

# Impact of Biochar Enriched with Dairy Manure Effluent on Carbon and Nitrogen Dynamics

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Amending soils with biochar can have multiple environmental benefits, including improvement in soil physicochemical properties, carbon sequestration, reduction in leaching losses of essential nutrients, and reduction in greenhouse gas (GHG) emissions. This study was conducted to determine the effect of enriched biochar amendments on leaching losses of essential nutrients and GHG emissions from soil. The enriched biochar was prepared by shaking biochar with dairy manure effluent for 24 h, which increased the C and N concentration of biochar by 9.3 and 8.3%, respectively. Incubation and leaching experiments were conducted for 8 wk with three treatments: soil, soil + 1% biochar, and soil + 1% enriched biochar. Amendment with biochar and enriched biochar relative to unamended soil resulted in 68 and 75% reduction in net nitrification, 221 and 229% reduction in net ammonification, 67 and 68% reduction in cumulative CO<sub>2</sub> flux, respectively, and 26% reduction in cumulative N<sub>2</sub>O flux for both biochar treatments. There were no significant differences among treatments in total leaching losses of C, N, and base cations. Our findings suggest that enrichment of biochar with dairy manure effluent can promote C and N storage in soil and provide additional environmental benefits.

THE POTENTIAL OF BIOCHAR (biomass-derived black carbon) application for long-term soil C sequestration has become the focus of a growing number of studies (Schmidt and Noack, 2000; Glaser, 2001) and commercial ventures, such as Biochar Solutions Inc. (Carbondale, Colorado), Biocarbo (Itabirito, Minas Gerais, Brazil), and Biochar Industries (Australia). Knowledge and experience gained from studies on the long-term enhanced productivity of the Brazilian *Terra Preta* soils (Glaser et al., 2002) have led to recent interest in biochar as a soil amendment. The ability of biochar to enhance soil productivity is partially attributed to its effect on increasing cation and anion exchange capacity of soils as well as its positive influence on soil structure and microbial dynamics (Lehmann et al., 2006; Liang et al., 2006). Studies have also reported the potential for reducing leaching losses of essential elements and reducing greenhouse gas (GHG) fluxes when biochar is incorporated into soil (Major et al., 2009; Singh et al., 2010a).

Understanding the effects of biochar on soil C and N dynamics is complicated by complex responses of soil C and N stocks and fluxes after biochar additions. For example, in New South Wales, Australia, Singh et al. (2010a) reported that biochar amendment reduced N<sub>2</sub>O emissions by 14 to 73% in an Alfisol and by 23 to 52% in a Vertisol and reduced NH<sub>4</sub> leaching by 55 to 94%. In Georgia, Steiner et al. (2010) reported that adding biochar to poultry litter during composting reduced ammonia emissions by 64% and reduced total N (TN) loss by 52%. Laird et al. (2010) reported that biochar addition along with swine manure reduced leaching losses of TN by 11% and total dissolved P by 69% for a Mollisol in Iowa as compared with soil amended with manure only. However, biochar has also been shown to immobilize N and thus reduce yields when added without fertilizers. Lehmann et al. (2002) reported reduction in the growth of *Inga edulis* seedlings when the soil was amended with biochar only. They found that charcoal amendments improved P and K supply but decreased N and Mg uptake by plants. Other studies have also reported N immobilization due to biochar additions (Gundale and DeLuca, 2007; Deenik et al., 2008). Beaton (1959) reported reduced P availability after forest fires and attributed

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**Abbreviations:** GHG, greenhouse gas; S, soil; S+B, soil + 1% biochar; S+EB, soil + 1% enriched biochar; TC, total carbon; TN, total nitrogen.

this effect to adsorption of P by biochar or formation of insoluble Ca-phosphates. The capacity of biochar to adsorb high amounts of P has been confirmed by Lehmann et al. (2006), who reported phosphate sorption capacity of 3 g kg<sup>-1</sup> for black locust biochar.

Application of biochar with fertilizer has been shown to improve plant growth compared with the addition of biochar alone (Lehmann et al., 2002). Combining fertilizer with biochar was shown to increase plant N uptake due to enhanced retention of NH<sub>4</sub> by biochar. Van Zwieten et al. (2010) reported up to 250% increase in wheat yield and increased N uptake due to the combined addition of fertilizer and biochar at a rate of 10 t ha<sup>-1</sup>. By contrast, Chan et al. (2008) reported that high-N charcoal produced from poultry litter increased dry matter yield of radish by 42 to 96% without fertilizer addition. On the other hand, N-poor biochar from green waste without N fertilizer did not increase radish yield even at the rate of 100 Mg ha<sup>-1</sup> (Chan et al., 2007).

These studies suggest that the addition of high-N biochar may overcome the problems associated with N immobilization. Hence, researchers have been studying the effectiveness of different nutrient enrichment techniques for biochar. For example, Day et al. (2005) used biochar to scrub and capture GHG emissions from fossil fuel burning and to produce a high-N fertilizer using a mechanical fluidized cyclone. Purevsuren et al. (2003) reported that pyrolysis of casein produced high-N biochar (9.02% N). Recent studies have tested the effectiveness of producing biochar from dairy, poultry, and other waste products (Ro et al., 2010; Singh et al., 2010b). However, to the best of our knowledge, the use of dairy manure effluent to enrich biochar (derived from excess biomass) with plant essential nutrients has not been evaluated. Using dairy manure effluent to enrich biochar can be an innovative and integrative solution. We hypothesize that biochar can be used as a means to (i) recapture excess nutrients from common agricultural pollutants, such as dairy manure effluent to reduce groundwater pollution; (ii) transport the captured nutrients to low-quality soils, where it can be used to supply essential nutrients and improve soil physical condition; (iii) improve the C sequestration potential of agricultural soils; and (iv) dispose of waste biomass from agriculture and forestry in an environmentally and economically sustainable manner. One of the superior qualities of this approach lies in its potential to address a series of disparate challenges concurrently (as a system) with potentially more significant environmental benefits, compared with addressing them individually.

Very little is known about how different methods proposed for enriching biochar could contribute to the dissolved and gaseous fluxes of C and N from the soil system. It is possible that a high concentration of labile N in enriched biochar can lead to larger N<sub>2</sub>O efflux from the soil to the atmosphere, especially under waterlogged conditions and inside anaerobic microsites in soil. Singh et al. (2010a) recently reported that poultry manure biochar, with a higher labile N content than biochar derived from wood, led to initially higher N<sub>2</sub>O emissions, whereas wood biochar showed consistently lower N<sub>2</sub>O emissions than the soil. Spokas and Reicosky (2009) also reported higher N<sub>2</sub>O losses after the addition of high-N

biochar. It is essential to ensure that the process of nutrient enrichment does not offset the environmental remediation potential of biochar. This study was conducted with the objective of assessing the effects of enriching biochar with nutrients from dairy manure effluent on N availability, GHG emissions from soil, and leaching losses of various cations and anions. Our hypothesis was that enriched biochar would increase dissolved and gaseous losses of N only immediately after application. We further hypothesized that biochar enrichment would not have a long-term detrimental effects on the ecosystem services offered by biochar, such as reduction in leaching losses and GHG emissions.

## Materials and Methods

### Biochar and Manure Source

The char was produced by slow pyrolysis at 300°C from a mixture of different hardwood shavings, including maple, aspen, choke cherry, and alder. No chemical preservatives were added during this process. There was no steam added externally, although some steam was produced during the production process. The biochar used for this study was commercially available Charcoal Gardens Biochar purchased from [http://www.buyactivatedcharcoal.com/charcoal\\_gardens](http://www.buyactivatedcharcoal.com/charcoal_gardens). Low-temperature biochar was used because it has been reported to increase microbial activity and N immobilization due to higher amounts of bioavailable C (Deenik et al., 2009), thus offering the potential for removing excess mineral N, by immobilization as well as adsorption, from the dairy manure effluent.

The total carbon (TC) and total nitrogen (TN) concentrations of the biochar were measured on four replicates using the dry combustion method on a Costech Elemental Analyzer (Costech Analytical Technologies Inc., Valencia, CA). Proximate analysis of the biochar was also done on four replicates according to the American Society for Testing and Materials (ASTM) D1762–84 method (ASTM, 1990). Briefly, four biochar properties—moisture, volatile matter, ash, and fixed carbon content—were determined through a series of heat treatments under specific conditions described in ASTM D1762–84.

Dairy manure effluent (liquid manure resulting from flushing of the dairy barns followed by mechanical separation of the solid and liquid parts) was collected from the sedimentation lagoon at the Vander Woude dairy farm in Merced County, California. The manure was centrifuged at 20,000 rpm (49,192 × *g*) and filtered through 0.45- $\mu$ m filters. To prepare the enriched biochar, 1% biochar (1 g 100 g<sup>-1</sup>) was added to the filtered manure, and the mixture was shaken for 24 h. The 24-h shaking time was used because previous sorption studies (unpublished data of the authors) showed that longer shaking time resulted in release of the adsorbed P. After shaking, the mixture was centrifuged and filtered, and the nutrient-enriched biochar was oven dried before use in the incubation experiment. Hereafter, this nutrient-enriched biochar is referred to as “enriched biochar,” as opposed to biochar that has not been enriched.

### Soil Sampling and Analysis

Bulk soil was collected from an almond orchard in Merced County, California (37.37° N, 120.66° W). The soil series

was Atwater (coarse-loamy, mixed, active, thermic Typic Haploxeralfs). The orchard was divided into four quadrants (northeast, northwest, southeast, and southwest). From each quadrant, one composite sample (~1 kg), representing three individual samples, was collected from the top 15 cm soil with a shovel. The four composite samples were used as replicates. In addition, three undisturbed soil cores per quadrant were collected using a bulk density corer for bulk density and moisture content determination. The soil samples were stored at 4°C until the analyses were performed. The TC and TN concentrations of the soil samples and the soil–biochar mixtures (on four replicates each) were measured using the dry combustion technique on a Costech Elemental Analyzer (Costech Analytical Technologies Inc., Valencia, CA).

## Incubation Experiment

The incubation study involved comparison between three treatments: soil (S), soil + 1% biochar (S+B), and soil + 1% enriched biochar (S+EB). The experiment was set up according to the procedure outlined by Hart et al. (1994). All the treatments were prepared using field moist soil that passed through 4-mm sieve. For the S, S+B, and S+EB treatments, field moist soil was mixed with nothing, 1% biochar, and 1% enriched biochar, respectively (10 g biochar per kg oven-dry weight of soil). The soil and soil–biochar mixtures (equivalent to 10 g oven-dry weight) were placed in 120-mL specimen cups and incubated at room temperature for 8 wk. The day the soil and biochar were mixed was considered Day 0 (1 d after field sampling). Soil and air samples were collected on Days 1, 3, 10, 20, 28, 35, 42, and 54. For each sampling time and treatment combination, four replicates were analyzed for the air sampling ( $n = 4 \times 8 = 32$  samples per treatment), and three were analyzed for  $\text{NO}_3$  and  $\text{NH}_4$  content ( $n = 3 \times 8 = 24$  samples per treatment). Soil  $\text{NO}_3$  and  $\text{NH}_4$  content was measured using a KCl extraction technique (Hart et al., 1994). Briefly, 10 g of soil were shaken with 50 mL of 2 mol L<sup>-1</sup> KCl in a stoppered 250-mL volumetric flask for 1 h. The suspension was filtered through preleached Whatman No. 1 filter paper and analyzed for  $\text{NO}_3$  and  $\text{NH}_4$  content on a Lachat Quickchem (method 12-107-04-1-B for  $\text{NO}_3$  and method 12-107-06-1-A for  $\text{NH}_4$ ; Lachat Instruments, Loveland, CO) (Sechtig, 1992; Prokopy, 1994). The preleaching of filter paper was done with four 50-mL aliquots of 2 mol L<sup>-1</sup> KCl followed by six 50-mL aliquots of deionized water and oven drying at 50°C. The samples were weighed each week. If the weight loss was >5%, deionized water was added by dropper to maintain the moisture content and mixed with soil by shaking lightly. Net nitrification and ammonification were calculated as the difference between measured amounts of  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  at time = 28 and 0 d, respectively. The duration of 28 d was chosen because it is a commonly used time period for determining N mineralization potential in laboratory and field conditions (Meason et al., 2004; Deluca and Sala, 2006). The analysis was continued for 4 wk to ensure that the GHG emissions were stabilized after this point. Net mineralization was calculated as the sum of total inorganic N ( $\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$ ) on Day 28 minus total inorganic N on Day 0 (Robertson et al., 1999).

One to three days before each sampling time (Day 1, 3, 10, 20, 28, 35, 42, and 54), corresponding specimen cups were sealed with a butyl rubber septum. Air samples were collected using vacutainers and two-way eclipse syringes (Becton Dickinson and Co., Franklin Lakes, NJ) and analyzed for  $\text{CO}_2$  and  $\text{N}_2\text{O}$  concentration on a Shimadzu GC-14A gas chromatograph (Shimadzu Scientific Instruments, Columbia, MD) with a thermal conductivity detector for  $\text{CO}_2$  and an electron capture detector for  $\text{N}_2\text{O}$ . The flux rates of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  per gram C and N, respectively, were calculated according to the methods of Robertson et al. (1999). Cumulative  $\text{CO}_2$  and  $\text{N}_2\text{O}$  production was calculated by integrating values under the curve (concentration values plotted against time) for the incubation experiment.

## Leaching Experiment

For the leaching experiment, the setup described in Neff and Hooper (2002) was used. For this, 250-mL Nalgene filter units were used with a Whatman GF-F glass fiber filters (0.7- $\mu\text{m}$  pore size) on top of glass wool separating the upper and lower chambers. Before incubation, each soil and soil–biochar mixture was added to the upper chamber (field moist, 10 g oven dry weight), and the chamber was covered with thin plastic film. Destructive sampling for KCl-extractable  $\text{NH}_4$  and  $\text{NO}_3$  measurement in the incubation study necessitated separate samples for each sampling time, whereas the same samples were used throughout the leaching study.

Leachate was collected at the same time intervals as the incubation experiment (i.e., at Days 1, 3, 10, 20, 28, 35, 42, and 54). For this, 100-mL water was added to the soil using a 10-mL pipette (10 mL water at 10-min intervals). Soil was allowed to drain completely, and leachate samples were collected from the lower chamber, filtered through a 0.45- $\mu\text{m}$  syringe filter, and analyzed for various cations, anions, and TC and TN concentrations. The ionic concentrations were measured on a Dionex ICS-2000 Reagent-Free Integrated Ion Chromatography System (Dionex Corp., Bannockburn, IL), and TC and TN concentrations were measured on a Shimadzu TOC/TN 5050 analyzer (Shimadzu Scientific Instruments, Columbia, MD) in the Environmental Analytical Laboratory at the University of California, Merced. Cumulative fluxes of different ions were calculated by integrating values under the curve for the leaching experiment over the 54-d study.

## Statistical Analysis

A Shapiro Wilks test of normality indicated that the data distribution was non-normal. Hence, nonparametric ANOVA calculated by the Kruskal-Wallis test was used to determine the effects of treatment (biochar addition) on all the variables measured in this study (PROC NPAR, SAS Institute). Differences were considered statistically significant at  $p < 0.05$ .

## Results

Proximate analysis showed that the moisture, volatile matter, ash, and fixed C content of the biochar (mean  $\pm$  SE;  $n = 4$ ) were 4.21 ( $\pm 0.02$ ), 19.74 ( $\pm 0.04$ ), 17.28 ( $\pm 0.02$ ), and 62.98 ( $\pm 0.06$ ), respectively. The total C and N concentrations of the soil, biochar, and soil + biochar mixtures are given in Table 1.

**Table 1. Total carbon and nitrogen concentrations of the treatments.**

	Total C	Total N
	mg g <sup>-1</sup>	
Biochar	725.4 ± 0.2a†	3.6 ± 0.003a
Enriched biochar‡	792.7 ± 0.5b	3.9 ± 0.006b
Soil	3 ± 0.02c	0.3 ± 0.002c
Soil + biochar	10.4 ± 0.02d	0.4 ± 0.002d
Soil + enriched biochar	11 ± 0.03e	0.4 ± 0.002d

† Values are mean ± SE. Values followed by the same letter indicate statistically significant differences ( $p < 0.05$ ) between the two biochar types and within the three soil and soil-biochar treatments ( $n = 4$ ).

‡ The enriched biochar was prepared by shaking biochar with filtered manure for 24 h. Biochar was added to the soil at the rate of 1% based on oven dry weight.

Shaking the biochar in filtered dairy manure effluent for 24 h increased the total C and N concentrations by 9.3 and 8.3%, respectively. The addition of 1% biochar to soil increased the soil C content from 3.0 to 10.4 mg g<sup>-1</sup> for the biochar and 11.0 mg g<sup>-1</sup> for the enriched biochar. The N content increased from 0.3 to 0.4 mg g<sup>-1</sup> for biochar and enriched biochar treatments (Table 1).

### Effect of Biochar Amendment on Soil Inorganic Nitrogen

The S+B and S+EB treatments resulted in significant reduction in KCl-extractable inorganic NH<sub>4</sub> and NO<sub>3</sub> compared with S (Fig. 1 and 2). The decrease in extracted NH<sub>4</sub> and NO<sub>3</sub> was accompanied by a reduction in the within-treatment variability, especially for NH<sub>4</sub> (Fig. 1). The S+B and S+EB treatments reduced net ammonification by >220%, and net nitrification for the S+B and S+EB treatments was reduced by 68 and 75%, respectively, compared with S (Fig. 3). The observed negative net ammonification for the S+B and S+EB treatments indicated that the rate of nitrification was higher than the rate of organic N mineralization (to NH<sub>4</sub>), which has previously been observed when the NH<sub>4</sub>-N pool is large (Nadelhoffer et al., 1984). Compared with S+B, the S+EB treatment showed slightly higher NH<sub>4</sub> concentrations on Day 1, but there were

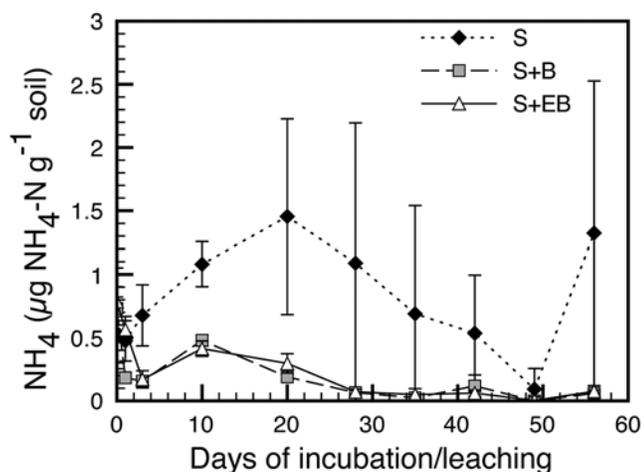


Fig. 1. Effect of biochar amendment on soil ammonium (KCl-extractable) concentration. Statistically significant differences ( $p < 0.05$ ) between the control and both treatments were observed on Days 1, 3, 10, 20, 28, and 42 of the experiment ( $n = 3$ ). S, soil; S+B, soil + 1% biochar; S+EB, soil + 1% enriched biochar.

no other significant differences between the two treatments (Fig. 1).

### Effect of Biochar Amendment on Greenhouse Gas Fluxes from Soil

The addition of biochar and enriched biochar led to significant reductions in the rate of CO<sub>2</sub> flux (mg CO<sub>2</sub> g<sup>-1</sup> C d<sup>-1</sup>) (Fig. 4) throughout the 8-wk incubation. The S+B and S+EB treatments led to a 67 and 68% reduction in cumulative CO<sub>2</sub> efflux per g C in soil, respectively, and reduced within-treatment variability compared with S. There were no significant differences in CO<sub>2</sub> losses between the two biochar treatments throughout the experiment.

The addition of biochar and enriched biochar also led to a decrease in the rate of N<sub>2</sub>O efflux (in µg N<sub>2</sub>O-N g<sup>-1</sup> N d<sup>-1</sup>) (Fig. 5). The S+B and S+EB treatments led to a 26% reduction in cumulative N<sub>2</sub>O efflux per g N in soil during the 8-wk incubation compared with S.

### Effects of Biochar Amendment on Leaching Losses of Carbon, Nitrogen, and Base Cations

We observed only small effects of the S+B or S+EB treatments on leaching losses of base cations (Na, Ca, K, and Mg). Biochar amendment led to increased leaching losses of base cations in the first few sampling periods (Na on Day 1, Ca and Mg on Day 3, and K until Day 20), but we observed no statistically significant differences in total leaching losses (Table 2). For the base cations, when an increase in leachate concentration was observed, we found that the effect of S+EB was less than that of S+B. The C/N ratio of the leachates was similar for the S and S+EB treatments (41.2) but higher for the S+B treatment (45.9), suggesting lower loss of water-soluble C or relatively higher loss of N from the S+B treatment.

### Discussion

Our results indicate that the addition of biochar enriched with dairy manure effluent to soil decreased gaseous fluxes

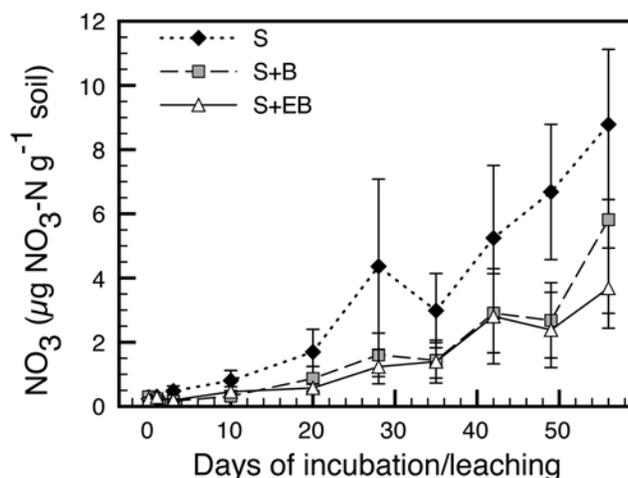


Fig. 2. Effect of biochar amendment on soil nitrate (KCl-extractable) concentration. Statistically significant differences ( $p < 0.05$ ) were only observed between soil and soil + enriched biochar treatments at Day 54 ( $n = 3$ ). S, soil; S+B, soil + 1% biochar; S+EB, soil + 1% enriched biochar.

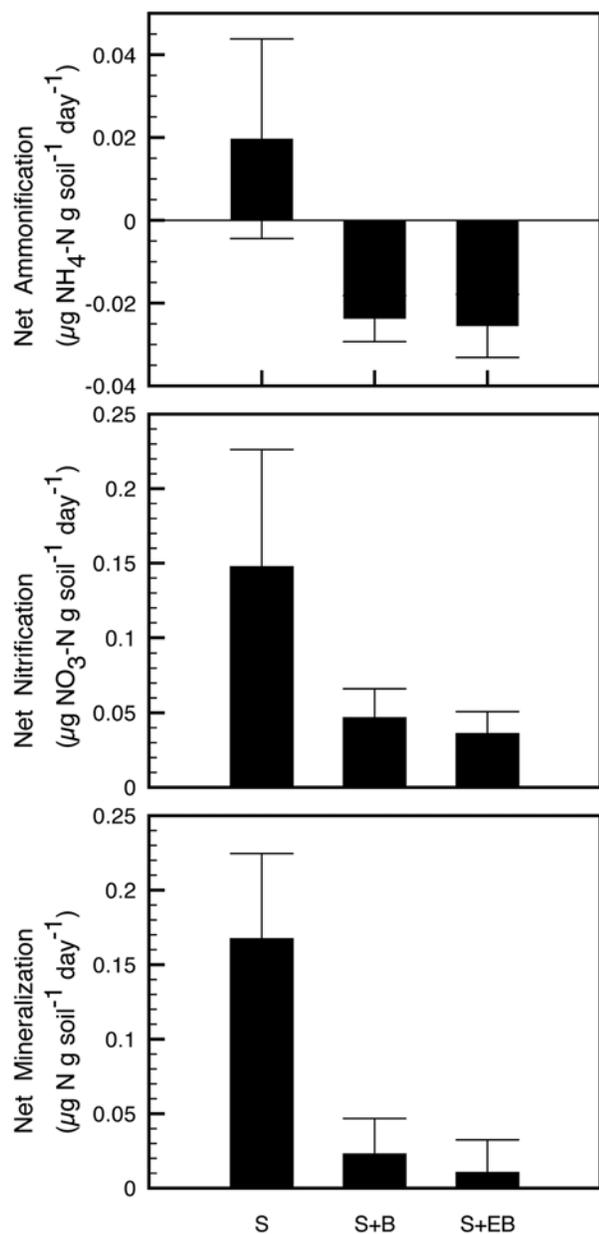


Fig. 3. Effect of biochar amendment on net ammonification, nitrification, and mineralization calculated according to the methods of Robertson et al. (1999). S, soil; S+B, soil + 1% biochar; S+EB, soil + 1% enriched biochar ( $n = 3$ ).

of C and N from the studied soil. In addition, we found that the effect of enriched biochar on soil-available N was comparable for the S+B and S+EB treatments, whereas leaching losses of TC, TN, and base cations were similar for all three treatments. This supported the hypothesis that, at least in the short-term, the biochar enrichment process does not have a detrimental effect on the environmental benefits derived from biochar.

### Effect of Biochar Enrichment on Available Nitrogen

The addition of biochar and enriched biochar to soil led to significant reductions in net ammonification, nitrification, and mineralization from soil as compared with the control. However, the differences in magnitude of net ammonification and nitrification between the S+B and S+EB treatments were

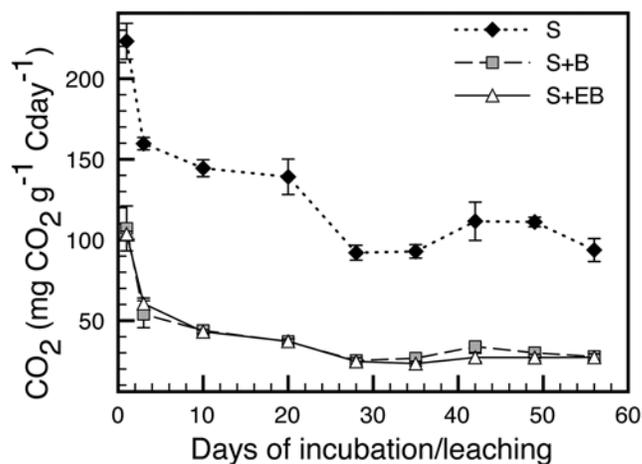


Fig. 4. Effect of biochar amendment on  $\text{CO}_2$  efflux from incubated soil. S, soil; S+B, soil + 1% biochar; S+EB, soil + 1% enriched biochar ( $n = 4$ ).

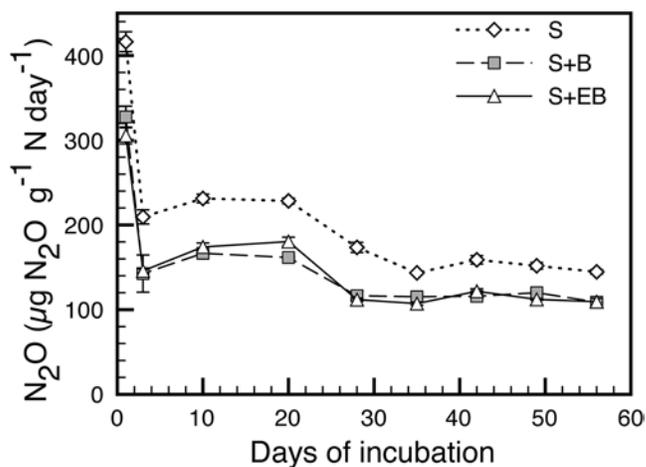


Fig. 5. Effect of biochar amendment on efflux of  $\text{N}_2\text{O}$  from incubated soil. S, soil; S+B, soil + 1% biochar; S+EB, soil + 1% enriched biochar ( $n = 4$ ).

not statistically significant, except for  $\text{NH}_4\text{-N}$  concentration measured for Day 1 and Week 7.

The patterns of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  release during the 8-wk experiment were different for S compared with the S+B and S+EB treatments. For S, a small  $\text{NO}_3$  peak was observed on Day 28 after the  $\text{NH}_4$  peak on Day 20, suggesting nitrification of the  $\text{NH}_4$  released during mineralization. On the other hand, the S+B and S+EB treatments showed consistently lower  $\text{NH}_4$  and  $\text{NO}_3$  concentrations in leachate than S, and the peaks on Days 20 and 28 were not prominent. These differences could be accounted for by the adsorption of  $\text{NO}_3$  (Mizuta, 2004) and  $\text{NH}_4$  (Lehmann et al., 2002) by biochar. Although an increase in microbial activity due to bioavailable C in biochar and the resultant immobilization of N was a possibility (Deenik et al., 2009), the  $\text{CO}_2$  efflux did not increase in S+B and S+EB treatments. Hence, it is likely that the reduction in  $\text{NH}_4$  and  $\text{NO}_3$  concentrations was due to adsorption rather than immobilization. The treatment differences were more pronounced for  $\text{NH}_4$  than  $\text{NO}_3$ , in agreement with previous studies showing that biochar has a high capacity to adsorb  $\text{NH}_4$  (Lehmann et al., 2002).

## Effect of Biochar Enrichment on Greenhouse Gas Fluxes from Soil

In this study, the biochar and enriched biochar treatments led to significant reductions in CO<sub>2</sub> fluxes during the 8-wk incubation. However, previous studies have reported increases and decreases of CO<sub>2</sub> fluxes after biochar additions to soil, at least in short-term incubations (Hamer, 2004; Steinbeiss et al., 2009). For example, Steinbeiss et al. (2009) reported that amendment with high-N yeast biochar showed significantly higher CO<sub>2</sub> losses initially, followed by rapid reduction in respiration rate after 4 wk of incubation. They also reported that addition of a N-poor glucose biochar amendment did not affect CO<sub>2</sub> efflux from soil. Hamer (2004) reported a priming effect of biochar addition on the rate of glucose mineralization. They reported that without biochar addition, 47% of the glucose-C was lost as CO<sub>2</sub> in the first 26 d after a lag phase (no CO<sub>2</sub> efflux) of 6 d. They showed that addition of charred rye grass and wood resulted in the loss of 64% of the glucose-C, whereas addition of charred maize residue resulted in the loss of 77% of the glucose-C in the first 26 d. In our study and in that of Hamer (2004), no lag phase was observed after the addition of biochar. The differences in results for these studies can be attributed to the differences in N concentrations (5% N in the study by Steinbeiss et al. [2009] versus 0.39% in our study) as well as in the presence of available C from glucose, which likely resulted in greater microbial activity in the previous studies.

The increase in CO<sub>2</sub> efflux in studies such as Hamer (2004) may raise concern for the effect of biochar on long-term C storage. However, as Spokas and Reicosky (2009) indicated, the effect of biochar on CO<sub>2</sub> emissions is likely to vary based on the characteristics of the biochar and soil type. Spokas and Reicosky (2009) found that in a forest nursery soil, three biochar types increased CO<sub>2</sub> emissions, while 13 biochar types suppressed CO<sub>2</sub> emissions. In an agricultural soil, three biochar types reduced emissions, five biochar types increased emissions, and eight biochar types had no effect on CO<sub>2</sub> emissions. Only two biochar types increased the CO<sub>2</sub> emissions in a landfill cover soil, whereas the remaining biochar types decreased emissions. Moreover, there is evidence that a significant portion of biochar added to soil persists for hundreds to thousands of years (Saldarriaga and West, 1986). Biochar-amended *Terra Preta* soils show significantly higher soil C content hundreds of years after the biochar additions (Glaser, 2001), further

**Table 2. Cumulative leaching losses of carbon, nitrogen, and base cations during 8 weeks in soil and in soil and biochar mixtures.**

	Soil	Soil + biochar	Soil + enriched biochar
	mg g <sup>-1</sup> of soil		
C	2.14 ± 0.1†	2.13 ± 0.2	2.05 ± 0.2
N	0.05 ± 0.004	0.05 ± 0.004	0.05 ± 0.003
Na	3.10 ± 0.2	3.20 ± 0.4	3.10 ± 0.3
K	0.12 ± 0.006	0.20 ± 0.02	0.15 ± 0.01
Mg	0.14 ± 0.01	0.16 ± 0.02	0.15 ± 0.01
Ca	0.44 ± 0.4	0.56 ± 0.06	0.49 ± 0.05

† Error values represent SE where *n* = 4 for all measured variables and measurement times.

supporting the hypothesis that the increased CO<sub>2</sub> losses due to biochar additions are likely to be short lived and that biochar amendments can be used to improve productivity without a negative effect on soil carbon storage.

In our study, the addition of biochar and enriched biochar led to a reduction in N<sub>2</sub>O efflux from soil during the 8-wk incubation. Our results are in agreement with the findings of other studies. For example, Singh et al. (2010a) reported 14 to 73% and 23 to 52% reduction in N<sub>2</sub>O flux due to biochar amendments from an Alfisol and a Vertisol, respectively. Similarly, Yanai et al. (2007) reported up to 89% reduction in N<sub>2</sub>O emissions due to the addition of biochar derived from municipal biowaste. Yanai and coworkers suggested that the effect of biochar in reducing soil N<sub>2</sub>O efflux was dependent on soil moisture content and the effect of high moisture content on inhibition of denitrifying bacteria. According to the authors, adsorption of water by biochar and improved aeration led to suppression of the activity of denitrifying bacteria and reduced loss of N<sub>2</sub>O. Rondon et al. (2006) reported that soil amendment with 20 t ha<sup>-1</sup> of biochar reduced the N<sub>2</sub>O emissions by 50 and 70% in soils under grass and maize, respectively. Reduction of N<sub>2</sub>O flux from soils amended with biochar was also reported by Spokas et al. (2009) and Van Zwieten et al. (2009). Although a few studies have shown increased N<sub>2</sub>O flux due to the addition of high-N biochar (Singh et al., 2010a; Spokas and Reicosky, 2009), enriched biochar in this study did not increase N<sub>2</sub>O flux. This was probably because the difference in N concentrations in this study was smaller (3.6 vs. 3.9 g kg<sup>-1</sup>) than in the studies by Singh et al. (2010a) (1.7–51.8 g kg<sup>-1</sup>) and Spokas and Reicosky (2009) (1–27 g kg<sup>-1</sup>).

These results support our hypothesis that, similar to biochar, biochar enriched with dairy manure effluent has the potential to reduce GHG emissions from soil and to increase terrestrial C sequestration. Improved aeration, as suggested by Yanai et al. (2007), is also likely to decrease CH<sub>4</sub> efflux from soil, providing additional reductions in GHG fluxes to the atmosphere, because methanogenic bacteria are obligate anaerobic organisms (Stadtman, 1967) and improved aeration reduces CH<sub>4</sub> production in soil (Sass et al., 1992). Further studies are needed to ascertain the role of the above-mentioned mechanisms on reducing gaseous fluxes of C and N from soil after biochar addition and the overall impact of biochar and enriched biochar additions on microbial biomass, community composition, and activity.

## Effect of Biochar Enrichment on Leaching Losses

There have been a limited number of studies investigating the effect of biochar on leaching losses of base cations from soil, and we are aware of no studies investigating the effect of biochar enriched with dairy manure effluent. It has been previously reported that biochar can be a source of nutrients when added to the soil. Lehmann et al. (2002) reported that biochar addition served as a direct source of P and K. This study supports the theory of biochar as a source of K, although the effect lasted only for 20 d. Others have also reported that the addition of biochar could lead to leaching losses of base cations and other essential nutrient elements (Laird et al., 2010). In a study that applied biochar and biochar followed by swine

manure application, Laird et al. (2010) reported that increasing amounts of biochar led to increased leaching losses of K, Mg, Ca, N, and P from soil. However, when coupled with swine manure additions, soils amended with biochar had reduced leaching losses of N and total dissolved P by 11 and 69%, respectively, compared with soils receiving only the manure treatment.

Biochar produced at 350°C was previously reported to have a negative effect on plant growth due to N immobilization (Gundale and DeLuca, 2007). Furthermore, studies have reported that combined fertilizer and biochar addition increased the crop yields significantly (Van Zwieten et al., 2010), whereas the addition of N-poor or high volatile matter-containing biochar without fertilizer resulted in yield decline due to N immobilization (Lehmann et al., 2002; Chan et al., 2007; Deenik et al., 2008). In this study, by using biochar produced at 300°C, we show that enriched biochar exhibited a similar reduction in soil-available N as biochar. This suggests that even though enriched biochar showed 8.3% higher N concentration than biochar, both biochar treatments were likely to require additional fertilizer to achieve optimum yield. Researchers have shown that it is possible to use charcoal with higher native N concentration, such as poultry litter biochar (Chan et al., 2008), or to add N from other sources, such as chemical fertilizers (Van Zwieten et al., 2010), to improve crop yields. However, other studies have reported increased GHG emissions and leaching losses due to the application of high-N biochars, such as poultry manure biochar (Singh et al., 2010a) and turkey manure + woodchip biochar (Spokas and Reicosky, 2009). On the other hand, an enrichment process, such as the one described in this paper, may be used to add nutrients in small increments without harmful effects. Further studies are required to optimize the nutrient enrichment process so that nutrient-enriched biochar amendments can offer improved crop yields without compromising the environmental services offered by biochar.

## Conclusions

Our findings show that enriched biochar produced by shaking charred woody biomass in dairy manure effluent has a similar potential for providing environmental benefits (e.g., reducing GHG emissions) when compared with biochar alone. Although enriched biochar has higher C and N concentrations, leaching losses from soil amended with enriched biochar were similar to leaching losses from unamended soil and soil amended with biochar. This suggests that enriched biochar can serve as a slow-releasing reservoir of nutrients in soil. In this study, we also found that biochar and enriched biochar treatments showed reduction in KCl-extractable  $\text{NH}_4$  and  $\text{NO}_3$ , suggesting the possibility of N immobilization. Further studies are necessary to understand the effect of enrichment on microbial activity and other mechanisms governing GHG emissions and to optimize the process of nutrient enrichment of biochar for achieving high crop yields without negative environmental impact.

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## References

- ASTM. 1990. Standard method for chemical analysis of wood charcoal. D1762–84. ASTM International, Philadelphia, PA.
- Beaton, J.D. 1959. The influence of burning on the soil in the timber range area of Lac le Jeune, B.C. II. Chemical properties. *Can. J. Soil Sci.* 39:6–11. doi:10.4141/cjss59-002
- Chan, K.Y., L. Van Zwieten, I. Meszaros, A. Downie, and S. Joseph. 2007. Agronomic values of greenwaste biochar as a soil amendment. *Aust. J. Soil Res.* 45:629–634. doi:10.1071/SR07109
- Chan, K.Y., L. Van Zwieten, I. Meszaros, A. Downie, and S. Joseph. 2008. Using poultry litter biochars as soil amendments. *Aust. J. Soil Res.* 46:437–444. doi:10.1071/SR08036
- Day, D., R.J. Evans, J.W. Lee, and D. Reicosky. 2005. Economical  $\text{CO}_2$ ,  $\text{SO}_x$ , and  $\text{NO}_x$  capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration. *Energy* 30:2558–2579. doi:10.1016/j.energy.2004.07.016
- Deenik, J.L., G. Uehara, Y. Sumiyoshi, A. Sidibe, A. McClellan, and M. Antal. 2008. Charcoal volatile matter content and its effects on plant growth and biological properties of an infertile tropical soil. Abstract #665–665. Proc. Joint Annual Meeting of GSA, ASA-CSSA-SSSA, and GCAGS 2008.
- Deenik, J.L., A.T. McClellan, and G. Uehara. 2009. Biochar volatile matter content effects on plant growth and nitrogen transformations in a tropical soil. Western Nutrient Management Conference. 2009. Vol. 8. Salt Lake City, UT.
- Deluca, T.H., and A. Sala. 2006. Frequent fire alters nitrogen transformations in ponderosa pine stands of the inland northwest. *Ecology* 87:2511–2522. doi:10.1890/0012-9658(2006)87[2511:FFANTI]2.0.CO;2
- Glaser, B. 2001. The 'Terra Preta' phenomenon: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften* 88:37–41. doi:10.1007/s001140000193
- Glaser, B., J. Lehmann, and W. Zech. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: A review. *Biol. Fertil. Soils* 35:219–230. doi:10.1007/s00374-002-0466-4
- Gundale, M.J., and T.H. DeLuca. 2007. Charcoal effects on soil solution chemistry and growth of *Koeleria macrantha* in the ponderosa pine/Douglas-fir ecosystem. *Biol. Fertil. Soils* 43:303–311. doi:10.1007/s00374-006-0106-5
- Hamer, U. 2004. Interactive priming of black carbon and glucose mineralisation. *Org. Geochem.* 35:823–830. doi:10.1016/j.orggeochem.2004.03.003
- Hart, S.C., J.M. Stark, E.A. Davidson, and M.K. Firestone. 1994. Nitrogen mineralization, immobilization, and nitrification. p. 985–1018. *In* R.W. Weaver et al. (ed.) *Methods of soil analysis, part 2: Microbiological and biochemical properties*. SSSA, Madison, WI.
- Laird, D., P. Fleming, B.Q. Wang, R. Horton, and D. Karlen. 2010. Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma* 158:436–442. doi:10.1016/j.geoderma.2010.05.012
- Lehmann, J., J. Gaunt, and M. Rondon. 2006. Bio-char sequestration in terrestrial ecosystems: A review. *Mitig. Adapt. Strategies Glob. Change* 11:403–427.
- Lehmann J., J.P. da Silva, Jr., M. Rondon, M.S. Cravo, J. Greenwood, T. Nehls, C. Steiner, B. Glaser. 2002. Slash-and-char: A feasible alternative for soil fertility management in the central Amazon? Paper no. 449. Proceedings of the 17th World Congress of Soil Science, 14–21 Aug. 2002, Bangkok, Thailand.
- Liang, B., J. Lehmann, D. Solomon, J. Kinyangi, J. Grossman, B. O'Neill, J.O. Skjemstad, J. Thies, F.J. Luizao, J. Petersen, and E.G. Neves. 2006. Black carbon increases cation exchange capacity in soils. *Soil Sci. Soc. Am. J.* 70:1719–1730. doi:10.2136/sssaj2005.0383
- Major, J., C. Steiner, A. Downie, and J. Lehmann. 2009. Biochar effects on nutrient leaching. p. 271–287. *In* J. Lehmann and S. Joseph (ed.) *Biochar for environmental management*. Earthscan, London.
- Meason, D.F., D. Markewitz, and R.E. Will. 2004. Annual fertilization and interspecific competition control: Effects on in situ forest floor nitrogen fluxes of different-aged *Pinus taeda* stands in southeast Georgia, USA. *Can. J. For. Res.* 34:1802–1818. doi:10.1139/x04-053
- Mizuta, K. 2004. Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. *Bioresour. Technol.* 95:255–257. doi:10.1016/j.

- Nadelhoffer, K.J., J.D. Aber, and J.M. Melillo. 1984. Seasonal patterns of ammonium and nitrate uptake in 9 temperate forest ecosystems. *Plant Soil* 80:321–335. doi:10.1007/BF02140039
- Neff, J.C., and D.U. Hooper. 2002. Vegetation and climate controls on potential CO<sub>2</sub>, DOC and DON production in northern latitude soils. *Glob. Change Biol.* 8:872–884. doi:10.1046/j.1365-2486.2002.00517.x
- Prokopy, W.R. 1994. Ammonia (phenate) in 2 M KCL soil extracts. Quikchem Method 12-107-06-1-A. Methods manual. Zellweger Analytics, Lachat Instruments Division, Milwaukee, WI.
- Purevsuren, B., B. Avid, B. Tesche, and Y. Davajav. 2003. A biochar from casein and its properties. *J. Mater. Sci.* 38:2347–2351. doi:10.1023/A:1023980429410
- Ro, K.S., K.B. Cantrell, and P.G. Hunt. 2010. High-temperature pyrolysis of blended animal manures for producing renewable energy and value-added biochar. *Ind. Eng. Chem. Res.* 49:10125–10131. doi:10.1021/ie101155m
- Robertson, G.P., D. Wedin, P.M. Groffman, J.M. Blair, E.A. Holland, K.J. Nadelhoffer, and D. Harris. 1999. Soil carbon and nitrogen availability: Nitrogen mineralization, nitrification and soil respiration potentials. p. 258–271. *In* G.P. Robertson, D.C. Coleman, C.S. Bledsoe, and P. Sollins (ed.) *Standard soil methods for longterm ecological research*. Oxford Univ. Press, New York.
- Rondon M.A., D. Molina, M. Hurtado, J. Ramirez, J. Lehmann, J. Major, E. Amezquita. 2006. Enhancing the productivity of crops and grasses while reducing greenhouse gas emissions through bio-char amendments to unfertile tropical soils. Presentation #138-68. 18th World Congress of Soil Science, 9–15 July 2006, Philadelphia, PA.
- Saldarriaga, J.G., and D.C. West. 1986. Holocene fires in the northern Amazon basin. *Quat. Res.* 26:358–366. doi:10.1016/0033-5894(86)90095-5
- Sass, R.L., F.M. Fisher, and Y.B. Wang. 1992. Methane emission from rice fields: The effect of floodwater management. *Global Biogeochem. Cycles* 6:249–262. doi:10.1029/92GB01674
- Sechtig, A. 1992. Nitrate in 2 M KCl soil extracts. QuikChem Method 12-107-04-1-B. Lachat Instruments, Milwaukee, WI.
- Schmidt, M.W.I., A.G. Noack. 2000. Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. *Global Biogeochem. Cycles* 14:777–793.
- Singh, B.P., B.J. Hatton, B. Singh, A.L. Cowie, and A. Kathuria. 2010a. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *J. Environ. Qual.* 39:1224–1235. doi:10.2134/jeq2009.0138
- Singh, B., B.P. Singh, and A.L. Cowie. 2010b. Characterisation and evaluation of biochars for their application as a soil amendment. *Aust. J. Soil Res.* 48:516–525. doi:10.1071/SR10058
- Spokas, K.A., and D.C. Reicosky. 2009. Impacts of sixteen different biochars on soil greenhouse gas production. *Ann. Environ. Sci.* 3:179–193.
- Spokas, K.A., W.C. Koskinen, J.M. Baker, and D.C. Reicosky. 2009. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. *Chemosphere* 77:574–581. doi:10.1016/j.chemosphere.2009.06.053
- Stadtman, T.C. 1967. Methane fermentation. *Annu. Rev. Microbiol.* 21:121–142. doi:10.1146/annurev.mi.21.100167.001005
- Steinbeiss, S., G. Gleixner, and M. Antonietti. 2009. Effect of biochar amendment on soil carbon balance and soil microbial activity. *Soil Biol. Biochem.* 41:1301–1310. doi:10.1016/j.soilbio.2009.03.016
- Steiner, C., K.C. Das, N. Melear, and D. Lakly. 2010. Reducing nitrogen loss during poultry litter composting using biochar. *J. Environ. Qual.* 39:1236–1242. doi:10.2134/jeq2009.0337
- Van Zwieten, L., B. Singh, S. Joseph, S. Kimber, A. Cowie, and K.Y. Chan. 2009. Biochar and emissions of non-CO<sub>2</sub> greenhouse. p. 227–249. *In* J. Lehmann and S. Joseph (ed.) *Biochar for environmental management*. Earthscan, London.
- Van Zwieten, L., S. Kimber, S. Morris, K.Y. Chan, A. Downie, J. Rust, S. Joseph, and A. Cowie. 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant Soil* 327:235–246. doi:10.1007/s11104-009-0050-x
- Yanai, Y., K. Toyota, and M. Okazaki. 2007. Effects of charcoal addition on N<sub>2</sub>O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. *Soil Sci. Plant Nutr.* 53:181–188. doi:10.1111/j.1747-0765.2007.00123.x