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# Biochar–manure changes soil carbon mineralization in a Gray Luvisol used for agricultural production<sup>1</sup>

T.L. Weber, C.M. Romero, and M.D. MacKenzie

**Abstract:** Biochar is a source of stable organic matter being explored as a manure additive. A 64 d incubation experiment was conducted to quantify the short-term effect of manure (RM), biochar–manure (BM), raw biochar (BC), RM + BC, and BM + BC amendment on soil carbon (C) and nitrogen (N) mineralization. Manure increased CO<sub>2</sub>-C emission rates, with the highest cumulative CO<sub>2</sub>-C emissions being observed for RM + BC. Treatments with BM halted soil C mineralization, indicating manure-C stabilization. By contrast, neither RM nor BM affected soil N mineralization. Applying BM might benefit soil C sequestration by lowering CO<sub>2</sub>-C emissions over the long term.

*Key words:* biochar, animal manure, soil carbon, feedlot cattle, nitrogen mineralization.

**Résumé :** Le biocharbon est une source de matière organique stable qu'on pourrait utiliser pour enrichir le fumier. Les auteurs ont effectué une expérience d'incubation de 64 jours en vue de quantifier les effets à court terme du fumier (RM), du fumier enrichi de biocharbon (BM), du biocharbon brut (BC), d'un amendement RM + BC et d'un autre amendement BM + BC sur la minéralisation du carbone (C) et de l'azote (N) dans le sol. Le fumier augmente les émissions de C-CO<sub>2</sub>, les émissions cumulatives les plus importantes du gaz ayant été observées avec le traitement RM + BC. Les amendements contenant du BM stoppent la minéralisation du C, signe qu'il y a stabilisation du C du fumier. En revanche, ni le RM ni le BM ne modifient la minéralisation du N dans le sol. L'application de BM pourrait concourir à la séquestration du C dans le sol par la réduction des dégagements de C-CO<sub>2</sub> à longue échéance. [Traduit par la Rédaction]

*Mots-clés :* biocharbon, fumier, carbone du sol, bovins de boucherie, minéralisation de l'azote.

## Introduction

Biochar is a promising avenue for carbon (C) sequestration in temperate soils of prairie eco-regions. Biochar is a form of pyrogenic-C produced by O<sub>2</sub>-limited thermal decomposition of organic matter (OM) at temperatures <700 °C. Amending soil with biochar, i.e., recalcitrant-C, has been shown to mitigate agricultural greenhouse gas emissions by altering soil biochemical properties, e.g., increasing cation exchange capacity and reducing microbial activity. Biochar stabilizes soil OM, thereby resulting in higher soil C benefits relative to more labile amendments such as manure and compost (Preston and Schmidt 2006; Whitman et al. 2015).

Applying biochar to croplands is also frequently associated with improved soil quality and crop productivity; biochar often increases soil pH and nutrient availability for plant uptake (Preston and Schmidt 2006).

Recently, findings that biochar use in animal feeding could lower enteric methane (CH<sub>4</sub>) emissions have expanded the prospect of its use in modern-day farming (Whitman et al. 2015). Similarly, biochar–manure manure may also stabilize manure OM, emitting less ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O), and CH<sub>4</sub> once applied to croplands (Kammann et al. 2017). Romero et al. (2021) demonstrated that biochar increases manure OM recalcitrance and its overall C sequestration potential,

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yet its effect on manure OM mineralization is mostly unknown.

Pyrogenic-C represents up to 20%–65% of total soil C in prairie soils (Preston and Schmidt 2006). Nevertheless, in cropped sites across central Canada, farming has removed pyrogenic-C by suppressing wildfires, thus altering its cycling in surface soil layers. Restoring pyrogenic-C levels, mainly through biochar additions, could increase crop production, particularly in Gray Luvisols, soils that are often difficult to farm due to their inherent low pH and poor nutrient availability. The objective of this work was to determine the effect of manure amendment, in the presence or absence of biochar, on soil C and N mineralization over a 64 d incubation period. Due to pyrogenic-C's recalcitrant nature, we hypothesized that biochar would retain some of its properties once excreted by feedlot cattle (Romero et al. 2021), thereby limiting microbial activity and associated soil C and N mineralization (Whitman et al. 2015).

## Materials and Methods

Solid manure was retrieved from a 235 d feeding trial conducted at the Lethbridge Research and Development Centre of Agriculture and Agri-Food Canada near Lethbridge, AB, Canada. Briefly, 80 yearling beef steers were fed a typical Canadian feedlot backgrounding diet consisting of 60% barley silage, 35% barley grain, and 5% mineral supplement (Terry et al. 2020). Treatments consisted of adding Southern yellow pine (*Pinus echinata*) biochar (National Carbon, Oakdale, MN, USA) at 0% (regular manure, RM) and 2% (biochar-manure, BM) of diet dry matter. Manure samples were collected in January 2019 and sent to the University of Alberta Campus in Edmonton, AB, Canada, for incubation and analysis. The biochar had a pH of 7.3, an electrical conductivity of 317 mS·cm<sup>-1</sup>, an H/C ratio of 0.29, as well as 733 g·kg<sup>-1</sup> and 2 g·kg<sup>-1</sup> of total C and N, respectively.

Surface soil (0–10 cm) was collected from the Breton Plots (53°07'N, 114°28'W) near Breton, AB, Canada. The soil, classified as a loamy Gray Luvisol (pH 6.3), was amended in four replications with (i) RM at 160 Mg·ha<sup>-1</sup>, (ii) BM at 160 Mg·ha<sup>-1</sup>, (iii) raw biochar (BC) at 10 Mg·ha<sup>-1</sup>, (iv) a combination of (ii) and (iii) (BM + BC), (v) combination of (i) and (iii) (RM + BC), and (vi) a non-amended control (soil without amendments) (CT). The rate of manure application was selected to mimic field applications for barley forage production in Alberta.

After collection, the soil was air-dried at room temperature, passed through a 2 mm sieve to remove plant litter, homogenized, and stored at room temperature (22 °C) for 30 d. Samples were incubated in a Forma Diurnal Growth Chamber-Model 3740 (Thermo Fisher Scientific, Waltham, MA, USA) at 25 °C. Two identical sets of 200 g (dry-weight basis) of air-dried soil

were weighed and placed into 500 mL Mason jars. One set was kept undisturbed for carbon dioxide (CO<sub>2</sub>) gas measurement. The second set was also kept undisturbed, but small cores were removed for inorganic N measurements at the same sampling intervals as for CO<sub>2</sub>. Water-holding capacity (WHC) was determined using a pressure plate analysis at field capacity (–0.33 MPa). Both sets were pre-incubated at 60% WHC for 7 d to avoid the initial flush of respiration after soil disturbance. Immediately after pre-incubation, manure/biochar amendments were applied to the soil. Jars were loosely capped, and caps were removed weekly for 10 min to ensure adequate aeration over the incubation period, during which samples were weighed and water added to maintain the 60% WHC condition.

CO<sub>2</sub>-C fluxes and inorganic N, nitrate (NO<sub>3</sub>-N), and ammonium (NH<sub>4</sub>-N), concentrations were measured every 3 d for the first week, once a week for the following 2 wk, and then biweekly for the remainder of the study (64 d). CO<sub>2</sub>-C fluxes were quantified using a LiCor LI-8100 Soil Gas Flux System and multiplexor (LI-COR, Lincoln, NE, USA) plumbed for flask measurements. Soil was extracted with a 2 mol·L<sup>-1</sup> KCl solution at a 1:5 (w:v) soil:extract ratio, shaken (250 r·min<sup>-1</sup>, 1 h), and then filtered using a Whatman No. 42 filter paper. Nitrate and NH<sub>4</sub>-N were determined via colorimetry using a Thermo Gallery Plus Autoanalyzer (Thermo Fisher Scientific).

Subsamples of soil and manure/biochar amendments were dried at 105 °C for 48 h, ball-milled (<0.15 mm), and stored in 20 mL scintillation vials. Total C (TC) and N (TN) were analyzed by dry combustion using a Thermo Flash 2000 Organic Elemental Analyzer (Thermo Fisher Scientific). Pyrogenic-C was measured using the benzene polycarboxylic acid method following Wiedemeier et al. (2016). Soil pH was measured in a 1:5 soil:water slurry, after samples were shaken for 1 h, vacuum filtered, and allowed to settle for 30 min.

## Statistical analysis

All statistical calculations were performed using R version 1.1 (R Core Team 2020). To predict soil C and N mineralization dynamics, we fit the data to a first-order reaction,

$$(1) \quad A_m = A_o(1 - e^{-kt})$$

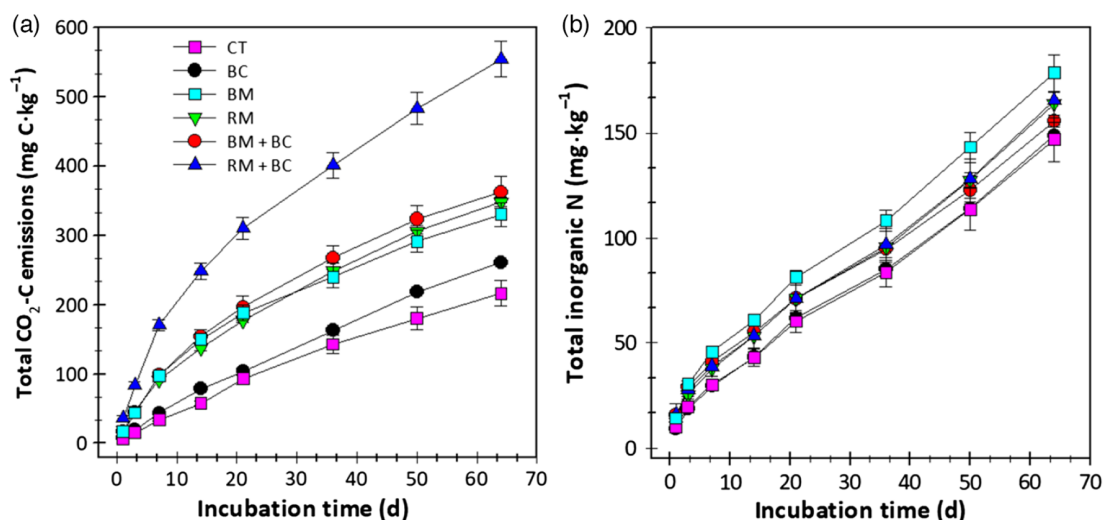
where  $A_m$  is the cumulative amount of soil C or N mineralized,  $A_o$  represents the labile pool of C or N,  $t$  is time, and  $k$  is the rate of mineralization constant (Riffaldi et al. 1996).

A one-way analysis of variance was used to analyze differences between manure/biochar amendments and soil properties, as well as the effect of manure/biochar treatments on soil C and N mineralization first-order kinetic curves. Assumptions of normal distribution and equal variance were confirmed using Shapiro and

**Table 1.** Respired soil carbon (C) and mineralized soil nitrogen (N) first-order kinetic parameters to amendment types over a 64 d incubation period and their corresponding *P* values (means  $\pm$  standard error) ( $n = 3$ ).

Amendment	Cm (mg CO <sub>2</sub> -C·kg <sup>-1</sup> )	Co (mg CO <sub>2</sub> -C·kg <sup>-1</sup> )	Kc (mg CO <sub>2</sub> -C·d <sup>-1</sup> )	Nm (mg N·kg <sup>-1</sup> )	No (mg N·kg <sup>-1</sup> )	Kn (mg N·d <sup>-1</sup> )
CT	215 $\pm$ 20d	397 $\pm$ 63ab	18.3 $\pm$ 1.9c	141 $\pm$ 10a	267 $\pm$ 10a	0.012 $\pm$ 0.001b
BC	260 $\pm$ 3cd	533 $\pm$ 65ab	16.0 $\pm$ 2.8c	143 $\pm$ 4a	276 $\pm$ 2a	0.012 $\pm$ 0.001b
BM	217 $\pm$ 18bc	397 $\pm$ 20b	54.9 $\pm$ 1.5a	169 $\pm$ 9a	229 $\pm$ 9a	0.021 $\pm$ 0.001ab
RM	340 $\pm$ 8bc	403 $\pm$ 9ab	41.8 $\pm$ 1.2b	155 $\pm$ 6a	246 $\pm$ 6a	0.017 $\pm$ 0.003ab
BM + BC	354 $\pm$ 22b	406 $\pm$ 31ab	47.9 $\pm$ 4.6ab	146 $\pm$ 2a	190 $\pm$ 2a	0.023 $\pm$ 0.002a
RM + BC	528 $\pm$ 25a	577 $\pm$ 28a	55.6 $\pm$ 1.5a	156 $\pm$ 10a	247 $\pm$ 10a	0.017 $\pm$ 0.003ab
<i>P</i> value	<0.001	<0.001	<0.001	0.130	0.130	<0.050

**Note:** Means followed by a common lowercase letter within a column are not significantly different ( $P < 0.05$ ). Cm, carbon mineralization; Co, labile pool of C; Kc, reaction rate coefficient; Nm, nitrogen mineralization; No, labile pool of N; Kn, rate of N mineralization constant; BC, biochar (10 Mg·ha<sup>-1</sup>); RM, manure from feedlot cattle on a control diet (160 Mg·ha<sup>-1</sup>); CT, control (no amendments); BM, manure from feedlot cattle on a control diet with the addition of BC at 2% of diet dry matter (160 Mg·ha<sup>-1</sup>).

**Fig. 1.** Respired soil carbon (C) (a) and mineralized soil nitrogen (N) (b) as affected by manure/biochar treatments. BC, biochar (10 Mg·ha<sup>-1</sup>); RM, manure from feedlot cattle on a control diet (160 Mg·ha<sup>-1</sup>); CT, control (no amendments); BM, manure from feedlot cattle on a control diet with the addition of BC at 2% of diet dry matter (160 Mg·ha<sup>-1</sup>). Whiskers above each shape indicate standard errors of the means ( $n = 3$ ).

Bartlett's tests, respectively. Means were compared using Tukey's honestly significant difference, where *F* values were significant at  $\alpha = 0.05$ .

## Results and Discussion

### Soil and manure characteristics

Manure pH ranged from 6.9 to 7.1, whereas the soil had a pH of 6.3. On average, manure contained 29% and 35% more TC and TN than soil, respectively (data not shown). Manure TN was unchanged ( $P > 0.05$ ) by dietary treatment, averaging 1.9 and 2.0 g·kg<sup>-1</sup> for RM and BM, respectively. By contrast, BM contained 11% more TC than RM. This response was likely associated with a higher ( $P < 0.05$ ) pool of pyrogenic-C within BM (6.3 m·g<sup>-1</sup>) relative to RM (2.0 m·g<sup>-1</sup>) (data not shown).

### Carbon mineralization

Carbon mineralization (Cm; 528 mg CO<sub>2</sub>-C·kg<sup>-1</sup>) was increased ( $P < 0.001$ ) with RM + BC relative to the other amendments (>354 mg CO<sub>2</sub>-C·kg<sup>-1</sup>) (Table 1), whereas Co (577 mg CO<sub>2</sub>-C·kg<sup>-1</sup>) was only augmented ( $P < 0.001$ ) with RM + BC compared with BM (397 mg CO<sub>2</sub>-C·kg<sup>-1</sup>). Mixing RM with BC stimulated a priming effect in soil, whereas BM and BC alone did not (Fig. 1a), supporting our hypothesis that biochar–manure would have a lower soil C mineralization potential relative to manure-only treatments. Carbon mineralization was reduced in BM (217 mg CO<sub>2</sub>-C·kg<sup>-1</sup>) compared with RM (340 mg CO<sub>2</sub>-C·kg<sup>-1</sup>) but was similar to CT (215 mg CO<sub>2</sub>-C·kg<sup>-1</sup>) (Table 1).

The reaction rate coefficient (Kc) was increased with RM + BC, BM, and BM + BC relative to CT and BC

treatments (Table 1). Apparently, there was a synergistic effect between RM and BC, considering that RM- and BC-only resulted in lower Kc values (Table 1). Lentz et al. (2014) found that applying manure with biochar improves the ability of heterotrophs to degrade biochar-C, which is in agreement with our findings of greater soil C mineralization under RM + BC. Adding biochar to manure may also improve aeration, further increasing microbial activity over labile-C (Whitman et al. 2015). Our observation supports this potential interaction as cumulative CO<sub>2</sub>-C emissions in RM + BC did not plateau as quickly as with the other treatments (Fig. 1a).

Interestingly, BM + BC and RM + BC exhibited distinct CO<sub>2</sub>-C emission patterns (Fig. 1a), despite soil C mineralization rates being similar between RM and BM treatments (Table 1). Romero et al. (2021) demonstrated that biochar passes through the gastrointestinal tract of feedlot cattle mostly unaltered. Based on this observation, we speculate that manure OM in BM is as labile as in RM, given that manure-C does not interact with biochar-C (Romero et al. 2021). However, biochar–manure is expected to be more aromatic than RM when considering the whole OM mixture (Romero et al. 2021). The latter supports our findings that adding biochar to BM does not increase CO<sub>2</sub>-C emissions as much as adding biochar to RM (Table 1).

#### Nitrogen mineralization

Nitrogen mineralization (Nm) and No were not affected ( $P = 0.130$ ) by amendment type, even though Kn was increased ( $P < 0.05$ ) with BM + BC relative to CT and BC treatments (Table 1). Joseph et al. (2015) demonstrated that biochar becomes enriched by organic-N within the rumen, potentially explaining higher manure TN contents in BM relative to RM (data not shown). Biochar may also stabilize N via sorptive reactions, limiting manure-N availability while prompting excess nutrient mining within BM + BC (Whitman et al. 2015). Amending soil with BM + BC increased NO<sub>3</sub>-N + NH<sub>4</sub>-N availability, in agreement with Lentz et al. (2014) who found that co-applying manure with biochar maximizes net N mineralization. Regular manure and RM + BC had closer soil N mineralization rates than BM and BM + BC (Table 1); cattle-ingested biochar was presumably more reactive than its raw counterpart (Joseph et al. 2015).

#### Conclusions

Application of manure, biochar, and biochar–manure impacted soil C mineralization, but did not affect soil N mineralization in the studied Gray Luvisol. Cumulative CO<sub>2</sub>-C emissions were higher with RM + BC than BM + BC and adding BC to RM or BM increased soil C and N mineralization rates. Our results indicate that BC and BM amendment might benefit soil C sequestration by lowering CO<sub>2</sub>-C emissions over time without limiting soil N availability. Further research calls for whole-farm

studies to validate the cascaded use of BM amendment in agroecosystems. Probing BM properties at a larger scale, utilizing different biochar feedstocks, is critical to identify BM types that maximize soil C benefits in Western Canada.

#### Conflicts of Interest

The authors declare there are no competing interests.

#### Contributions

Investigation: T.L.W; writing and editing: C.M.R, M.D.M, T.L.W; resources and supervision, M.D.M. All authors have read and agreed to the published version of the manuscript.

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