Biochar and Manure Affect Calcareous Soil and Corn Silage Nutrient Concentrations and Uptake

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Carbon-rich biochar derived from the pyrolysis of biomass can sequester atmospheric CO_2, mitigate climate change, and potentially increase crop productivity. However, research is needed to confirm the suitability and sustainability of biochar application to different soils. To an irrigated calcareous soil, we applied stockpiled dairy manure (42 Mg ha^{-1} dry wt) and hardwood-derived biochar (22.4 Mg ha^{-1}), singly and in combination with manure, along with a control, yielding four treatments. Nitrogen fertilizer was applied when needed (based on preseason soil test N and crop requirements) in all plots and years, with N mineralized from added manure included in this determination. Available soil nutrients (NH_4–N; NO_3–N; Olsen P; and diethylenetriaminepentaacetic acid–extractable K, Mg, Na, Cu, Mn, Zn, and Fe), total C (TC), total N (TN), total organic C (TOC), and pH were evaluated annually, and silage corn nutrient concentration, yield, and uptake were measured over two growing seasons. Biochar treatment resulted in a 1.5-fold increase in available soil Mn and a 1.4-fold increase in TC and TOC, whereas manure produced a 1.2- to 1.7-fold increase in available nutrients (except Fe), compared with controls. In 2009 biochar increased corn silage B concentration but produced no yield increase; in 2010 biochar decreased corn silage TN (33%), S (7%) concentrations, and yield (36%) relative to controls. Manure produced a 1.3-fold increase in corn silage Cu, Mn, S, Mg, K, and TN concentrations and yield compared with the control in 2010. The combined biochar-manure effects were not synergistic except in the case of available soil Mn. In these calcareous soils, biochar did not alter pH or availability of P and cations, as is typically observed for acidic soils. If the second year results are representative, they suggest that biochar applications to calcareous soils may lead to reduced N availability, requiring additional soil N inputs to maintain yield targets.

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The manufacture of biochar (biomass-derived black carbon) via pyrolysis of photosynthetically fixed C biomass, along with the subsequent storage of biochar in soil, provides a real means of reducing atmospheric CO_2 and mitigating climate change (Laird, 2008; Woolf et al., 2010; Matovic, 2011). However, research is needed to evaluate the expediency and sustainability of storing recalcitrant biochars in different types of soils (Matovic, 2011).

Research has evaluated biochar effects on highly weathered soils of the humid tropics and acidic forest soils. The addition of charcoal to these soils increased the pH and decreased aluminum saturation of highly weathered soils via the addition of K, Ca, magnesium (Mg), and sodium (Na) cations, which are present in the biochar or associated ash (Tryon, 1948; Chidumayo, 1994; Glaser et al., 2002). Charcoal also increased the cation exchange capacity, total N (TN), and the availability of P in these soils, and the charcoal itself is an efficient adsorber of polar and hydrophobic molecules (Glaser et al., 2002). Another study found that a forest soil amended with 1% charcoal increased net nitrification rates (DeLuca et al., 2006). Researchers hypothesized that charcoal may adsorb organic compounds that inhibit nitrification or compounds that might otherwise stimulate immobilization (Wardle et al., 1998; Fierer et al., 2001; DeLuca et al., 2006; Gundale and DeLuca, 2007). Charcoal may bind NH_4^+ in the soil or stimulate N immobilization by microbes (Steiner et al., 2008; Deenik et al., 2010), with the latter accomplished by binding organic compounds that inhibit microbial activity (Iswaran et al., 1980; Wardle et al., 1998; DeLuca et al., 2006).

As a result of these effects, charcoal amendments can substantially increase seed germination, crop yields, and crop quality (Glaser et al., 2002; Kadota and Niimi, 2004; Rondon et al., 2007: Steiner et al., 2007; Mu et al., 2004). In some cases, however, negative effects have been described. Deenik et al. (2010) observed reductions in vegetable growth with increasing macadamia nut (*Macadamia integrifolia* Maiden & Betche) charcoal applications when fertilizer was not applied. Growth reduction was attributed to phenolic and other C compounds in the charcoal, which may have stimulated microbial growth and immobilization. This negative C mineralization

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Abbreviations: DTPA, diethylenetriaminepentaacetic acid; EC, electrical conductivity; ICP–AES, inductively coupled plasma atomic emission spectrometry; OC, organic carbon; TC, total carbon; TN, total nitrogen; TOC, total organic carbon.

priming effect of biochar was also reported by Zimmerman et al. (2011), who found that its magnitude was a function of soil organic C (OC) concentration and type of biochar.

Because biochar properties vary with the source of biomass and conditions of pyrolysis (Novak et al., 2009b; Spokas et al., 2010; Zimmerman et al., 2011), comparisons among experiments that use different biochars can be problematic. A number of studies have used the same type of biochar derived from hardwood waste biomass (CQuest; Dynamotive Energy Systems, West Lorne, Ontario, Canada). Experiments using CQuest biochar are underway at various locations across North America, including several that are part of a national effort by the USDA Agricultural Research Service to assess the biochar's effect on soil properties and crop production.

In 2008, a commercial-scale demonstration study applied 3.9 Mg ha^{-1} CQuest to acidic soils in Quebec, Canada. In the following 3 yr, the biochar treatment produced 1.04- to 1.2-fold greater yields than the control (Husk and Major, 2011). When added to a peat-based, acidic nursery container substrate (pH 3.9), the CQuest biochar increased water-extractable Fe, K, Na, P, and B and decreased Al, Ca, Mg, Mn, and S (Dumroese et al., 2011). Other researchers grew asparagus in a New Haven, Connecticut soil (pH 6.9) amended with CQuest, which increased K, S, Mn, and B nutrient concentrations in crop tissue while decreasing N, Mg, and Fe concentrations relative to the control (Elmer and Pignatello, 2011). Minnesota researchers reported that relatively large CQuest biochar additions to an acidic silt loam soil (pH 6.5) generally suppressed CO_2, CH_4, and N_2O production rates during a 100-d incubation (Spokas et al., 2009). This result suggested that the biochar stabilized soil OC, which has implications for N and S availability because they are substantially derived from organic sources.

Before the current study, little published research has evaluated the influence of CQuest or other types of biochar on field soils over several years or determined its effects on soil chemical properties of semiarid, calcareous soils. A few recent studies have evaluated biochar effects on soils with pH values >7, but the soils were developed in wetter climates and contained little if any free lime (Iswaran et al., 1980; Smith et al., 2010; Zimmerman et al., 2011). Blackwell et al. (2010) studied the effect of banded biochar on first-year wheat yields after biochar application to a calcareous soil with relatively high OC (17.2–21.5 g kg^{-1}) in southwestern Australia. When fertilizer was applied, the biochar had little influence on wheat grain yield (Blackwell et al., 2010).

Arid soils tend to have low organic matter concentrations and alkaline pH values, but many are irrigated and intensively cropped under light and temperature regimes that produce near optimal yields (Lobell et al., 2009). Fertility demands on these irrigated soils are high, and adding biochar might benefit soils by increasing their OC content. However, biochar's observed positive impacts on fertility may partially be related to its ability to raise the pH of acidic soils, which is unlikely to occur in biochar-amended calcareous soils. In general, the influence of biochar additions on the fertility of agricultural soils in temperate regions is not well understood (Atkinson et al., 2010). The objective of this study was to determine the effect of CQuest biochar and dairy manure amendments and their interaction on soil chemical properties and crop nutrient uptake of an irrigated, calcareous field soil in southern Idaho.

Materials and Methods

Site, Soils, and Amendments

Experimental plots were established in fall 2008 on sprinkler-irrigated Portneuf silt loam (coarse-silty, mixed superactive, mesic Durinodic Xeric Haplocalcids) with 1.4% slopes near Kimberly, Idaho (42°31′ N, 114°22′ W, elevation of 1190 m). The surface soil contained 200 g kg^{-1} clay, 560 g kg^{-1} silt, 12 g kg^{-1} OC, and 8.8% calcium carbonate equivalent. The soil has a saturated paste extract electrical conductivity (EC) of 0.05 S m^{-1}, exchangeable sodium percentage of 1.5, pH of 7.6 (saturated paste), and a cation exchange capacity of 19 cmol$_c$ kg^{-1}. Soils on the site have been cropped to an alfalfa–corn–bean–grain rotation for the previous 33 yr. No manure had been applied to the soils since 1986.

Solid manure from dairy cattle (*Bos* species) was retrieved from an open pen at a local dairy, where it had been stockpiled through summer 2008 in 1.7-m-high, unconfined piles. The material contained little or no straw bedding and comprised 55.3% solids at time of application. Total C and TN of the organic amendments were determined on a freeze-dried sample with a CN analyzer (Thermo-Finnigan FlashEA1112; CE Elantech Inc., Lakewood, NJ). Total elements were determined by $HClO_4$–HNO_3–HF-HCl digestion (Soltanpour et al., 1996) followed by analysis using inductively coupled plasma atomic emission spectrometry (ICP–AES). Manure NO_3–N and NH_4–N were determined using a 2 mol L^{-1} KCl extract (Mulvaney, 1996). Manure volatile solids were determined gravimetrically by ashing at 550°C for 12 h.

Dry biochar (CQuest) with a <0.5-mm particle size was shipped to the laboratory and stored in sealed steel barrels. The charcoal was manufactured from oak and hickory hardwood sawdust using fast pyrolysis at 500°C. It had a 14% ash content, an O:C ratio of 0.22, and a surface area of 0.75 m^2 g^{-1}. The pH of CQuest was near neutral, at the low end of the pH range observed for biochars, and was preferable to more alkaline amendments for these higher pH soils. Ash content of the biochar was determined using ASTM methods for wood charcoal (600°C). Other chemical characteristics were determined as previously described. Soil, manure, and biochar chemical characteristics are presented in Table 1.

Experimental Design

The experimental design was a randomized complete block with three replicates. Four amendment treatments included (i) a control (no manure or biochar application); (ii) manure application (42 Mg ha^{-1} dry wt. application of stockpiled dairy manure); (iii) biochar application (22.4 Mg ha^{-1} dry wt); and (iv) manure+biochar combined application using rates identical to manure-only and biochar-only treatments. The soil amendments were applied only once, in fall 2008. Spring 2009 soil sampling indicated that plot soils needed to be supplemented only with N to meet the corn silage yield target of 67 Mg ha^{-1} (22.2 Mg ha^{-1} dry wt) for 2009 and 2010. Inorganic N fertilizer was supplied as needed to each plot each spring assuming that 21% of the total manure N added would become available in the first growing season and 12% in the second growing saeson (local unpublished data) and that biochar supplied little N to soils in either year. Plots were 4.6 m wide and 5.2 m long and included six planted rows. Limited biochar availability precluded larger plot sizes and additional experimental blocks. Plots were separated by a 1.5-m-wide planted buffer, and a 4-m-wide planted border strip comprised the perimeter.

Field Operations

Spring barley (*Hordeum vulgare* L.) was grown on the site in 2008. After harvest, the field was moldboard plowed to 0.20-m depth. On 21 Nov. 2008, solid manure from a local dairy was collected and hand-applied to designated plots. The manure was subsampled during application, and the composite volume was stored at 4°C for later analysis. Biochar was hand-applied to designated plots on 24 Nov. 2008, and immediately thereafter all plots were rototilled to 0.15-m depth. The field was roller harrowed on 21 Apr. 2009, and Round-Up ready silage corn (*Zea mays* L.) (Monsanto, St. Louis, MO) was planted on 12 May 2009 in 0.76-m spaced rows. On 8 June 2009, 200 kg N ha^{-1}, as ammonium sulfate, was applied by hand to all nonmanured plots, followed by sprinkler-applied 21-mm irrigation. The initial soil N levels and N from mineralization in manured soils was determined to be adequate for the 2009 corn crop. Two postemergence applications of 2,4D-amine and glyphosate were used in June 2009 to control weeds. Irrigation through the growing season was supplied via sprinkler every 7 to 14 d to meet crop evapotranspiration requirements. Irrigation water had an average electrical conductivity of 0.05 S m^{-1} and sodium adsorption ratio of 0.5. The crop was harvested for silage on 18 Sept. 2009, with the remaining corn stover (15- to 30-cm-tall stems with leaves) flail chopped in preparation for a no-till planting in the spring 2010.

Round-Up ready silage corn was planted into the row spaces of the previous corn crop on 19 May 2010. Planting into the low-lying interrow spaces proved inconsistent across all plots; thus, any skips in emerged seedlings observed within plots were replanted by hand 5 d after the original seeding had emerged. On 25 June 2010, urea was applied to plots by hand at 224 kg N ha^{-1} for nonmanured treatments and 67 kg N ha^{-1} for manured treatments, immediately followed by a 57-mm irrigation. An application of 2,4-dichlorophenoxyacetic acid and dicamba and diflufenzopyr (Distinct; BASF, Florham Park, NJ) was applied on 14 July 2010 to control weeds. Irrigation was applied using the same method as in 2009. Silage corn was harvested in 15 Oct. 2010.

Soil and Plant Sampling and Analyses

Soil samples were collected on 20 Nov. 2008 before amendment applications and again on 21 Apr. 2009, 19 Oct. 2009, and 14 Apr. 2010. Four 0- to 30-cm soil samples were taken from each plot, composited, air dried at 35°C, and crushed to pass a 2-mm screen. Although it is likely that biochar effects were more intense within the layer of incorporation, we anticipated that particulates and dissolved OC from biochar would move downward in the soil profile (Major et al., 2010) and influence mineralization/immobilization in a like manner as manure (Lentz et al., 2011). Thus, we considered that the 0- to 30-cm depth may better incorporate biochar's real affects on soil and crops. The soil-available P was estimated using the Olsen-P method S-4.10 (Gavlak et al., 2003). Soil NO_3–N and NH_4–N were extracted using 2 mol L^{-1} KCl and measured within 6 h of extraction with an automated flow injection analyzer (Lachat Instruments, Loveland, CO). The availability of soil K, Na, Mg, Zn, Mn, Cu, and Fe was estimated by extracting with diethylenetriaminepentaacetic acid (DTPA) (method S-6.10) (Gavlak et al., 2003) and analysis using ICP–AES. We determined soil total C (TC) and TN by combustion using a FlashEA1112 CN analyzer (Thermo-Finnigan, Waltham, MA), total inorganic C using a pressure-calcimeter (Sherrod et al., 2002), and TOC by difference.

Standing above-ground corn biomass and silage yields were measured by hand clipping plants (30 mm above soil surface) from 3 m of two rows. The sample was weighed and chopped, and a subsample was collected, dried at 65°C, and ground in a Thomas Wiley mill (Thomas Wiley, Swedesboro, NJ) to pass an 865-μm screen. The TC and TN concentrations of the subsample were determined as previously described. A 0.50-g subsample was placed in a 100-mL beaker and dry ashed at 500°C for 5 h. The samples were allowed to cool and weighed, and 10 mL of 1 mol L^{-1} HNO_3 were added. The samples were then heated on a hot plate until condensation no longer occurred on the inside of the beaker. Then, all samples were brought to a 50-mL final volume by weight

Table 1. Chemical properties and total mineral and extractable inorganic nitrogen concentrations (all on a dry wt. basis) in amendments and soil.

Material	Volatile solids	EC†	pH	C:N	C	N	NO_3–N‡	NH_4–N‡	Ca	K	P	Na
	g kg^{-1}	dS m^{-1}			g kg^{-1}							
Manure	521	13.4	8.8	11.8	264	22.4	<0.01	<0.01	22.0	13.5	4.1	3.8
Biochar	707	0.7	6.8	208.2	662	3.2	0.2	0.1	3.7	3.4	0.3	0.2
Soil§	–	0.4	7.7	16.4	18	1.1	<0.01	<0.01	33.3	26.8	4.2	10.4
	Mg	Al	Fe	S	Mn	Zn	Cu	B	Ni	Mo	Cd	Pb
	g kg^{-1}			mg kg^{-1}								
Manure	8.2	3.5	4.5	10‡	169	167	77	27.3	3.4	0.5	0.3	1.9
Biochar	1.5	0.3	1.4	80	118	14	17	12.1	4.9	<0.05	<0.05	2.0
Soil§	11.9	52.7	21.4	789	–	71	21	27.3	18	4.7	<1	17

† Electrical conductivity.

‡ Estimated.

§ Values for soil EC, pH, C, and N components are averages for the control treatment (0–30 cm). Values for remaining soil elements are averages for soils from the local area and are included solely to provide a relative comparison with the manure and biochar. Source: US Geological Survey (1975).

with deionized H_2O, stirred, filtered through Whatman #50 filter paper, and analyzed for P, K, Ca, Mg, and trace elements by ICP–AES

Calculations and Statistical Analysis

A repeated measures ANOVA, PROC Mixed (SAS Institute, 2008) was used to test the significance of amendment, sampling time, and their interactions on soil chemical properties. Where needed to stabilize variances and improve normality, soil nutrient concentrations were transformed using common Log or square root. For all significant fixed effects, means were separated using 95% confidence intervals. The means and confidence interval values were back transformed to original units for reporting. An ANOVA, PROC Mixed (SAS Institute, 2008) was used to test the significance of amendment effects on above-ground biomass nutrient and trace element concentrations, total above-ground nutrient uptake, and silage yields. Biomass and yield data for 2009 and 2010 were analyzed separately. Again, transformations of concentration and uptake data were used where appropriate. We also included several more powerful, single-degree-of-freedom contrast tests in the ANOVA analyses. These tested the effect of amendments across all sampling times and compared manure and manure+biochar together as a class vs. no-manure treatments (control, biochar) and compared biochar treatments (biochar, biochar+manure) as a class vs. no biochar treatments (control, manure). All analyses were conducted using at the $P = 0.05$ significance level.

Results

Late spring (May and June) was unusually cool during both years of the study. In 2009 this period was the fourth coldest, and in 2010 late spring was the coldest of all May–June periods in the previous 14 yr. Thus, in 2009 and 2010 corn emergence and seedling establishment was delayed by 1 to 2 wk relative to more typical growing seasons.

Soil Chemical Properties

The ANOVA (Table 2) indicated that amendment, sample date, and their interaction significantly influenced soil chemical properties. Of the main factors, amendment affected all soil properties except pH, DTPA-extractable Fe, and TN, whereas sample date affected all measured soil properties. Biochar itself influenced only soil TC, TOC, and Mn, whereas mean separations and contrast tests indicated that manure had a broader influence on measured soil properties as compared with biochar alone, affecting all soil properties except pH and Fe.

Biochar and manure effects on soil TC and TOC were similar, and the amendments increased TC and TOC in an additive manner (Fig. 1a,b). In 2009, biochar increased soil TOC 1.4-fold, compared with a 1.2-fold increase from manure and a 1.7-fold increase from the biochar+manure treatment relative to the control (Fig. 1b). These proportions remained similar for the April 2010 sampling, even though soil TOC trended lower overall. The April 2009 increase in soil TOC for biochar plots represented 134 ± 57% of the C added, whereas the values for manure and for biochar+manure were 117 ± 71% and 127 ± 62%, respectively (assuming TC = TOC for added biochar and manure and 4.48×10^3 Mg ha^{-1} soil mass for the 0- to 30-cm layer). Total N trended upward in manure applications with or without biochar (Fig. 1c), although the differences were not significant.

Relative to the control in 2009, biochar increased available soil Mn 1.5-fold, while manure produced a 1.4-fold increase (Fig. 2c). Adding biochar with manure produced a synergistic 2.1-fold increase in soil Mn compared with the control (i.e., this increase exceeded the sum of the two amendments individual effects). The influence of biochar and manure on soil Mn was temporary, however, being significant for the two 2009 sampling times but not for April 2010.

Manure treatments generally increased soil nutrient concentrations and EC in 2009. During the 2-yr period, the manure effect varied depending on the nutrient; it was consistent across 2009–10 for Cu and Zn (Fig. 2a,d); decreased with time for Mn, EC, NH_4–N, Mg, K, and Na (Fig. 2c,e and Fig. 3a,d,e,f); or increased with time for NO_3–N and Olsen P (Fig. 3b,c). Across all sampling times, manure treatments as a class increased availability of trace nutrients 1.1- to 1.2-fold and increased macronutrients and EC 1.4- to 1.7-fold as compared with no-manure treatments as a class (Table 3).

Table 2. The influence of amendment and sampling date on soil nutrients, electrical conductivity, and pH at the 0- to 30-cm depth.

Source of variation	NH_4–N	NO_3–N	Olsen P	DTPA† K	DTPA Na	DTPA Mg	DTPA Cu	DTPA Fe	DTPA Mn	DTPA Zn	EC‡	pH	Total C	Total N	Total organic C
	P values§														
Amendment (Amend)	*	***	*	***	***	***	***	ns¶	**	*	**	ns	*	*	**
Sample date (date)	***	***	***	***	***	***	**	***	***	***	***	***	***	*	****
Amend × date	***	ns	**	***	***	**	**	ns	**	*	**	ns	**	ns	**
Contrasts#															
Manure vs. no manure	**	***	**	**	***	***	***	ns	**	*	**	ns	*	*	*
Biochar vs. no biochar	ns	ns	ns	ns	ns	ns	ns	ns	***	ns	ns	ns	**	ns	**

† Diethylenetriaminepentaacetic acid.

‡ Electrical conductivity.

§ *P* values for treatment effects and interaction terms and single-degree-of-freedom orthogonal comparisons derived from an ANOVA (* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$).

¶ Nonsignificant ($P > 0.05$).

Classes compared comprise the following treatments: manure = manure, combined manure+biochar; no manure = control, biochar; biochar = biochar, manure+biochar; no biochar = control, manure.

Biochar had a synergistic effect on soil Mn and K availability when combined with manure, although the benefit faded with time (Fig. 2c and 3d). Similar synergistic trends were observed for Cu and Olsen P, but the differences were not significant (Fig. 2a and 3c).

Corn Silage Yield and Nutrient Concentrations

The statistical analysis (Table 4) indicated that the amendment factor had no significant effect on silage yield and nutrient concentrations in 2009, except that biochar treatments as a class affected silage B concentrations (contrast test). However, in 2010 amendments did influence silage yield and silage Cu, S, and TN concentrations. Manure treatments as a class influenced various silage nutrient concentrations, but only in 2010.

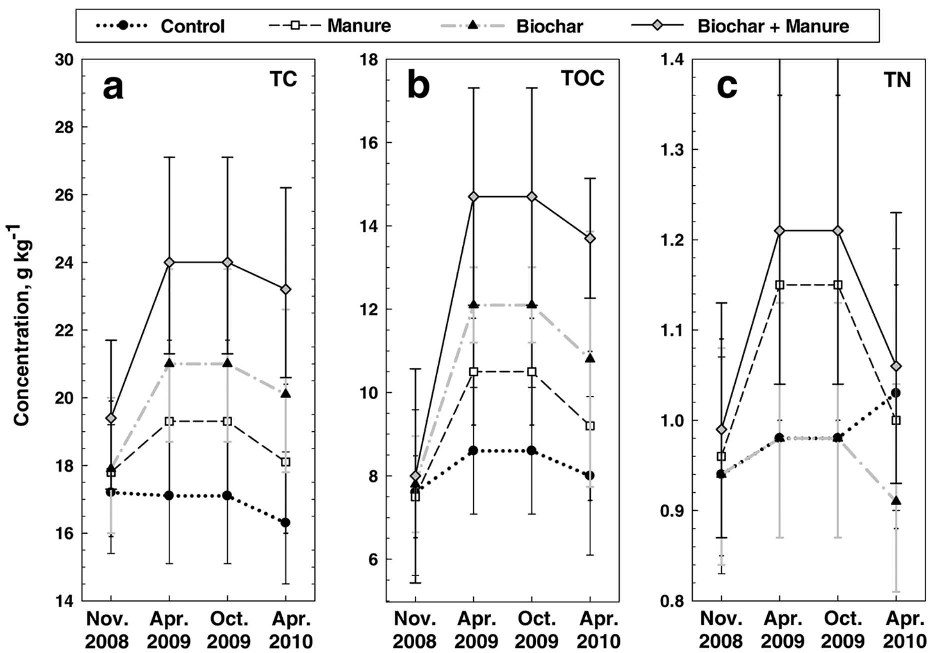

Fig. 1. The effect of organic amendments on 0- to 30-cm soil concentrations. (a) Total carbon (TC). (b) Total organic carbon (TOC). (c) Total nitrogen (TN). Amendments were added immediately after the November 2008 soil sampling. Error bars represent 95% confidence limits on the treatment means.

In 2009 corn silage yields were similar among all treatments and averaged 18.4 Mg ha^{-1} (Table 5), which exceeded our yield target. However, in 2010 the biochar treatment reduced silage yield 36% (to 13.2 Mg ha^{-1}) relative to the average yield of the other three treatments (20.6 Mg ha^{-1}). The 2010 biochar yield was 19% below our target value, whereas other treatments exceeded our target. By contrast, manure as a class increased 2010 silage yields 1.3-fold relative to the mean value for no-manure treatments (Table 5).

In 2009 contrast tests showed that biochar treatments increased silage B concentration 1.5-fold compared with its average concentration in the two no-biochar treatments, 9.45 mg kg^{-1} vs. 6.35 (Table 4). In 2010 biochar decreased silage concentrations 33% for TN and 7% for S (Table 5) compared with the control. Corn leaves in the biochar plots exhibited chlorotic symptoms in 2010, particularly late in the growing season. Like biochar, manure had little effect on silage nutrient concentrations in 2009, but as a class manure produced a mean 1.3-fold increase in 2010 concentrations of Mg, K, TN, Cu, Mn, and S (Table 5) relative to the no-manure treatment class.

Nutrient Uptake in Corn Silage

The ANOVA showed no significant amendment effects on nutrient uptake in 2009, although the contrast tests indicated that biochar treatments as a class increased 2009 B uptake 1.5-fold (0.18 kg ha^{-1} vs. 0.12) compared with that of no-biochar treatments (Table 6). Amendment effects were significant in 2010, indicating that the uptake of the various nutrients was influenced by biochar or manure.

In 2010 treatment mean separations revealed that biochar decreased uptake of Cu, S, Mg, and TC by an average 32% and decreased TN by 52% relative to the control (Table 7). The contrast tests also showed that biochar treatments as a class decreased 2010 B uptake 27% (0.19 kg ha^{-1} vs. 0.26) relative to the mean value for the no-biochar treatments (Tables 6 and 7). This effect on 2010 B uptake was the reverse of that observed in 2009.

In 2010 the contrast tests indicated that manure treatments as a class increased uptake of all measured nutrients relative to the average of no-manure treatments. Manure produced an average 1.5-fold increase in B, Al, Fe, Zn, Mg, Ca, P, and TC uptake; a 1.7-fold increase in Cu, S, K, and TN uptake; and a 2.1-fold in Mn uptake (Table 7).

Discussion

The addition of biochar (0.5% g g^{-1} averaged over the 0- to 30-cm soil depth) increased TC and TOC, as did the manure and biochar+manure treatments. During the April 2009 to April 2010 period, the biochar soil lost 10.7% OC, compared with 12.4% for manure, 7% for biochar+manure, and 7% for the control (Fig. 1). This result suggests not only that biochar is more recalcitrant than manure but also that when the amendments were combined the biochar may have inhibited manure OC losses during the period. The biochar-only soil OC losses were similar to those reported by Steiner et al. (2007) for a tropical soil, and manure-only soil OC losses were on par with values reported for manure applied to local soils (Robbins et al., 2000).

Manure and biochar treatments had little influence on soil pH and had no effect on extractable soil nutrients other than increasing Mn availability in 2009. These results differ from those of many earlier biochar studies, which were commonly conducted with potted, acidic soils and greater biochar additions over <6-mo periods (e.g., Lehmann et al., 2003; Chan et al., 2007). These previous studies indicated that biochar increased soil pH and available K and Na and decreased Al. Other studies reported that biochar additions of as little as

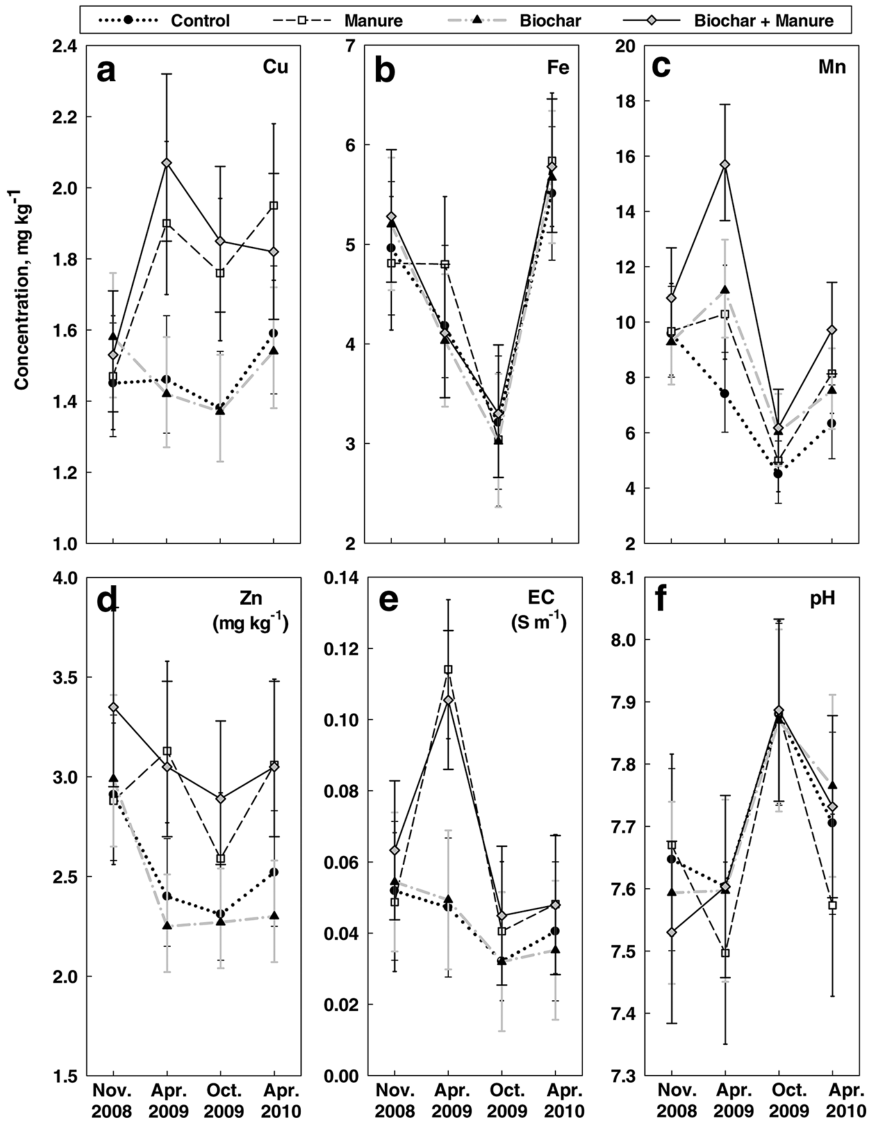

Fig. 2. The effect of organic amendments on 0- to 30-cm soil concentrations. (a) Ammonium N. (b) Nitrate N. (c) Olsen-P. (d–f) Diethylenetriaminepentaacetic acid–extractable K (d), Mg (e), and Na (f). Amendments were added immediately after the November 2008 soil sampling. Error bars represent 95% confidence limits on the treatment means. EC, electrical conductivity.

0.36 to 0.5% increased available P, K, Mg, Mn, Ca, and As and decreased available S, Zn, and Pb (Novak et al., 2009a; Laird et al., 2010; Namgay et al., 2010). The exception to this was a van Zwieten et al. (2010) study for a sandy pH 4.5 soil for which only N was influenced by biochar. Longer-term field research on acid soils (pH <5.6) using ≤1% biochar additions showed increases in soil Ca, K, and Mg in some cases but not in others (Steiner et al., 2007; Major et al., 2010; Gaskin et al., 2010) and that feedstock source influenced the outcome (Gaskin et al., 2010).

The total nutrient concentrations in the calcareous soil we evaluated exceeded those in the added biochar (except C and N), which explains in part why biochar failed to increase soil K and Mg. To increase extractable soil nutrient levels, the CQuest biochar likely would need to provide a more available form of the nutrient or, by decreasing soil pH, make intrinsic nutrient forms more available. Available soil P, Cu, Mn, Zn, and to some extent Fe concentrations did respond to temporal changes in soil pH (Fig. 2a,b,c,d,f and 3c), indicating their sensitivity to this soil property. This suggests the importance of biochar's pH-altering capability for increasing nutrient availability in acid soils. However, in our calcareous soil, the biochar effect on soil pH (i.e., lowering the soil pH using the near-neutral CQuest biochar) was minimal due to buffering by $CaCO_3$ present in the system.

Biochar's temporary boosting of soil Mn availability in 2009 suggests that another factor besides a direct pH effect is responsible. Because biochar and manure included Mn and had a similar positive effect on soil Mn, we assumed both amendments acted as a source of the micronutrient. However, biochar's Mn effects were synergistic when combined with manure, indicating that an additional process affected Mn availability (Fig. 2c). It is not clear if this additional process operates only in the short-term. Biochar may promote or inhibit microbial activity that influences Mn availability (Meek et al., 1968; Abou-Shanab et al., 2003) via changes in microbial populations and activity (Khodadad et al., 2011) or mycorrhizal root colonization (Solaiman et al., 2010). These shifts may result from biochar effects on physical soil properties (e.g., soil water retention) (Glaser et al., 2002; Laird et al., 2010) or release or sorption of microorganism-inhibiting or -promoting chemicals (Uusitalo et al., 2008; Clough and Condron, 2010; Deenik et al., 2010; Spokas et al., 2010) or because biochar provides additional habitat or refugia for organisms (Pietikainen et al., 2000; Warnock et al., 2007). The increased soil Mn availability due to biochar had little impact on silage Mn concentrations. The uptake of Mn concentration by the corn was low (Table 5) relative to the range of values considered to be sufficient (Adriano, 1986). Thus, biochar's enhancing effect on soil Mn availability is not likely to have a negative impact on corn silage yields. Increased Mn availability may be an important benefit in these calcareous soils because of glyphosates's negative influence on Mn and Fe uptake in genetically modified (Round-Up ready) crops (Eker et al., 2006). The increased availability of soil nutrients from manure was expected because manure acts as a mineral source (Table 1) (Eghball et al., 2002) and supports a more active microbial biomass (Burger and Jackson, 2003).

Silage Nutrient Concentrations and Yields

That manure had a greater influence on silage nutrient concentrations than biochar (Table 4) follows from its markedly greater influence on soil nutrient availability. Compared with the control, manure produced the greatest increase in soil NH_4–N, K, Mg, Cu, and Mn in spring 2009 (Fig. 2 and 3), yet these increases did not result in increased corn silage nutrient concentrations or yields until 2010 (Table 5). The reason for this is unclear.

Biochar had little influence on corn silage nutrient concentrations in 2009 but decreased silage TN and S concentrations and yields in 2010 (Table 5). When CQuest biochar was added to slightly acidic soils, Elmer and Pignatello (2011) also reported a decrease in TN in a subsequent asparagus crop relative to the control, but, unlike the current study, they saw an increase in asparagus S concentrations. Other field studies using different biochars and conducted on acidic soils reported that biochar yields were the same as or greater than controls in the second year after biochar application (Steiner et al., 2007, 2008; Gaskin et al., 2010).

Based on nutrient concentration in the silage corn, the yield reduction in 2010 may have resulted from reduced availability or uptake of one or more nutrients. The silage N concentrations for all treatments in 2010 were below typical levels of 10 to 15 mg kg^{-1} (Patni and Culley, 1989; Eghball et al., 2004), and the biochar silage contained the least N of all treatments. Silage S concentrations were also low, and S deficiency produces chlorotic symptoms in corn similar to that of N deficiency; however, the N in biochar corn did not increase with decreased S intake, suggesting that S availability was not limiting (Stewart and Porter, 1969). Finally, Mn and Cu concentrations in biochar silage were below the typical range for Idaho (Mahler, 2004); although concentrations were not always significantly different from other treatments, reduced Mn and Cu uptake may have contributed to reduced yields.

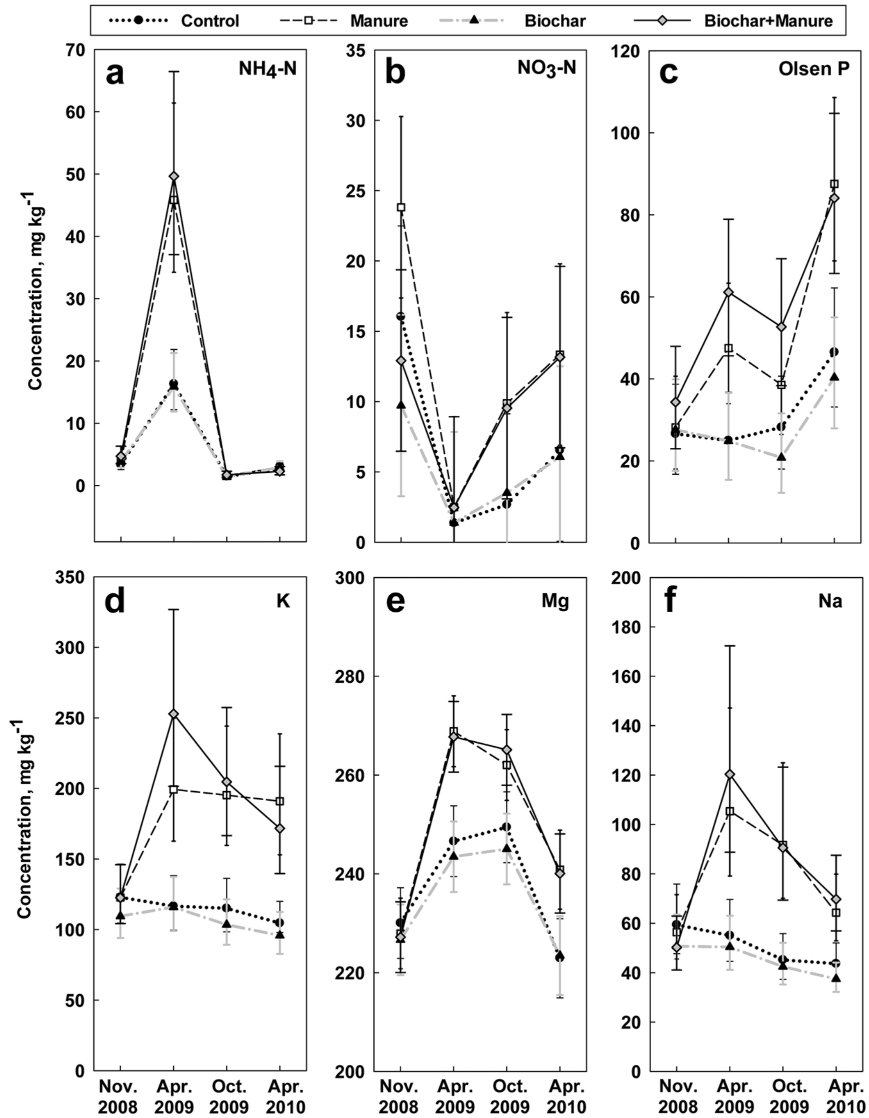

Fig. 3. The effect of organic amendments on 0- to 30-cm soil concentrations. (a–f) Diethylenetriaminepentaacetic acid–extractable Cu (a), Fe (b), Mg (c), and Zn (d); soil electrical conductivity (e); and soil pH (f). Amendments were added immediately after the November 2008 soil sampling. Error bars represent 95% confidence limits on the treatment means.

In the current study, the belated effect of biochar on corn silage N, micronutrient uptake, and yield suggests (i) that the mechanism involved was delayed until the amendment had

Table 3. Soil chemical properties for 0- to 30-cm depth as affected by amendment classes across all sampling times for two contrast tests.

Class comparison†	NH_4–N	NO_3–N	Olsen P	DTPA‡ K	DTPA Na	DTPA Mg	DTPA Cu	DTPA Fe	DTPA Mn	DTPA Zn	EC§	pH	Total C	Total organic C	Total N
	mg kg^{-1}										S m^{-1}		g kg^{-1}		
Manure	5.4a¶	8.3a	49.6a	182a	81a	250a	1.8a	5.0	9.0a	3.0a	0.06a	7.67	20.6a	11.1a	1.09a
No manure	3.9b	4.2b	28.4b	110b	48b	236b	1.5b	4.9	7.8b	2.5b	0.04b	7.70	18.5b	9.5b	0.97b
Biochar	10.3	7.3	43.2	147	64	242	1.6	5.3	9.6a	2.8	0.05	7.70	21.3a	11.7a	1.04
No biochar	9.8	9.5	41.0	146	65	244	1.6	5.2	7.8b	2.7	0.05	7.68	17.8b	8.8b	1.02

† Classes compared comprise the following treatments: manure = manure, combined manure+biochar; no manure = control, biochar; biochar = biochar, manure+biochar; no biochar = control, manure.

‡ Diethylenetriaminepentaacetic acid.

§ Electrical conductivity.

¶ For a given soil parameter, treatment class means followed by the same letter are not significantly different ($P < 0.05$). Letters are not displayed if the effect was not significant in the ANOVA (see Table 1).

Table 4. The influence of amendments on silage corn mineral concentrations for years 2009 and 2010.

Source of variation	Year	B	Al	Cu	Fe	Mn	Zn	S	Mg	Ca	P	K	C	N	Silage yield
		P values†													
Amendment‡	2009	ns§	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	2010	ns	ns	*	ns	ns	ns	***	ns	ns	ns	ns	ns	*	**
Contrasts¶															
Manure vs. no-manure	2009	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	2010	ns	ns	**	ns	*	ns	***	*	ns	ns	*	*	*	**
Biochar vs. no biochar	2009	*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	2010	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

† The significance of *P*-values for treatment effect and single-degree-of-freedom contrasts were derived from an ANOVA (* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$).

‡ This factor includes control, manure, biochar, and combined biochar+manure amendment treatments.

§ Nonsignificant ($P > 0.05$).

¶ Classes compared comprise the following treatments: manure = manure, combined manure+biochar; no manure = control, biochar; biochar = biochar, manure+biochar; no biochar = control, manure.

Table 5. Macronutrient, micronutrient, and total nitrogen and carbon concentrations in above-ground crop tissue and silage corn yield for 2009 and 2010. Values are given for treatments and classes associated with the contrast test that was most significant across the uptake components.

Amendment/class	Mg		Ca		P		K		C		N		S	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
	g kg^{-1} dry wt												mg kg^{-1} dry wt	
Control	1.42	1.25	1.91	1.57	1.39	1.50	7.21	8.53	440	439	12.5	8.0a†	458	373b
Manure	1.47	1.44	1.93	1.95	1.58	1.51	7.90	11.29	431	442	12.4	8.7a	470	432a
Biochar	1.45	1.32	2.11	1.97	1.46	1.49	6.82	10.71	441	441	12.2	5.4b	469	348c
Biochar+manure	1.40	1.43	1.95	1.84	1.5	1.78	6.67	11.08	441	432	12.8	9.2a	460	464a
Contrasts‡														
Manure	1.44	1.43a	1.94	1.90	1.54	1.64	7.28	11.19a	436	437	12.6	9.0a	466	449a
No manure	1.43	1.29b	2.01	1.77	1.43	1.49	7.02	9.62b	440	440	12.4	6.7b	466	361b
	Al		Cu		Fe		Mn		Zn		B		Silage yield (dry wt)	
	mg kg^{-1} dry wt												Mg ha^{-1}	
Control	73	69	1.6	1.2bc†	77	79	35	19	20	17	6.7	11.3	18.1	19.1a
Manure	67	90	2.5	2.1a	75	95	41	27	19	20	6.0	14.3	18.0	21.2a
Biochar	86	102	1.6	1.2c	92	102	37	16	19	17	9.3	11.5	19.45	13.2b
Biochar+manure	70	99	1.6	1.6b	77	104	38	24	21	20	9.6	10.5	18.6	21.6a
Contrasts														
Manure	69	95	1.6	1.9a	85	100	39	25a	20	20	7.8	12.4	18.3	21.4a
No manure	80	85	2.1	1.2b	76	91	36	18b	20	17	8.0	11.4	18.6	16.2b

† For a given soil parameter, treatment class means followed by the same letter are not significantly different ($P < 0.05$). Letters are not displayed if the effect was not significant in the ANOVA (Table 7).

‡ Classes compared comprise the following treatments: manure = manure, combined manure+biochar treatments; no manure = control, biochar.

Table 6. The influence of amendments on mineral uptake in silage corn for 2009 and 2010.

Treatment	Year	B	Al	Cu	Fe	Mn	Zn	S	Mg	Ca	P	K	C	N
		P values†												
Amendment‡	2009	ns§	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	2010	ns	ns	**	*	*	ns	***	**	ns	ns	***	**	**
Contrasts¶														
Manure vs. no-manure	2009	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	2010	*	*	***	**	**	*	***	**	*	*	***	**	**
Biochar vs. no biochar	2009	*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	2010	*	ns	ns	ns	ns	ns	*	ns	ns	ns	ns	ns	ns

† The significance of *P* values for treatment effect and single-degree-of-freedom contrasts were derived from an ANOVA (* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$).

‡ This factor includes control, manure, biochar, and biochar+manure treatments.

§ Nonsignificant ($P > 0.05$).

¶ Manure = manure, combined manure+biochar; no manure = control, biochar; biochar-manure = manure+biochar; other = control, manure, biochar; biochar = biochar, manure+biochar; no biochar = control, manure.

aged or (ii) that biochar interacted with an unknown factor in 2010 (as compared with 2009) that altered its influence on the soil or crop. Some properties or effects of soil-applied biochar are time dependent. Cheng et al. (2008) reported that the nature of biochar surface chemistry changes after a year of residence in soil. Time may also be required for bacteria to populate biochar pores. Because of the biochar's small pore size, the inhabiting bacteria may be protected from grazers and predators, preventing the bacterial biomass from becoming available for plant uptake (Clarholm, 1985; Lehmann et al., 2011).

Biochar's effect on soil respiration and in some cases soil priming (i.e., accelerated mineralization of less recalcitrant soil OC in response to the addition of new C) appears to be time dependent, particularly in soils with low OC. An initial flush of soil microbial growth, respiration, and N immobilization occurs in the first 1 to 2 wk after biochar addition, and biochar with high volatile matter contents produces a greater and longer flush than low-volatile-matter biochar (Deenik et al., 2010). Smith et al. (2010) concluded that pyrolysis-derived condensates adhering to the biochar during cooling are the source of labile C that support this immediate increase in soil respiration. Four to five days after application, little if any of the added biochar C continued to be mineralized (Smith et al., 2010). In the longer term, biochars produced from hardwoods at high temperatures (like CQuest) and added to low OC soils were found to have little effect on soil priming in the first year after application. However, in the second year the biochar had a negative priming effect (i.e., the soil C was stabilized and its rate of mineralization was reduced) (Zimmerman et al., 2011). If CQuest amendment caused a second-year reduction in mineralization in the current study, it could have contributed to the observed decrease in N and S availability, uptake, and yield.

In 2009 biochar treatments as a class increased corn silage B concentrations relative to treatments without biochar (Table 5). For all treatments, the silage B concentrations were on the low end of the typical range (15–90 mg kg^{-1}) but above the 9 mg kg^{-1} value thought to indicate deficiency (Adriano, 1986). Thus, the enhanced B uptake from biochar did not present a toxicity problem and may have contributed to the trending mean silage yield increase for biochar relative to the control in 2009 (Table 5).

Corn Silage Nutrient Uptake

In 2010, the biochar-induced reduction in uptake of Mg, TN, TC, Cu, and S (Table 7) by corn silage relative to the control was largely caused by a corresponding yield reduction. The exception was for S and TN, where accompanying reduced biomass nutrient concentrations contributed to the uptake reduction. The increased nutrient uptake in manure-treated 2010 corn silage (Table 7) was primarily caused by a corresponding increase in biomass nutrient concentrations, although the mean 2010 manure silage yield was slightly greater than that for the control and contributed some to the increased uptake.

Conclusions

The addition of hardwood-derived biochar to irrigated calcareous soils increased soil TC and TOC concentrations over the 2-yr period and may have inhibited mineralization of manure C when both were added to soil simultaneously. Biochar and manure produced a synergistic increase in available soil Mn in the first year (relative to the control), suggesting that at least two processes control Mn availability in the combined treatment. Biochar effects on calcareous soils were unlike those reported for acidic profiles in that pH changes and increases in available P and cations were not observed. Biochar did not affect corn silage nutrient concentrations or yields in year 1, but in year 2 biochar decreased silage TN and S concentrations and yield as well as cumulative uptake of TN, Mg, Cu, Mn,

Table 7. The uptake of macro- and micronutrient in corn silage for 2009 and 2010. Values are given for treatments and classes associated with the contrast test that was most significant across the uptake components.

	Mg		Ca		P		K		S		N		C	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
	kg ha^{-1} (dry wt)												Mg ha^{-1}	
Control	25.5	24.1b†	34.4	29.9	25.2	29.2	130.1	163b	8.3	7.2b	227.8	153.3b	7.9	8.4a
Manure	26.5	30.9a	34.8	42.0	28.4	32.6	142.6	240a	8.5	9.3a	220.5	184.3a	7.8	9.4a
Biochar	28.3	17.4c	41.2	25.6	28.4	19.8	133.0	139b	9.1	4.6c	235.2	74.9c	8.5	5.8b
Biochar+manure	26.1	31.0a	36.4	39.9	27.9	38.7	124.2	241a	8.6	10.1a	242.5	200.4a	8.2	9.4a
Contrasts ‡														
Manure	26.3	31.0a	35.6	41.0a	28.1	35.6a	124.2	240a	8.5	9.7a	231.5	192a	8.0	9.5a
No manure	26.9	20.7b	37.8	27.8b	26.7	24.5b	135.2	151b	8.7	5.9b	232.2	114b	8.3	7.1b

	Al		Cu		Fe		Mn		Zn		B	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
Control	1.32	1.39	0.03	0.02c	1.39	1.53b	0.64	0.36bc	0.36	0.34	0.12	0.22b
Manure	1.25	1.93	0.04	0.05a	1.36	2.03a	0.74	0.58a	0.35	0.43	0.11	0.30a
Biochar	1.72	1.44	0.03	0.01c	1.78	1.41b	0.73	0.21c	0.38	0.23	0.18	0.15b
Biochar+manure	1.35	2.38	0.03	0.03b	1.43	2.42a	0.70	0.51ab	0.39	0.44	0.18	0.23a
Contrasts												
Manure	1.52	2.15a	0.03	0.04a	1.40	2.23a	0.72	0.54a	0.37	0.43a	0.15	0.26a
No manure	1.30	1.41b	0.03	0.02b	1.59	1.47b	0.68	0.29b	0.37	0.28b	0.15	0.19b

† For a given soil parameter, treatment class means followed by the same letter are not significantly different ($P < 0.05$). Letters are not displayed if the effect was not significant in the ANOVA.

‡ Manure = manure, combined manure+biochar treatments; no manure = control, biochar.

and S and was accompanied by general foliar chlorosis. This was consistent with a biochar-induced, second-year reduction in soil C mineralization rate like that observed in low-OC soils by Zimmerman et al. (2011), which may have reduced soil N and S availability in year 2. Our results suggest that biochar application to calcareous soils should be monitored closely in case fertility management adjustments are needed to achieve yield targets. Further research is needed to determine longer-term impacts of biochar on these soils.

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