochar ha^{-1}) and full recommended fertilization. Animal manure biochars increased biomass by up to 43% and corn stover biochar by up to 30%, while food waste biochar decreased biomass by up to 92% in relation to similarly fertilized controls (all $P<0.05$). Increasing the pyrolysis temperature from 300°C to 600°C decreased the negative effect of food waste as well as paper sludge biochars. On average, plant growth was the highest with additions of biochar produced at a pyrolysis temperature of 500°C ($P<0.05$), but feedstock type caused eight times more variation in growth than pyrolysis temperature. Biochar application rates above 2.0% (w/w) (equivalent to 26 t ha^{-1}) did generally not improve corn growth and rather decreased growth when biochars produced from dairy manure, paper

sludge, or food waste were applied. Crop N uptake was 15% greater than the fully fertilized control ($P<0.05$, average at 300°C) at a biochar application rate of 0.2% but decreased with greater application to 16% below the N uptake of the control at an application rate of 7%. Volatile matter or ash content in biochar did not correlate with crop growth or N uptake ($P>0.05$), and greater pH had only a weak positive relationship with growth at intermediate application rates. Greater nutrient contents (N, P, K, Mg) improved growth at low application rates of 0.2% and 0.5%, but Na reduced growth at high application rates of 2.0% and 7.0% in the studied fertile Alfisol.

Keywords Biochar · Black carbon · Corn · Nitrogen uptake · Sodium

Introduction

Biochar applications to soil are motivated by the findings that anthropogenic char found in Terra Preta de Indio in the Amazon improves soil fertility for millennia (Lehmann et al. 2003a). Investigation of the effects of biochar on crop growth has increased over the past years but has mainly concentrated on tropical soil (Lehmann et al. 2003b; Yamato et al. 2006; Chan et al. 2007, 2008; Steiner et al. 2007; Kimetu et al. 2008; Hidetoshi et al. 2009; Yeboah et al. 2009; Gaskin et al. 2010; Major et al. 2010; Van Zwieten et al. 2010a, b). An important aspect for improving crop growth in highly weathered soils is the liming effect of biochars that typically have a high pH (Yamato et al. 2006; Van Zwieten et al. 2010a; Yuan and Xu 2011) and the generation of cation exchange capacity (CEC) (Liang et al. 2006) to reduce nutrient leaching (Lehmann et al. 2003b). However, there is a lack of studies that investigate

S. Rajkovich · A. Enders · K. Hanley · C. Hyland ·
J. Lehmann (✉)
Department of Crop and Soil Sciences, Cornell University,
Ithaca, NY 14853, USA
e-mail: CL273@cornell.edu

A. R. Zimmerman
Department of Geological Sciences, University of Florida,
Gainesville, FL 32611, USA

biochar effects on crop growth in temperate soils that are not primarily limited by pH or CEC.

Biochars can have very different properties depending on the feedstock they are produced from and the pyrolysis conditions used to generate them (Antal and Grønli 2003; Chan and Xu 2009; Bonelli et al. 2010). The feedstock mainly affects the elemental composition of nutrients and metals (Chan and Xu 2009), whereas pyrolysis temperature largely controls the proportion of volatiles (Zimmerman 2010) and surface properties (Amonette and Joseph 2009). Considering the large variation in biochar properties, it is not surprising that crop yields vary with different biochars (Chen et al. 2010; Gaskin et al. 2010; Makoto et al. 2011). Few studies have been published that compare a wide range of well-characterized biochars in their performance with respect to crop growth (Chan et al. 2008), and none has been reported for temperate soils.

In addition to the mentioned beneficial effects on soil productivity, biochars may also reduce plant growth (Devonald 1982; Gaskin et al. 2010). In some cases, an unfavorably high pH of the biochar in relation to already high pH in the studied Calcarosol was identified as the reason for yield depressions (Van Zwieten et al. 2010a). In other cases, the reason is less clear and may include direct phytotoxicity possibly of the volatile fraction or negative effects of metals (Devonald 1982). Also N immobilization after addition of fresh biochar has been observed to decrease N availability (Lehmann et al. 2003b; Bridle and Pritchard 2004) which may result in growth depression. The relationship of biochar chemical and physical properties and these growth-depressing effects have not been systematically examined. Microbiological interactions between roots and biochar may also occur (Lehmann et al. 2011) which are not investigated further here.

To address these knowledge gaps, we investigated the short-term effects of a large and diverse set of biochars on corn growth in the greenhouse. The experiments were conducted with a temperate Alfisol that had no significant fertility constraints. The specific objectives were (a) to quantify the effects of varying biochar characteristics on corn growth and N uptake, (b) to assess whether feedstock properties or pyrolysis temperature are more important in determining initial plant growth, and (c) to identify the optimum rate of biochar application considering both positive and negative effects on growth.

Materials and methods

Soil type

The soil used in this experiment was taken from the Cornell Musgrave Research Farm in Aurora, New York,

continuously cropped to corn for over 20 years. The soil is classified as a Junius loam (0–2% slopes, overtill), Kendaia silt loam (2–5% slopes), and Lima loam (2–6% slopes), or fine-loamy, mixed, mesic Glossoboric Hapludalf. It had a pH of 6.85 in 1 N KCl (ratio of 1:20 w/v), CEC of 97.6 mmol$_c$ kg^{-1}, clay content of 27%, total C content of 16.2 mg g^{-1}, total N of 1.62 mg g^{-1}, and Mehlich-3 extractable P of 35.8 mg g^{-1}, K of 84.1 mg g^{-1}, Ca of 3,739 mg g^{-1}, Mg of 483 mg g^{-1}, and Na of 75 mg g^{-1}. The soil was air-dried for several days and subsequently shredded using a Royer Soil Conditioner to create soil uniformity. Excess organic material was then removed by passing the soil through a 5-mm sieve.

Biochar production

Biochar was produced from corn stover, hazelnut shells, oak wood, pine wood, digested dairy manure, food waste, paper mill waste (sludge), or poultry with sawdust bedding (Table 1). The raw organic material for the crop residues and poultry manure was collected in Wisconsin; the food waste from Cornell dining facilities; the paper mill waste from Mohawk Paper in Waterford, NY consisting of white, uncolored paper pulp waste; and the digested dairy manure from AA Farms in Candor, NY (operating with more than 1,000 milking cows). Feedstock was oven-dried to approximately 10% moisture before pyrolysis. Biochars were produced using slow pyrolysis (Daisy Reactor, Best Energies, Inc., Cashton, WI, USA). Approximately 3 kg of feedstock was manually placed into the reactor, which was thoroughly purged with N$_2$ (with the mixer running). The material was charred for 80–90 min, including rising temperature to the target with a few degrees per minute and holding at final temperature for 15–20 min. Different biochars were generated with target temperatures of 300°C, 400°C, 500°C, or 600°C. Subsequently, the furnace was turned off and the main chamber was allowed to cool before collecting the biochar under N$_2$ purge to reduce rapid oxidation (leading to a more homogeneous product) and auto-ignition. In addition to this set of biochars that was produced using the identical kiln and production procedure (except for the systematic variation in pyrolysis temperatures), a wider set of biochars was procured from companies and research groups which were generated using other thermochemical techniques such as torrefaction, fast and flash pyrolysis, and gasification (see Supplementary material for detailed description of production conditions). After transportation to the analytical laboratories, biochars were stored dry under argon gas to limit oxidation on air. All biochars were ground with a mortar and pestle and passed through a 2-mm sieve just before experimentation.

Table 1 Selected physical and chemical characteristics of the studied biochars

Biochar	Bulk density (Mg m⁻³)	SSA (N₂) (m² g⁻¹)	SSA (CO₂)	pH (water)	EC (mS m⁻¹)	C (mg g⁻¹)	N	$\delta^{15}N$ (‰)	C/N	Ash (%)	Fixed carbon	Volatile matter	CEC	Available ($mmol_c$ kg⁻¹) Ca	K	Mg	Na	Total (mg kg⁻¹) P	Ca	K	Mg	Na
Corn 300°C	0.120	4.7	141	7.33	189	595	11.6	2.29	51	10.70	37.43	51.87	708	105	309	212	2	1,369	6,480	17,052	5,883	492
Corn 400°C	0.102	3.9	282	9.17	177	626	11.0	2.13	58	12.90	42.37	44.73	796	55	249	93	3	1,812	7,254	20,234	6,583	904
Corn 500°C	0.103	3.2	494	9.92	203	687	11.1	1.76	62	17.60	51.32	31.08	517	54	403	87	4	1,852	11,699	24,817	9,510	1,384
Corn 600°C	0.113	3.4	531	9.95	196	698	10.1	2.04	70	16.72	59.80	23.49	385	41	230	53	4	2,114	9,383	24,616	8,582	1,539
Hazelnut 300°C	0.336	1.3	224	6.35	38	699	5.4	2.95	159	1.98	49.23	48.79	59	10	5	bd	bd	397	3,726	5,166	790	471
Hazelnut 400°C	0.411	1.6	493	7.66	14.2	758	5.1	1.88	158	1.69	54.83	43.48	102	11	18	1	1	298	2,821	4,285	554	488
Hazelnut 500°C	0.464	3.8	521	8.60	10.6	801	5.1	3.48	177	1.94	60.88	37.19	118	21	41	4	3	275	2,693	4,297	494	447
Hazelnut 600°C	0.449	0.9	632	8.85	18.8	841	5.2	3.53	181	2.18	68.19	29.63	56	12	27	2	0	329	3,262	5,162	587	407
Oak 300°C	0.264	nd	163	4.25	11.6	639	1.3	bd	520	0.35	38.52	61.13	414	4	6	1	3	6	752	725	46	297
Oak 400°C	0.241	3.5	450	4.58	7.6	788	1.7	bd	468	0.78	58.30	40.93	261	6	3	1	3	5	1,061	1,462	61	321
Oak 500°C	0.197	1.5	600	5.78	4.8	839	1.8	bd	474	3.72	65.58	30.70	147	5	4	0	3	5	1,538	1,171	57	330
Oak 600°C	0.208	0.7	635	6.38	4.8	876	1.7	bd	510	1.31	71.16	27.53	126	7	5	1	3	bd	1,210	2,061	100	52
Pine 300°C	0.141	nd	157	6.74	19.2	621	1.0	bd	676	1.48	43.20	55.32	289	19	6	4	3	255	2,927	692	680	327
Pine 400°C	0.167	1.4	413	4.57	10.8	744	0.9	bd	900	1.05	53.48	45.47	304	5	3	1	2	35	2,247	373	482	351
Pine 500°C	0.138	4.7	524	5.62	4.6	834	1.0	bd	896	1.00	62.05	36.95	240	3	5	1	3	1	2,741	682	796	332
Pine 600°C	0.161	1.8	611	5.97	3.8	870	1.3	bd	725	1.07	71.22	27.70	153	4	2	0	2	14	2,167	775	604	320
Dairy manure 300°C	0.172	nd	nd	8.92	211	561	26.6	8.08	21	39.23	10.29	50.48	444	450	303	316	148	5,391	20,185	14,954	8,757	3,808
Dairy manure 400°C	0.169	nd	nd	9.22	201	577	24.2	7.85	26	14.50	26.91	58.58	297	393	340	252	151	6,446	22,552	16,604	9,733	4,405
Dairy manure 500°C	0.120	nd	nd	9.36	217	594	25.8	8.26	23	14.74	42.59	42.67	478	453	330	325	158	3,945	18,505	14,937	8,498	3,861
Dairy manure 600°C	0.120	nd	nd	9.94	234	628	22.5	6.56	28	18.84	41.73	39.43	151	291	413	164	257	8,269	26,518	20,852	11,744	5,051
Food waste 300°C	0.428	nd	nd	7.52	465	653	58.8	4.60	11	23.30	31.28	45.42	104	57	307	27	255	5,874	28,177	13,018	3,337	9,852
Food waste 400°C	0.500	nd	nd	8.27	423	524	36.5	4.06	14	45.96	18.32	35.72	98	157	560	32	413	5,007	51,745	14,557	5,341	9,008
Food waste 500°C	0.457	nd	nd	9.67	573	367	25.6	4.25	14	52.70	13.59	33.71	88	229	388	37	328	7,524	53,779	21,340	4,461	13,708
Food waste 600°C	0.475	nd	nd	10.53	645	232	10.3	4.95	23	51.95	13.56	34.48	34	569	110	266	98	8,150	73,534	27,949	6,567	14,503
Paper waste 300°C	0.230	nd	nd	7.44	71.6	212	0.9	bd	234	50.35	0.00	49.65	83	1,046	0	17	6	827	258,128	2,783	2,428	256
Paper waste 400°C	0.269	nd	nd	8.18	63	200	1.1	bd	185	54.58	1.23	44.20	62	1,210	5	22	9	830	266,234	3,279	2,831	453
Paper waste 500°C	0.315	nd	nd	9.28	25.2	192	0.7	bd	258	57.45	0.03	42.52	29	905	1	19	6	818	289,226	3,339	2,739	295
Paper waste 600°C	0.352	nd	nd	11.14	71.6	192	0.8	bd	250	59.05	0.00	39.95	34	990	bd	20	3	937	311,232	3,848	2,940	370
Poultry 300°C	0.520	1.2	55	8.12	495	259	21.5	10.78	13	46.71	6.54	46.76	362	260	422	149	74	26,414	157,531	40,013	8,914	3,868
Poultry 400°C	0.631	4.0	47	9.85	333	268	12.4	12.66	46	51.74	4.47	43.79	166	273	299	80	49	17,957	265,729	31,751	7,164	3,209
Poultry 500°C	0.549	4.7	88	10.57	419	254	14.1	13.60	18	52.62	4.16	43.22	78	304	379	96	65	30,555	204,205	28,109	10,436	4,537
Poultry 600°C	0.646	6.7	93	10.65	377	236	9.4	13.32	28	55.80	0.00	44.20	59	329	316	100	58	23,596	242,788	27,400	8,769	3,457

SSA specific surface area, *EC* electric conductivity, *CEC* cation exchange capacity, *bd* below detection, *nd* not determined

Experimental setup

A greenhouse experiment was set up using pots with a height of 360 mm and average diameter of 100 mm (Treepots Short One, Stuewe and Sons, Tangent, OR, USA). Each pot received a uniform volume of 1.65 L of either soil or a soil and biochar mixture. Application rates of biochar included 0.0%, 0.2%, 0.5%, 2.0%, and 7.0% on a dry weight basis (w/w), except for the wider set of biochars, which were applied only at a rate of 2%. These biochar application rates correspond to 0.0, 2.6, 6.5, 26, and 91 t biochar ha^{-1}. The amount of biochar required for each application rate was combined with the soil in a V-Mixer for a minimum of 15 revolutions. The greenhouse at the Guterman Bioclimatic Laboratories, Cornell University, was maintained at temperatures recommended for corn growth, at 24°C during day and 18°C at night. The pots were randomly positioned on benches. For each biochar, the experiment included two replicate pots of each application rate at each production temperature, and three replicates for the wider set of biochars. Controls without biochar addition had six replicates. The drainage holes of the pots were fitted with fiberglass window mesh to prevent soil loss from irrigation, but pots were otherwise allowed to drain freely. After the soil had been prepared and biochar added, three seeds (Yieldguard Hybrid treated seed, Dyna-Gro, Loveland, CO, USA) were planted approximately 40 mm deep in the center of the pots. At 9 days after germination, the two weakest seedlings were culled. All pots received the same amount of irrigation initiated at the first signs of leaf curl to minimize drought stress, with a total of 24 watering events over the course of the corn growth. The amount added was adjusted to match or exceed the water holding capacity and to initiate leaching as determined from measurements of field capacity and preliminary column experiments without plants on all mixtures as well as the control. This procedure would minimize effects of biochars on water availability, but maximize biochar effects on nutrient retention as percolation would occur.

Each pot was given an identical dose of starter fertilizer via fertigation. The recommended treatment for a corn crop was 10–20–20 (NPK: N as urea, P as diammonium phosphate, K as muriate of potash) at 123 kg ha^{-1}, with an application of 12 kg N ha^{-1}, 10 kg P ha^{-1}, and 10 kg K ha^{-1}. The fertilizer was ground to pass a #50 mesh sieve to ensure uniform application and accurate weighing. The fertilizer was then dissolved into water and administered via fertigation in three consecutive applications of 136 mL per pot to prevent leaching losses during application. All of the pots received an additional application of N fertilizer in the form of uncoated granular urea topdressing (46–0–0) in the amount of 134 kg N ha^{-1}. The

fertilizer was ground to pass a #50 mesh sieve to ensure uniform application and accurate weighing. The fertilizer was then dissolved into water and administered via fertigation in one application of 136 mL per pot. The control pots, which did not receive biochar, received the same amount of fertilizer and were replicated six times. No pesticides or herbicides were applied, since no weeds were expected and no disease or pest symptoms were visible.

Plant sampling

The corn plants were harvested 46 days after planting. The above ground biomass was collected by severing at the base of the corn stalk. The below ground biomass was manually separated from the potting soil and washed off soil and biochar particles. All biomass was dried to constant weight at 60°C, weighed, and finely ground with a ball mill. A weighted average of above and below ground biomass was composited before chemical analyses.

Plant and biochar analyses

Biochar pH values were obtained in duplicate using a ratio of 1.0 g of biochar in 20 mL deionized water with the modification that the time on the shaker was increased to 1.5 h to ensure sufficient equilibration between solution and biochar surfaces. Electric conductivity (EC) was then determined with an Orion model 115A plus conductivity meter (Thermo Fisher Scientific, Waltham, MA).

Biomass N analysis, biochar C and N analyses as well as N isotope determination were performed after sample combustion to CO_2 and N_2 at 1,000°C in an online elemental analyzer (PDZEuropa ANCA-GSL, Crewe, UK) coupled to a continuous flow isotope ratio mass spectrometry (20–20 mass spectrometer, Sercon, Crewe, UK). Nitrogen uptake was calculated by multiplying N concentration with biomass production.

Potential CEC was determined by saturating 1.0 g of the biochar with 50 mL of 1 N ammonium acetate at pH 7 and placing on a shaker table overnight. The shaking ensured sufficient wetting of the biochar surfaces. After shaking, the initial 50 mL of 1 N ammonium acetate was extracted by vacuum with an automatic extractor, and a second addition of 40 mL ammonium acetate was added. The samples were then washed with ethanol three times with a total volume of 60 mL and then received 50 mL of 2 N KCl. This initial 50-mL addition of 2 N KCl was allowed to stand 16 h to ensure adequate time for replacement of the absorbed NH_4^+ cations. The initial 50 mL was extracted and then immediately followed by a second addition of 40 mL of 2 N KCL and subsequent extraction. The extracted NH_4^+ was quantified using a continuous flow analyzer (Technicon

Auto Analyzer, Chauncey, CT, USA). Exchangeable cations in the biochars were quantified in the ammonium acetate extract by inductively coupled plasma spectrophotometry (ICP-AES, Spectro CIROS, CCD, Germany).

Total P, Ca, Mg, K, and Na were obtained after dry combustion by heating to 500°C over 2 h and holding at 500°C for 8 h. Five-milliliter HNO_3 were added to each vessel and digested at 120°C until dryness. Tubes were removed from the block and allowed to cool before adding 1.0 mL HNO_3 and 4.0 mL H_2O_2. Samples were placed back into a preheated block and processed at 120°C to dryness, then dissolved with 1.43 mL HNO_3, made up with 18.57 mL deionized water to achieve 5% acid concentration, sonicated for 10 min, and filtered.

Bulk density of the biochars was quantified, after sieving to achieve a particle size range of 149–850 μm, by tamping biochar in a glass cuvette with a diameter of 25 mm and a height of 70 mm. Specific surface area was assessed using two different methods, BET-N_2 and CO_2 sorption isotherms collected on a Quantachrome Autosorb 1. External surface area (pores >1.5 nm) was calculated using multipoint adsorption data from the linear segment (in partial pressure range of 0.001 to 0.03) of the N_2 adsorption isotherms (at 77 K) using Brunauer–Emmett–Teller theory. Total surface area (including pores <1.5 nm) was determined using CO_2 adsorption isotherms (at 273 K) generated in the partial pressure range <0.02. These isotherms were interpreted using Grand Canonical Monte Carlo simulations and the non-local density functional theory. Biochars were degassed under vacuum at 200°C for at least 24 h prior to analysis. Proximate analyses were used to assess volatile matter, "fixed carbon," and ash according to ASTM D1762-84 Chemical Analysis of Wood Charcoal, on a mass weight basis. In brief, volatile matter was quantified as the mass loss by heating to 950°C for 10 min, ash by heating to 750°C for 6 h, and mass of fixed carbon calculated by difference. Biochar samples were analyzed in duplicate.

Mixtures of soil and biochar at all rates as well as the control were analyzed for field capacity and permanent wilting point, from which plant-available water capacity (AWC) was calculated by difference between water retained at permanent wilting point and at field capacity. Soil or mixtures were filled in rings with a height of 10 mm and an interior diameter of 35 mm. The installations were carefully wetted from below and drained in a pressurized chamber to either 1.1 or 15 bar on ceramic plates specific to each pressure (Chamber 1600 and 1500, Soil Moisture Equipment, Santa Barbara CA, USA), allowed to equilibrate for 5 days, and weighed after reaching constant water contents. Water content was determined by drying at 105°C for 8 h, and field capacity and permanent wilting point were calculated.

Statistical analyses

Three-way analysis of variance (ANOVA) with the factors application rate, feedstock, and pyrolysis temperature was performed using a completely randomized design (JMP 8 software, SAS, Cary, NC, USA). Adequacy of replication was verified by three-way interactions. Post hoc comparisons were conducted using least significant difference (LSD) at $P < 0.05$, but only broad trends across factors and with pooled treatments were considered (due to low replication of individual treatments). Pair-wise linear correlations and multiple regressions were computed at $P < 0.05$ unless otherwise noted.

Results

Biochar properties

Bulk density of the biochars (Table 1) was not affected by pyrolysis temperature ($P = 0.969$), but mainly by feedstock type ($P < 0.05$). The lowest densities were observed with biochars made from corn stover, wood, and dairy manure, the highest with biochars made from food waste, hazelnut shells, and poultry manure with sawdust ($P < 0.05$). Poultry manure biochar had five times the density of corn stover biochar. Specific surface areas determined with N_2 indicating pores >2 nm was low for all biochars. Specific surface area including pores <2 nm determined with CO_2, however, increased two to four-fold with charring temperature and was nearly one order of magnitude lower for biochar made from poultry manure than from any other feedstock studied. AWC in mixtures of biochar and soil was either not significantly different from the control or increased with no discernable effect of application rate across feedstocks (Supplementary Fig. S1). Mixtures with biochars produced at intermediate pyrolysis temperatures had greater AWC than those produced at high or low temperatures ($P < 0.01$). On average, biochar made from corn increased AWC more than biochar made from woody feedstock (oak, pine) or paper mill waste ($P < 0.05$).

The pH values were the lowest in wood biochars (4.25–6.38) and the highest in animal manure biochars (8.12–10.65) (contrasts significant at $P < 0.05$). Pyrolysis temperature caused pH values to vary less than half as much as feedstock properties among the biochars studied here. CEC was the highest ($P < 0.05$) in corn stover, oak, and manure biochars and the lowest in biochars made from food waste, paper mill waste, and hazelnut shells, with a trend toward decreasing CEC with increasing pyrolysis temperature. Total C, N, P and metal contents as well as EC and ash content of the studied biochars varied to the largest extent with feedstock type and less with pyrolysis temperature.

However, volatile and fixed carbon contents varied to a greater degree with pyrolysis temperature.

Biomass production

Across all biochar types, average total biomass production was similar for application rates of 0.2%, 0.5%, and 2%, but significantly lower at 7%. However, there were large differences between individual biochars (significant interaction between application rate, pyrolysis temperature, and feedstock; Supplementary Table S1). For our selection of biochars, feedstock type had an eight times greater effect on corn biomass production than pyrolysis temperature (Supplementary Table S2). Except for large applications (7%), biochar made from corn stover, oak, and pine wood and animal manures generated positive or no growth responses (Fig. 1). Biochar from hazelnut shells did not significantly affect growth. At lower pyrolysis temperatures of 300°C and 400°C, biochar made from food waste and paper mill waste resulted in significant growth reductions. With increasing pyrolysis temperature, however, the negative effects of food and paper mill waste biochars decreased. On average, biochars produced at 500°C had significantly ($P<0.05$) better growth than those produced at 300°C and 400°C. Biochar made from poultry litter maintained greater plant growth than the control without biochar additions irrespective of application rate and pyrolysis temperature. The shoot-to-root ratio was the highest ($P<0.05$) at 2% application rate and significantly greater for biochar made from dairy manure than any of the other biochars (Supplementary Table S7).

Nitrogen concentration and uptake

Tissue N concentration (Table 2) and total N uptake (Fig. 2) decreased, on average, with increasing pyrolysis temperature and application rate ($P<0.05$; Supplementary Table S3). Differences in tissue N concentration between treatments were consistent between application rates (no significant interaction with application rate, $P=0.666$). Across all feedstocks, corn grown with food waste biochar showed the highest N concentrations ($P<0.05$; Supplementary Table S6) but had low total N uptake (Fig. 2). Pyrolysis temperature had a significant influence on the extent to which biochars produced from different feedstocks influenced tissue N concentration. At low pyrolysis temperatures, poultry manure biochars had 33% higher average N tissue concentrations than the unamended control, but this decreased for corn grown in biochar charred at greater temperatures (Table 2). Total N uptake after application of low-temperature biochar made from poultry manure increased with greater application rates while N uptake decreased for biochars made from all other feedstocks.

Nitrogen isotope values

The N isotope values of all of the biochars ($\delta^{15}N$ between 1.8 and 13.6; Table 1) were greater than that of the added starter fertilizer ($\delta^{15}N$ of −0.13‰), and many were greater than that of the granular topdressing (4.94‰). However, the $\delta^{15}N$ values of the corn tissue (Fig. 3) were little influenced by biochar additions. Minor increases were observed when biochars made at low temperature from N-rich poultry manure were added.

Correlation between biochar properties and corn growth or N uptake

Simple linear correlation analysis revealed large differences in responses depending on application rate (Table 3). At low application rates (0.2%), only CEC correlated weakly with crop growth (Table 3). Similarly, multiple regressions did not explain biomass production at low application rates well ($r^2<0.3$; $P>0.6$). However, N uptake at 0.2% application rate correlated positively with tissue N concentrations and negatively with the C/N ratios (Table 3). At a higher level of biochar application (0.5%), these relationships between N or C/N ratios and N uptake were even more apparent, even between N or C/N ratios and total biomass production.

At 0.5% and 2%, the amount of P, K, and Mg uptake in the corn correlated well with biomass production (Table 3), which was also reflected in a positive correlation with pH and EC. At the highest application rate of 7%, biochar Na contents dominated the correlations by negatively affecting crop growth. Still, greater K contents had a positive influence on growth also at these high application rates (multiple regression with all total elemental contents at 7%, K: $\beta=0.675$, $P=0.026$; $r^2=0.746$), which was not apparent in simple regressions due to the overwhelming negative effect of Na. None of the ASTM properties (fixed carbon, volatile matter, ash) or the AWC was significantly correlated with crop growth or N uptake ($P>0.05$).

Discussion

Crop growth with biochar

Feedstock type was more important than pyrolysis temperature for understanding to what extent biochars on average influenced crop growth in the present short-term experiment. However, some biochars triggered improved growth with increasing pyrolysis temperatures, whereas others caused decreased growth. Therefore, pyrolysis temperature remains an important variable to improve biochar performance for soil fertility management, as indicated by
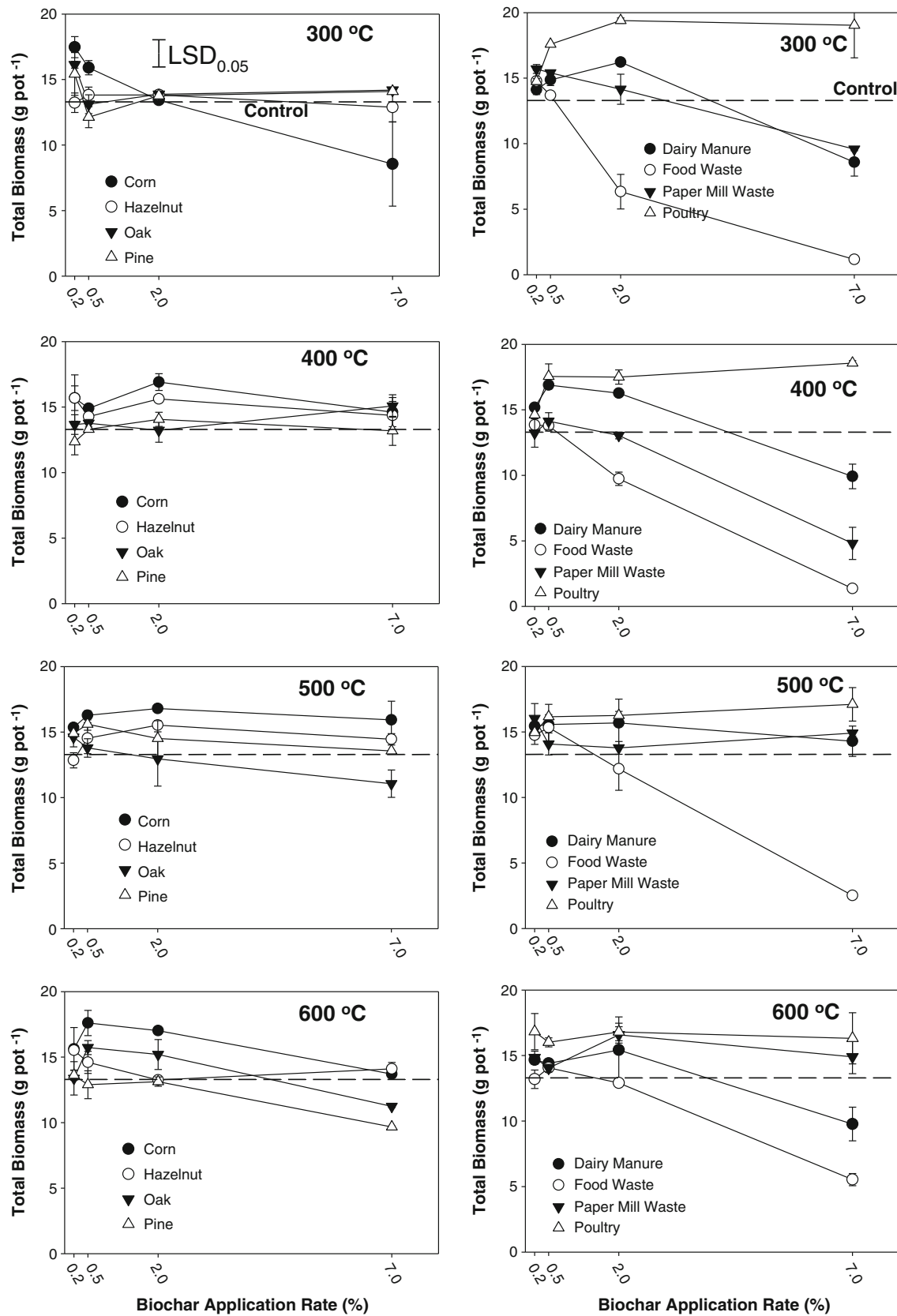
Fig. 1 Total biomass production (root and shoot) of corn with different biochars added (*symbols*) in comparison to the control (*dashed horizontal line*) without biochar additions (means and standard errors; *N*=2 for biochar-amended soils; *N*=6 for control without biochar additions; temperature refers to pyrolysis temperature; *LSD* least significant difference)

Table 2 Tissue N concentration of total corn plants grown in soil with different biochars additions ($LSD_{0.05}$=2.55 between feedstocks, 2.64 in comparison to control; N=2 for biochar-amended soils; N=6 for control without biochar additions)

Biochar	Tissue N concentrations (mg g^{-1})				
	Biochar application rates (w/w)				
	0.0%	0.2%	0.5%	2.0%	7.0%
Corn 300°C	10.07	9.55	9.68	10.57	8.56
Corn 400°C	10.07	9.43	9.57	9.59	8.15
Corn 500°C	10.07	10.13	9.85	8.10	8.97
Corn 600°C	10.07	8.76	8.47	8.64	8.55
Hazelnut 300°C	10.07	11.25	10.12	9.55	10.08
Hazelnut 400°C	10.07	9.80	9.95	9.21	8.52
Hazelnut 500°C	10.07	11.56	9.71	9.83	9.08
Hazelnut 600°C	10.07	9.07	10.21	9.43	8.64
Oak 300°C	10.07	9.98	10.32	9.51	9.75
Oak 400°C	10.07	10.69	9.69	10.21	10.24
Oak 500°C	10.07	11.95	10.30	8.95	9.88
Oak 600°C	10.07	9.62	9.26	8.73	8.43
Pine 300°C	10.07	10.50	9.56	10.71	10.02
Pine 400°C	10.07	10.18	10.85	10.24	9.34
Pine 500°C	10.07	9.19	10.08	9.77	10.16
Pine 600°C	10.07	10.05	9.78	10.11	9.36
Dairy manure 300°C	10.07	10.13	8.93	9.16	9.16
Dairy manure 400°C	10.07	9.96	9.59	10.26	8.47
Dairy manure 500°C	10.07	8.14	9.27	9.10	9.89
Dairy manure 600°C	10.07	8.88	9.59	9.15	8.93
Food waste 300°C	10.07	12.03	16.89	13.56	9.37
Food waste 400°C	10.07	11.84	9.31	13.45	9.76
Food waste 500°C	10.07	14.12	12.62	10.41	9.88
Food waste 600°C	10.07	11.25	10.07	9.92	10.56
Paper waste 300°C	10.07	9.57	9.72	10.36	9.73
Paper waste 400°C	10.07	10.48	10.87	9.65	9.31
Paper waste 500°C	10.07	10.53	10.06	9.99	9.20
Paper waste 600°C	10.07	10.37	10.47	9.87	9.66
Poultry 300°C	10.07	15.99	10.90	11.31	15.21
Poultry 400°C	10.07	9.25	10.16	9.26	9.64
Poultry 500°C	10.07	10.16	8.65	9.19	9.39
Poultry 600°C	10.07	9.68	8.92	8.69	8.68

Makoto et al. (2011) for biochar made at 400°C and 800°C which was added to larch seedlings.

A comparison of biochars made by a variety of technologies, including flash pyrolysis, fast pyrolysis, torrefaction, or gasification (Supplementary Table S8), did not show a systematic difference that superseded the effect of feedstock (Fig. 4). The nutrient-rich biochars such as those produced from animal manures or graminaceous plants (switchgrass, corn, rice husks) generally improved crop growth over the short period of this experiment,

irrespective of production technology (Fig. 4). However, direct comparisons between different pyrolysis technologies by using identical feedstocks are needed in future studies to avoid biases due to different starting materials. In addition, these results are only valid for corn grown on a relatively fertile Alfisol under optimal fertilization. Improvements in pH or nutrient retention observed for many other locations with poorer soils (Lehmann et al. 2003b; Steiner et al. 2007; Van Zwieten et al. 2010b) did not have a large effect on crop growth especially at high application rates, as expected for this experiment. In addition, soil water availability was maintained at levels that would minimize growth reductions due to water stress, and AWC of biochar–soil mixtures did not correlate with plant growth. Therefore, this experiment rather tested what biochar properties would reduce plant growth under otherwise optimum conditions. However, even on the relatively fertile Alfisol investigated here, half of the studied biochars showed average growth improvements of 20% at application rates of 2.6 and 6.5 t ha^{-1} compared to a fully fertilized control without biochar additions.

Biochar made from plant residues such as hazelnut shells, pine, and oak showed little improvement of the relatively fertile Alfisol, with the exception of biochar from corn stover which significantly improved crop growth on average by 16% (range between −36% and +32% depending on pyrolysis temperature and application rates). Pyrolysis of animal manures, food waste, and paper mill waste generated biochars that were either beneficial or detrimental to crop performance. Similarly, very different growth responses were found for sugar cane grown with biochar made from either bagasse or biosolids (Chen et al. 2010). These results stress the importance of quantifying yield responses to biochars made from different feedstocks before large-scale application.

Increasing application rates in our study beyond 26 t ha^{-1} (2%) had either positive, negative, or no effects on corn growth, depending on the biochar. In comparison, Lehmann et al. (2003b) found improved rice growth in an Oxisol when application rates of biochar made from woody material was increased from 95 to 180 t ha^{-1}. Similarly, Chan et al. (2007, 2008) showed increasing crop growth from 50 to 100 or 10 to 50 t ha^{-1} of green waste or poultry manure biochar added to an acid Alfisol. Rondon et al. (2007) reported improved bean growth in response to increasing rates of eucalyptus wood biochar from 66 to 122 t ha^{-1} added to a highly weathered savanna soil, but decreasing growth upon further increases to 188 t ha^{-1}. Our results expand these findings by clearly showing the short-term growth dependency on primarily feedstock type and secondarily pyrolysis temperature of a wider selection of biochars. The responses to increasing rates of biochar application may also depend on the crop, which was not
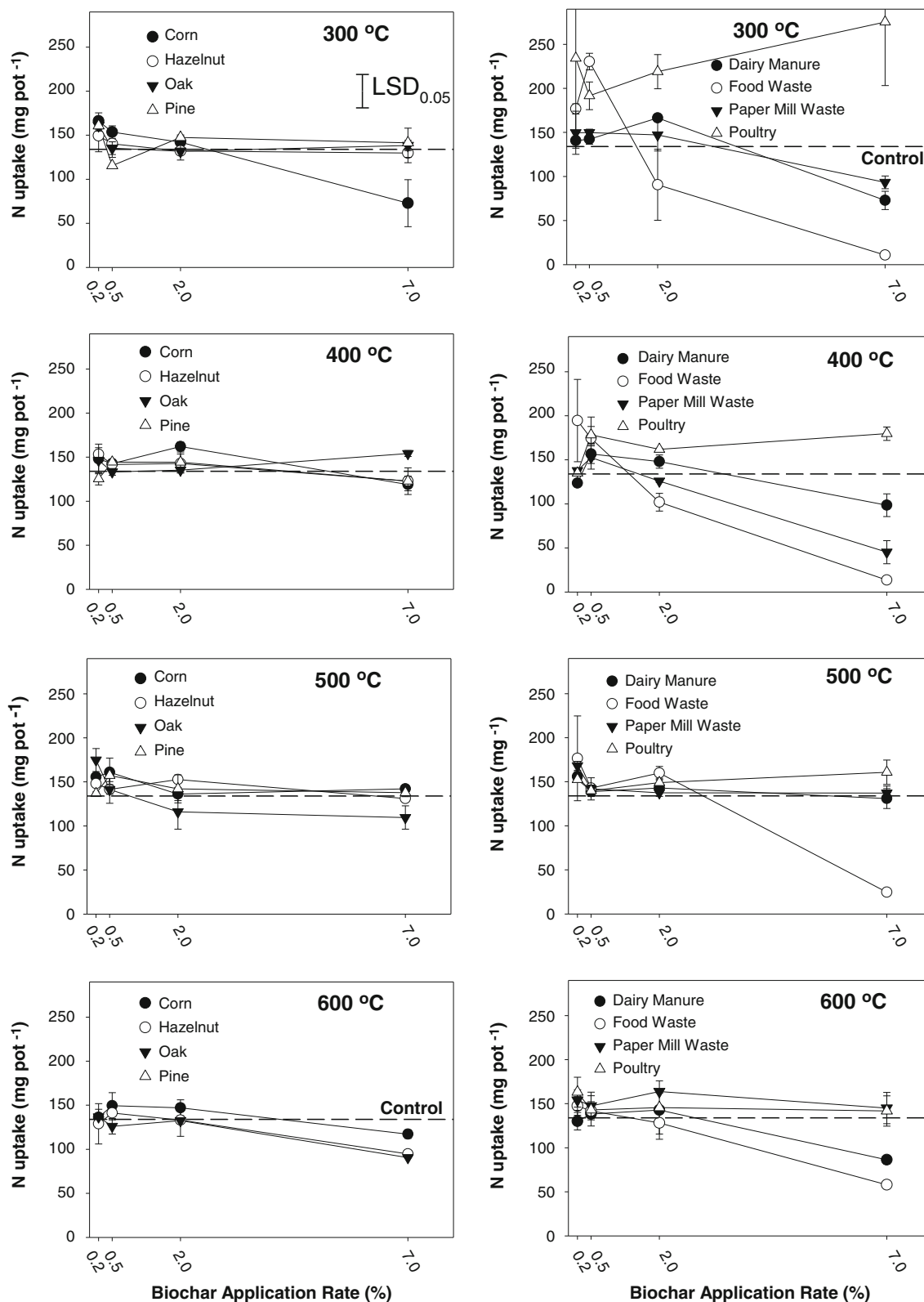
Fig. 2 Total N uptake (root and shoot) of corn with different biochars added (*symbols*) in comparison to the control (*dashed horizontal line*) without biochar additions (means and standard errors; *N*=2 for biochar-amended soils; *N*=6 for control without biochar additions; temperature refers to pyrolysis temperature; *LSD* least significant difference)
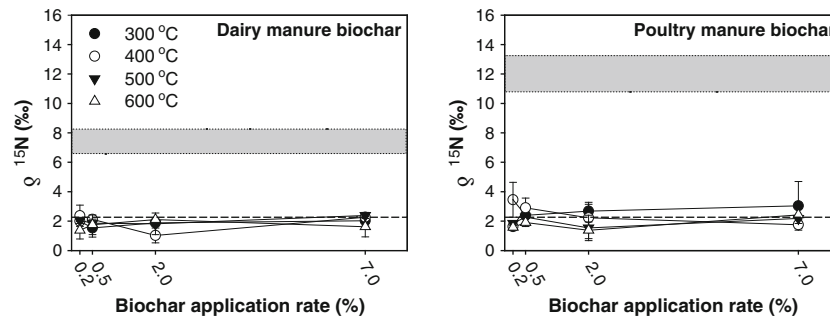
Fig. 3 Nitrogen stable isotope values ($\delta^{15}N$) of the total corn biomass amended with biochar made from either digested dairy manure or poultry with sawdust at different pyrolysis temperatures in comparison to the control (*dashed line*) without biochar additions (means and

standard errors; $N=2$ for biochar-amended soils; $N=6$ for control without biochar additions; *gray area* indicate the $\delta^{15}N$ values of the original biochar) ($\delta^{15}N$ of −0.13‰ for the starter and $\delta^{15}N$ of 4.94‰ for the granular topdressing)

Table 3 Correlation coefficients (r^2) for linear relationships between biochar properties and biomass production or N uptake ($N=32$; except SSA $N=20$); significant correlations at $P<0.05$ are shown in bold

Biochar properties	Biomass production			
	Biochar application rates (w/w)			
	0.2%	0.5%	2.0%	7.0%
Bulk density	−0.005	0.026	−0.002	0.002
SSA (CO_2)[a]	−0.144	−0.060	−0.163	**−0.246**
Available water capacity	0.017	0.018	0.005	0.014
pH (water)	0.063	**0.234**	**0.124**	0.001
EC	0.003	**0.146**	−0.006	−0.108
Fixed Carbon (ASTM)	−0.036	−0.053	0.012	0.013
Volatile Matter (ASTM)	0.078	−0.013	0.004	−0.007
Ash (ASTM)	0.100	0.088	0.009	−0.025
C	−0.036	−0.062	−0.031	0.000
N	0.002	0.033	**−0.131**	**−0.261**
C/N ratio	−0.077	**−0.241**	−0.020	−0.025
CEC	**0.134**	0.059	0.100	0.041
Available Ca	0.006	0.002	0.002	−0.026
Available K	0.042	**0.261**	0.002	−0.017
Available Na	−0.007	−0.000	**−0.178**	**−0.447**
Available Mg	0.006	**0.140**	0.109	0.003
Total P	0.021	**0.289**	**0.136**	0.071
Total Ca	−0.023	0.055	0.049	0.029
Total K	0.051	**0.498**	**0.167**	0.015
Total Mg	0.084	**0.411**	**0.192**	0.004
Total Na	−0.020	−0.006	**−0.133**	**−0.358**
	N uptake			
N	**0.269**	**0.342**	**0.152**	0.011
C/N	**−0.226**	**−0.239**	**−0.208**	−0.100

[a] The correlation was skewed by the low surface area of poultry manure biochar, excluding poultry manure biochar yields $r^2 <0.15$ ($P>0.1$)

addressed in our study. Wheat biomass production on an acid tropical soil increased linearly up to an application of 10 t ha^{-1} (2.2%) and decreased with 20 and 50 t ha^{-1} (4.4% and 11%), whereas growth of radish did not decrease at high application rates (Van Zwieten et al. 2010b).

Biochar properties and corn growth

Among the measured biochar properties, nutrient contents were largely responsible for positive crop responses at low to intermediate application rates of 0.2% to 2%, whereas the Na contents limited growth at high application rates of 7%. Additions of P, K, or Mg are expected to improve plant growth. The positive correlation between pH values and crop growth (Table 3) may not be a result of an actually improving pH but a correlation with base cations ($r^2>0.35$; $P<0.05$), since the pH of the studied soil is already at pH 6.85 and an improvement with greater pH is not expected.

The reduction of plant growth by Na may be partly explained by increases in osmotic potential that reduces water uptake. The lack of a significant negative relationship between growth and other metals or EC may indicate, however, that Na also directly affected plant growth. Sodium has been found to be the most toxic ion to corn grown in slightly saline soils (Fortmeier and Schubert 1995) and may explain growth reductions at high biochar application rates of 91 t ha^{-1}, which added 1.3 t ha^{-1} of Na with biochar made from food waste. Direct salinity is likely to have played a role, as Ca additions alone added 14 to 28 t ha^{-1} with biochars made from food or paper mill waste, which contained almost no Na and still caused growth reductions at high application rates.

Nitrogen was likely immobilized with addition of some of the biochars as evident from the low foliar N concentrations and low N uptake. This was most visible at high application rates (with the lowest tissue N concentrations; Table 2) and likely the most important effect reducing plant
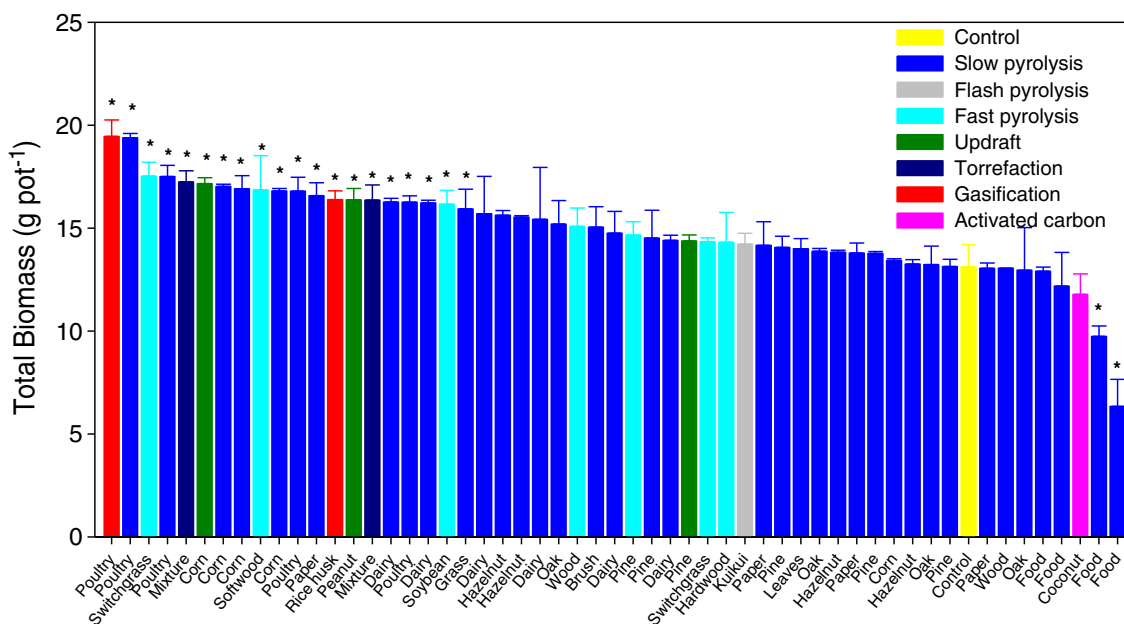
Fig. 4 Biomass production (root and shoot) of corn with additions of 2% by weight of biochars (26 t ha^{-1}) produced using different thermal procedures in comparison to an unamended control (means and standard errors; $N=2$–3 for biochar-amended soils; $N=6$ for control without biochar additions; ANOVA $P<0.0001$; treatments marked with an asterisk are significantly different from the control; crop names indicate biochars made from their residues and animal names indicate those made from their manures; further explanation of production conditions and feedstocks are given in Supplementary Materials)

growth for biochars with low C/N ratios made at low pyrolysis temperatures. Lower foliar N and N uptake was also observed in biochar-amended tropical soils cropped to rice and beans (Lehmann et al. 2003b; Rondon et al. 2007). Immobilization of inorganic N by microorganisms is common during the decomposition of organic materials that have low N contents (Parton et al. 2007). Despite the high stability of most biochars over long periods of time, a small portion may remain mineralizable over short periods of time (Lehmann et al. 2010) and may cause the observed reduction in N availability. Typically, a few percent of biochar is mineralized within weeks or months (Kuzyakov et al. 2009; Nguyen et al. 2010) and can stimulate growth of microbial populations (Steiner et al. 2008b). This effect is expected to be transient and limited to the period of initial mineralization of the more labile fraction of biochars. The proportion of such a labile fraction decreases with increasing pyrolysis temperature which may be indicated by the volatile matter contents (Zimmerman 2010). A lower proportion of the mineralizable biochar fraction may at least partly explain why yield reductions became less pronounced with increasing pyrolysis temperature (Fig. 1) but does not constitute a dominant effect as shown by the poor correlations between volatile matter and growth across all biochars (Table 3).

On the other hand, biochars with high N contents improved N nutrition which was most important in comparison to other growth-controlling factors at low application rates. Improved N nutrition was not a result of a direct N addition by the biochars, since we would expect a ^{15}N isotope change in the corn. A stable N isotope change in corn was not even observed with addition of the N-rich biochars (Fig. 3), which is unlikely a result of different N isotope enrichment of the labile biochar fraction since the δ^{15}N did not change with increasing pyrolysis temperature. Similarly, Gaskin et al. (2010) did not find uptake of N from an N-rich biochar made from peanut shells. Therefore, improved N use efficiency is the most likely explanation, which has been observed after biochar additions to various tropical soils (Chan et al. 2007; Steiner et al. 2008a; Van Zwieten et al. 2010b). A reduction of ammonium leaching by adsorption is possible (Lehmann et al. 2003b), but CEC of the fresh biochars is still low and sufficiently high in the studied soils without biochar additions. Therefore, an improvement in cation adsorption may not be expected at application rates between 0.2% and 7%. More likely is a microbial cycling of applied N as hypothesized by Steiner et al. (2008a). Nitrogen fertilizer may have been immobilized in the microbial biomass and adsorbed in organic form to biochar surfaces (Steiner et al. 2008a). Such cycling of N in microbial biomass and organic N forms may also reduce the opportunity of ammonium to become unavailable to plants by fixation in clay minerals dominated by vermiculites and illites (Nieder et al. 2011) as these are likely present in our soils (USDA 1965). Similarly possible is a reduction in gaseous N losses by denitrification that has

been observed after additions of biochar and high N applications (Taghizadeh-Toosi et al. 2011).

Even though AWC was in some cases significantly improved with biochar additions confirming earlier results (Tryon 1948; Kishimoto and Sugiura 1985; Brockhoff et al. 2010), AWC did not correlate with plant growth. This may not necessarily be explained by a lack of relevant changes in AWC but rather by the way in which the experiment was designed, since watering was done before significant water stress occurred. Under field or greenhouse conditions where water is limiting, the measured differences in AWC may be relevant for plant growth, which warrants further research.

Biochar characterization

The most important measured characteristics of biochars that allowed prediction of the studied short-term crop performance on the studied soil were their element contents. The nutrient elements such as P, K, or Mg improved crop growth, whereas Na reduced crop growth. There was no advantage of quantifying available element contents (using ammonium acetate extraction) over total contents (Table 3). Given the different protocols to determine plant-available nutrient contents, quantification of total elemental contents would also be easier to standardize with appropriate methodology (Enders and Lehmann 2011).

Quantification of total ash did not succeed as a predictor of short-term corn growth, despite the importance of metal contents for plant growth in our experiment. The reason may be that ash contains both beneficial nutrients as well as salts that are detrimental to plants at high concentrations, as shown here for Na. Therefore, individual elements must be quantified rather than total ash.

Neither volatile matter nor fixed carbon contents were related to differences in plant growth. However, the short-term nature and the dominance of the nutrient and salt effects in this experiment may have obscured the effect of C quality. The volatile matter content is expected to relate to the easily mineralizable fraction of biochars (Zimmerman 2010). Yet, the volatile matter did not correlate with crop growth. This lack of correlation may indicate that volatile matter is not representing the microbially mineralizable fraction of biochars that may either cause N immobilization or N input depending on its C/N ratios. Either the differences between the biochars were not sufficiently large or the method did not sufficiently capture the proportion that was mineralizable. The relatively wide spread of volatile matter from 23% to 61% suggests that indeed a more appropriate method may need to be applied to determine the fraction that causes differences in N availability.

The C/N ratios provided some predictive capacity for reduced N availability (Table 3), even though it was

measured on the total biochar, of which the largest fraction is likely stable and does not readily decompose. Total N contents proved equally useful to estimate N availability, despite the fact that C contents varied widely (19–87%) and immobilization depends on relative amounts of C sources and N availability.

Several biochar properties and their potential effects on corn were not measured, but may have affected growth. Growth stimulation has been observed through organic substances in the biochar such as phenols and carboxylic acids or shifts in microbial populations toward known growth-promoting microorganisms (Graber et al. 2010). Spokas et al. (2010) showed significant production of ethylene that may promote growth as a plant hormone. Disease resistance was greater with biochar additions to soil (Elad et al. 2010; Elmer and Pignatello 2011). It cannot be excluded that these mechanisms played a role, but were not captured in our study.

Biochar optimization

To optimize crop responses in the short term, nutrient and salt contents in the biochar must be managed such as P, K, Mg, or Na. For the studied biochar, soil, and crop type, there are two options for addressing the negative effects of Na on plant growth: (a) to limit the total Na concentration in the biochar to values around 5,000 mg kg^{-1} or (b) to limit the application rate to between 0.5% and 2% (6.5–26 t ha^{-1}) (Supplementary Fig. S2). Options not studied here also include post-treatment of the biochars such as rinsing that would reduce Na loadings or application at a time of year that would ensure leaching of Na by rainfall before a crop is planted, with the caveat that beneficial nutrients are leached, as well. Blending of different biochars and judicious dosing may be the preferred strategy to avoid the need for post-treatment, minimize nutrient leaching, and maximize resource use efficiency.

In addition, N deficiency may need to be addressed. Higher pyrolysis temperatures of 500–600°C may minimize N immobilization, as the mineralizable fraction of the biochar decreases. Post-treatment to remove mineralizable C from biochars with high C/N ratios may be achievable and should be tested more rigorously. However, effects of treatments such as steam activation on other nutrients have to be considered. Chan et al. (2008) found lower N use efficiency of steam-treated poultry manure biochar made at 550°C compared to untreated biochar made at 450°C, which the authors explained by lower available P contents through steam treatment. In addition to changes in biochar production conditions, also the cropping system can be adapted to such initially lower N availability after biochar addition by choosing legume crops that fix atmospheric N and where biological N$_2$ fixation may even be stimulated by lower N availability (Rondon et al. 2007).

Conclusions

The short-term data shown here apply primarily to the studied biochars and corn crop under the specific soil conditions. The conclusions are not necessarily applicable to field settings, since, for example, Na may have been leached from the studied soil under the temperate climate conditions that it occurs in during early-season rains, and not caused growth depression as shown in the greenhouse experiment with initially little leaching. However, they are directly relevant to horticultural applications that utilize pots and have to be considered for short-term responses even under field conditions.

In addition to biochar properties, growth responses will vary on different soils and with different crops. The complexity of possible interactions between crop, soil, and biochar may be very large, as evident from the present experiment with only one crop and one soil. Decision tools need to be developed that capture this complexity and should be continuously refined.

Post-treatment of biochars may provide useful opportunities to alleviate possible negative effects on crop growth as shown here for Na. In addition, the long-term effect of biochars that may become oxidized in soils over time and from which minerals have been leached should be examined across a similarly wide range of feedstocks and production conditions as in the present study.

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