

Contrasting effects of wheat straw and its biochar on greenhouse gas emissions and enzyme activities in a Chernozemic soil

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Abstract Biochar produced from plant biomass through pyrolysis has been shown to be much more resistant to biodegradation in the soil as compared with the raw biomass, such as cereal straw that is routinely shredded and discharged on to farm fields in large amounts. Biochar application to soil has

also been reported to decrease greenhouse gas (GHG) emissions, although the mechanisms are not fully understood. In this study, the emissions of three main GHGs (CO₂, CH₄, and N₂O) and enzyme activities (urease, β-glycosidase, and dehydrogenase) were measured during a 100-day laboratory incubation of a Chernozemic soil amended with either straw or its biochar at rates of 0.67 and 1.68 % (based on the amount of C added) for the low and high rates, respectively. The biochar application dramatically reduced N₂O emissions, but CO₂ or CH₄ emissions were not different, as compared with the unamended soil. At the same C equivalent application rate, CO₂ and N₂O emission rates were greater while CH₄ emission rates were lower in straw than in biochar application treatments. The activities of both the dehydrogenase and β-glycosidase significantly declined while that of urease significantly increased with the biochar as compared with the straw treatment. We conclude that pyrolysis of cereal straw prior to land application would significantly reduce CO₂ and N₂O emissions, in association with changed enzyme activities, while increasing the soil C pool through the addition of stable C in the form of biochar.

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Introduction

Increases in atmospheric concentrations of greenhouse gases (GHGs) such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) are of major concerns as factors affecting global climate warming (Gärdenäs et al. 2011; Snyder et al. 2009). It has been reported that the global atmospheric concentrations of CO₂ and CH₄ have exceeded the natural range that has likely occurred over the last 650,000 years (IPCC 2007). Much of the anthropogenic C in the atmosphere is of a soil origin because the soil has lost on average

over half of its C content as a result of massive expansion of arable lands and excessive use of mineral fertilizers that destabilizes the otherwise stable Ca-forms of soil organic C contained in aggregates, leading to the formation of labile humic substances (Muñoz et al. 2010; Shevtsova et al. 2003). Soils produce CO₂ mostly under aerobic conditions, CH₄ under anaerobic conditions, and N₂O under either aerobic (nitrification) or anaerobic (denitrification) conditions. More than a third of all N₂O emissions are from anthropogenic activities and primarily due to agricultural activities (IPCC 2007). Over the past few decades, the temperatures of the atmosphere and oceans have increased due to GHG emissions. The global warming potential, which is related to the catalytic destruction of stratospheric ozone, of CH₄ and N₂O are 23 and 296 times greater than CO₂ in a 100-year period (Muñoz et al. 2010). Therefore, reducing emissions of GHGs, particularly that of N₂O, can make a substantial contribution to decreasing the effect of GHG emissions on the global climate.

The production of CO₂, N₂O, and CH₄ are affected by biophysical conditions and the incorporation/decomposition of organic residues in the soil. It is widely accepted that the addition of crop residues to the soil helps to maintain soil organic matter levels, thereby affecting soil structure, soil fertility, and crop production. Crop residue additions to the soil also have significant effects on the sustainable development of agriculture as the incorporation of crop residue alters the soil environment, physical properties, nutrient supply, and the subsequent improvement of soil productivity, which offers a way to resolving the conflict between maximizing short-term production at minimum cost versus providing sustainable health and long-term productivity of the soil. (Gao et al. 2010; Han et al. 2003; Janzen 2006; Kumar and Goh 2000) and for the reduction of N₂O emissions in fertilized and irrigated soils in southern Alberta (Hao et al. 2001). However, application of crop residues may also result in the temporary immobilization of soil nutrients during their decay, delay soil warming in the spring, and increase the risk of disease, weed, and pest transfer from the previous crop (Procházková et al. 2003). The conversion of crop residues into biochar prior to soil application could present a viable alternative to eliminate these problems.

Biochar is a stable (relative to its raw biomass C form) and C rich material produced by the pyrolysis of organic material in the absence of oxygen or in a low oxygen environment (Sohi et al. 2009). In the pyrolysis process, approximately 50 % of the C contained in the biomass is immediately released as bioenergy, leaving the remaining 50 % of the C in a stable form called biochar (Day et al. 2005; Katyal et al. 2003; Lehmann et al. 2002). Unpyrolyzed organic material decomposing in the soil initially releases C quickly and then slows over time. However, the

release of C continues until less than 10–20 % of the added C remains in agricultural soils after 5–10 years depending on C quality and the environment. Thus, in the long term, biochar application ultimately leads to greater amounts of C remaining in the soil than the direct application of un-charred organic matter (Lehmann et al. 2006; Woolf et al. 2010).

The application of biochar can increase plant growth by improving soil physical, chemical, and biological properties, including soil structure, nutrient availability, and water and nutrient retention (Glaser et al. 2002; Lehmann et al. 2003; Lehmann and Rondon 2005; Sombroek et al. 1993). Biochar application has also been reported to reduce CO₂ and N₂O production and reduce ambient CH₄ oxidation (Major et al. 2010; Spokas et al. 2009), while reduced N₂O emission and no effects on CO₂ emission were observed by Wang et al. (2011), indicating that biochar application has the potential to reduce GHG emissions and increase C sequestration. In biochar-amended soils with or without N fertilization, total N₂O emissions decreased by 40–51 and 21–28 %, respectively, while CH₄ emissions increased by 34 % with biochar addition relative to treatments without biochar and by 41 % by N fertilizer addition as compared with treatments without N fertilizer addition (Zhang et al. 2010).

Soil GHGs are mostly produced from microbiological processes, i.e., biological oxidation of organic matter in the soil (soil respiration), CH₄ oxidation, and nitrification and denitrification (Brzezińska et al. 2004; Tiedje 1998). Enzyme activities are critical in maintaining nutrient availability, and their activities are “sensors” of soil microbial function and soil physicochemical conditions (Asmar et al. 1994; Baum et al. 2003; Nannipieri et al. 2003; Sparling 1997; Wick et al. 1998). For example, soil urease activity reflected N₂O emission because of the close relationship between urease activity and nitrification (Bai et al. 2003), while the highest dehydrogenase activities occurred in the period of rapid depletion of CH₄ and O₂ and simultaneous CO₂ production due to the adaption of soil methanotrophic microorganisms in this period (Brzezińska et al. 2004). The emission of N₂O was found to be significantly related to dehydrogenase activities as the N₂O was produced during NO₃⁻ transformation in which dehydrogenation of the organic matter was catalyzed by dehydrogenases (Włodarczyk et al. 2002). Fluxes of N₂O during the dry season were positively correlated to microbial biomass N and β-glucosidase activities as heterotrophic nitrifying and denitrifying bacteria (which can both produce N₂O) require an organic form of C as energy source and may depend on β-glucosidase activities for their C supply (Wick et al. 2005). However, there have been few studies on the effects of biochar application on GHG emissions and their relationship with soil enzyme activities (Bailey et al. 2011; Lammirato et al. 2011; Paz-Ferreiro et al. 2011).

Evaluating the effects of crop residue and its biochar on soil processes is particularly interesting due to the fact that discharge of shredded straw in large amounts on to the fields during crop harvest is a common agricultural practice. The amount of crop residue returned to the soil is not based on the requirement for soil enhancement for the next crop. Indeed, excessive loading of straw can delay seed germination and lead to the oversupply of fertilizers to compensate for the N that would be locked up during the critical early summer crop growing period (Graham et al. 1986; Procházková et al. 2003).

An important anthropogenic source of GHGs was agriculture which accounts for approximately 20 % of the annual increase in radioactive forcing on climate change (Cole et al. 1997). Moreover, many of the earlier investigations only focused on the biochar effects on mitigating GHG emissions, as well as on increasing crop production and changing soil physical and chemical properties, while very few studies made comparison of the effects of biochar and its straw on GHG emissions and microbiological properties such as changes in enzyme activities that are considered as soil quality indicators that may respond to alterations in soil management on a shorter period of time than those based on physical or chemical properties (Paz-Ferreiro et al. 2011; Roldán et al. 2005). The objective of this study was to compare the effects of applying wheat straw and its biochar on GHG emissions from a Chernozemic soil as well as on enzyme activities in a laboratory incubation experiment. More specifically, we tested the hypothesis that the conversion of straw residues to biochar will suppress GHG emissions.

Materials and methods

The soil, wheat straw, and biochar

Surface soil (0–6 cm) was obtained from Flagstaff County (52°46'N, 111°41'W) in southeast Alberta, for the laboratory incubation experiment reported here. The soil is an Orthic Black Chernozem based on the Canadian system of soil classification with the following properties: loam texture, pH (1:2 v/v soil/water) 5.6 (see the “[Analysis of soil, straw, and biochar properties](#)” section below for the methods of analysis), cation exchange capacity (CEC) 13.5 cmolkg⁻¹, organic C 2.41 %, total N 0.24 %, total P 597 mgkg⁻¹, total K 5390 mgkg⁻¹, available NO₃-N 21.9 mgkg⁻¹, available PO₄-P 38.5 mgkg⁻¹, and available K 274 mgkg⁻¹. The soil was sieved to pass a 2-mm sieve and homogenized for the incubation experiment.

The biochar was produced from wheat straw using a fast pyrolysis process (450 °C and at a heating rate of 15 °Cmin⁻¹) by Alberta Innovates—Technology Futures (AITF; Vegreville,

AB, Canada), which yields approximately 30 % biochar (by weight, same below), 35 % oil, and 35 % gases. The biochar had a pH of 9.93, fixed C (or stable C, C leftover after the majority of the volatile organic matter was lost after heating) of 81 %, aeration porosity of 51 %, bulk density of 54 kg m⁻³, volatile matter of 5.0 %, water holding capacity of 44 %, and ash content of 13.8 %. The biochar contained 72.6 % total C, 0.32 %N, 2.8 %H, 15.4 % O, and 0.02 %S on an oven-dry weight basis (Waste Materials Engineering Lab., AITF). The wheat straw had 46 % C, 1.0 %N, 6.25 %H, 0.24 %S, and 6.78 % ash on an oven-dry basis. The wheat straw used in this experiment was the same as that used for biochar production.

Experimental design and treatments

The straw and biochar were ground to <2 mm. Three levels of soil amendments with straw and biochar were established, based on an equivalent amount of elemental C added by weight (0, 0.67, and 1.68 %). Since pyrolysis increased the C concentration in the final product, the dry weight percentages of added wheat straw and biochar were different: 0, 0.99, and 2.44 % for biochar (treatments CK, B1, and B2) and 0, 1.48, and 3.61 % for straw (treatments CK, S1, and S2). The equivalent field rates of these amendments incorporated into the 0–10-cm layer would be about 0, 10, and 25 t ha⁻¹ of biochar and 0, 15, and 37.5 t ha⁻¹ of straw.

For each treatment, the soil (100 g per jar) and amendments were mixed and placed into 1,000 mL sterilized glass jars and then moistened with distilled water to 80 % water filled pore space (WFPS) as calculated using the following equation (Yanai et al. 2007):

$$\text{WFPS} = \left(\frac{\theta_m \cdot P_B}{\rho_{\text{H}_2\text{O}} \cdot \text{TP}} \right) \cdot 100\% \quad (1)$$

where WFPS = water fill pore space, in percent; θ_m = gravimetric water content, megagrams per megagram; P_B = soil bulk density, in megagrams per cubic meter; $\rho_{\text{H}_2\text{O}}$ = density of water, 1 Mg m⁻³; TP = total soil porosity = $1 - P_B/P_P$, in percent; and P_P is soil particle density, megagrams per cubic meter.

Five replications were established for a 100-day incubation experiment. All 25 jars were sealed with air-tight lids and kept at 25 °C in the dark. The water content was kept constant during the incubation period by adding distilled water twice a week.

Gas sampling and analysis

Gas samples were periodically collected from the incubators for analysis: daily for the first 7 days, then once every 4 days for the next 47 days, and weekly thereafter (Cheng et al. 2012; Wang et al. 2011). Before each air sample collection, the lids were opened for half an hour to ensure thorough gas

exchange between the atmosphere and the inside of the jar. The lids were then sealed before sampling. Gas samples were taken at time 0 and 1 h incubation time using a 20-mL gas-tight syringe (BD Luer-Lok™ Tip) and injected into pre-evacuated 12-mL Exetainer® vials with septa. Gas samples were analyzed on a gas chromatograph (Varian GC-3800) fitted with a COMBI PAL autosampler. The CO₂, CH₄, and N₂O concentrations were analyzed by thermal conductivity, flame ionization, and electron capture detectors, respectively. The change in the gas concentrations was used to calculate the greenhouse gas emission rates.

Measurement of soil enzyme activities

Soil samples were collected from each jar immediately at the end of each incubation period, stored at 4 °C and processed within 24 h. Enzyme activities were determined in triplicates and expressed on an oven-dry soil basis. The experimental setup only allowed us to determine enzyme activities at the end of the incubation to evaluate the impact of the treatments on enzyme activities.

For the determination of urease activities, 5 g of moist soil (≤2 mm) was incubated at 37 °C for 5 h after adding a 5-mL (2 mg mL⁻¹) urea solution (controls were processed by adding 5 mL of distilled water instead of a urea solution). Urea remaining after the incubation was extracted with 2 mol L⁻¹ KCl-PMA (potassium chloride–phenylmercuric acetate) solution (Tabatabai 1994). Soil suspension was filtered under suction after the incubation. And then 30 mL of a color reagent (2.5 % diacetylmonoxime solution and 0.25 % thiosemicarbazide solution in H₃PO₄ and H₂SO₄) was added to 2 mL filtrate in 50 mL volumetric flask. The intensity of the red color developed was measured at 527 nm. The remaining urea was calculated using a calibration curve established with standards containing 0, 0.5, 1, 2, and 4 μg mL⁻¹ of urea. Urease activity ω (N) was expressed as the reduction of milligrams of urea-N per kilogram of dry soil per hour.

$$\omega(N) = \frac{\left[10 - m_1 \times \left(\frac{V_1}{(V_2 \times 1,000)}\right)\right] \times 0.466}{m_2 \times t} \times 1,000 \quad (2)$$

where: m_1 = urea content in soil samples, in micrograms; V_1 = total volume of extraction solution, in milliliter; V_2 = volume of extraction used to determine urea concentration, in milliliter; 0.466 = N content (as a fraction) in urea; m_2 = the amount of soil used for the incubation, in grams; and t = incubation time, in hours.

The method used to determine β-glucosidase activity was based on the colorimetric determination of *p*-nitrophenyl released by β-glucosidase when 1 g of soil was incubated for 1 h at 37 °C with a buffered PNG (*p*-nitrophenyl-β-D-glucoside) solution (pH 6.0) and toluene (Tabatabai 1994). The amount of *p*-nitrophenyl released from the substrate was determined

by measuring the yellow filtrate colorimetrically after color development of the soil suspension with 1 mL 0.5 mol L⁻¹ CaCl₂ and 4 mL of tris (hydroxymethyl) aminomethane buffer (pH=12). Three replicates and two controls were set up during the assay with the same procedure, except that the substrate (PNG) was added to controls after the incubation described above, immediately prior to the end of the reaction. The mean control value was subtracted from the corresponding sample values. The intensity of the color of the filtrate that developed was determined at 400 nm, and the amount of *p*-nitrophenyl released was calculated using a calibration curve established with standards containing 0, 1, 2, 3, 4, and 5 μg mL⁻¹ of *p*-nitrophenyl. The β-glucosidase activity ω (PN) was expressed as milligrams of *p*-nitrophenyl released per kilogram dry soil per hour.

$$\omega(\text{PN}) = \frac{A \cdot 1,000}{m \cdot b} \quad (3)$$

where A = the amount of *p*-nitrophenyl in a soil sample, in milligrams; m = the amount of soil used, in kilograms; and b = 1 – soil moisture content, in percent.

The method used to determine dehydrogenase activity was based on extraction with methanol and colorimetric determination of the triphenyl formazan (TPF) produced from the reduction of 2,3,5-triphenyltetrazolium chloride (TTC) in soils (Tabatabai 1994). Six grams of soil was mixed with 1 mL 3 % TTC, 0.07 g CaCO₃, and 2.5 mL distilled water and then incubated at 37 °C for 24 h. The TPF in the filtrate produced from TTC was extracted with four successive portions of methanol totaling 100 mL. The control was processed using the same procedure except that the substrate (TTC) was added to the control after the incubation. The intensity of the reddish color developed was measured at a wavelength of 485 nm. The amount of TPF produced was calculated using a calibration curve prepared from TPF standards containing 0, 5, 10, 15, and 20 μg mL⁻¹ of TPF. Dehydrogenase activity ω (TPF) was expressed as milligrams of TPF produced per kilogram of dry soil per hour.

$$\omega(\text{TPF}) = \frac{m_1 \times 1,000}{m_2} \times t \quad (4)$$

where m_1 = TPF produced by soil samples, in milligrams; m_2 = the amount of soil used for the assay, in grams; and t = incubation time, in hours. The color of the filtrate and solution described above was measured with a Spectronic 10 Genesys spectrophotometer (Thermo Electron Scientific Instruments Corp., Madison, WI, USA).

Analysis of soil, straw, and biochar properties

Soil texture was determined using the hydrometer method (Gee and Or 2002). The pH of the soil and biochar was measured with a pH meter in 0.01 mol L⁻¹ CaCl₂ (pH_{CaCl2})

using 10 g of soil/biochar in 20 mL of solution. CEC was determined after extracting the sample with 1 mol L⁻¹ NH₄OAc at pH 7 following Carter and Gregorich (2006). The total C, N, H, O, and S concentrations of the soil, straw, or biochar samples were analyzed using a CHNS/O elemental analyzer. Soil total P and K concentrations were determined on an autoanalyzer (for P) or an atomic absorption spectrophotometer (K) after the samples were digested in a HNO₃/HClO₄ solution (Sparks et al. 1996). Soil available NO₃⁻N was measured on an autoanalyzer after extracting the soil sample with 2 mol L⁻¹ KCl. Available soil PO₄-P and K were determined following a modification of Kelowna extraction (Qian et al. 1994). The ash content was determined after burning off the organic matter in a sample in a muffle furnace at 500 °C. The volatile matter content was determined following American Society for Testing and Materials method E872, by placing 1 g sample in a lidded silica crucible in a 950±20 °C furnace for 7 min and determining the weight loss. The amount of fixed C in a sample of material was determined by subtracting water, ash, and volatile matter content from the total mass. The bulk density of the biochar was determined by placing and weighing the material in a container with a known volume. Aeration porosity and water holding capacity were measured following the methods in Ingram et al. (1990).

Statistical analysis

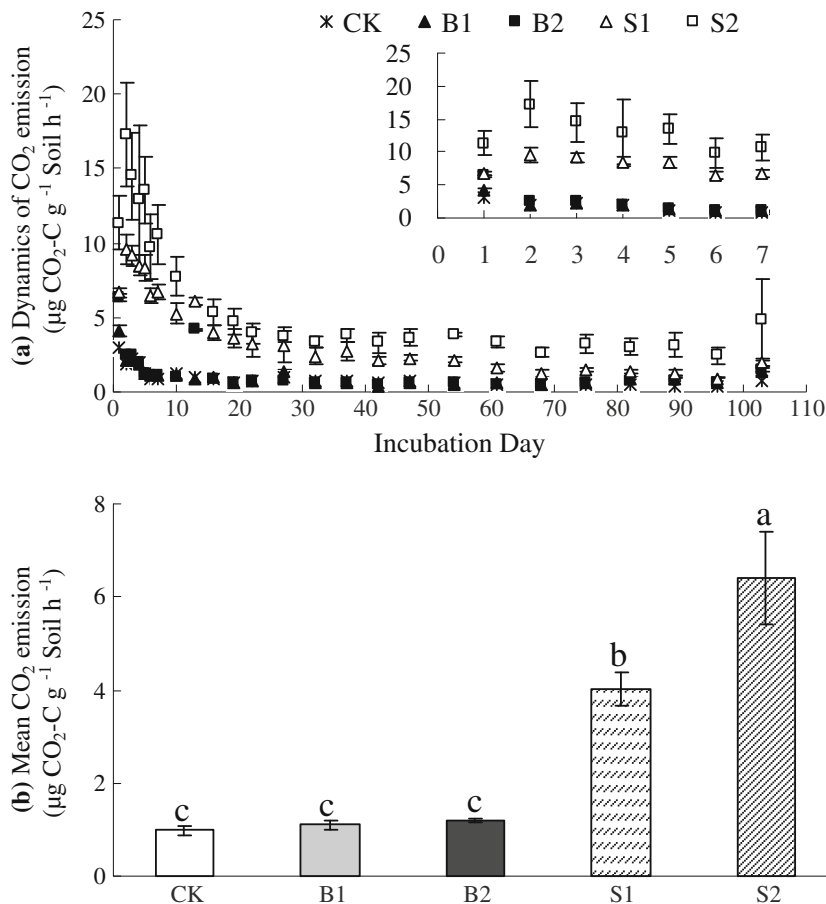
The rates of CO₂, CH₄, and N₂O emissions were determined from the increase in gas concentrations in the headspace over the 1-h incubation period, and the values are expressed as arithmetic means (n=5) and standard deviations (SD) of the replications. Variances were analyzed using the repeated measures analysis, the treatments consisted of a control (CK), two levels of biochar amendments (B1 and B2), and two levels of straw amendments (S1 and S2). One-way analysis of variance was applied to determine treatment efforts, and significance level was assumed at p=0.05. Mean separations were conducted using the LSD multiple range test. All statistical analyses were performed using version 9.01 of SAS (SAS Institute, Inc., Cary, NC, USA).

Results

Soil trace gas emissions

Straw treatments had greater CO₂ emission rates than the biochar treatments during the incubation, and the difference between the treatments gradually decreased over time in the

Fig. 1 The effects of straw and its biochar application on **a** the dynamics of CO₂ emission (mean±SD) and **b** mean CO₂ emission rates during a 100-day incubation experiment. The *insert* plots the data from the first 10 days of the incubation. Treatment codes are CK control, no biochar or straw application; B1 biochar application at a rate equivalent of 10 tha⁻¹; B2 biochar application at a rate equivalent of 25 tha⁻¹; S1 straw application at a rate equivalent of 15 tha⁻¹; and S2 straw application at a rate equivalent of 37.5 tha⁻¹



first 30 days (Fig. 1a). The straw treatments had greater mean CO_2 emission rates than the biochar treatments (which was not different from the CK) during the 100-day incubation period, with CO_2 emission rates increased with increased rate of straw addition (Fig. 1b). Overall, CO_2 emissions in the biochar treatments were reduced by 73 and 81 % for the low and high rates of biochar C addition, respectively, as compared with the corresponding straw treatments.

The rates of CH_4 emissions were generally similar across the treatments over the incubation period (Fig. 2a). Rates of CH_4 emissions fluctuated over the incubation period with minimal emission rates observed on day 5, and obvious absorption of CH_4 was found in all treatments on day 68. Biochar addition increased mean CH_4 emission rates in comparison with the CK (Fig. 2b). There were no significant differences in the mean CH_4 emission rates among the B1, B2, and CK treatments. Rates of CH_4 emissions in the straw treatments (S1 and S2) were lower than that in the biochar treatments. Compared to straw addition (S1 and S2), biochar application (B1 and B2) increased mean CH_4 emission rates by 13 and 35 %, respectively.

The highest N_2O emission rates were observed between days 2 and 4, and then the rates decreased to their lowest level on day 13 in all treatments, thereafter N_2O emission

rates stabilized or increased with time (the CK in particular) in the incubation period (Fig. 3a). The N_2O emission rates from treatment with the high rate of biochar addition (B2) were negligible during the entire incubation period. There was an increasing trend of N_2O production after day 36 in all treatments, with N_2O production from the CK greater than that from the other treatments. Both biochar and straw application suppressed the production of N_2O based on the mean emission rates, with the suppressing effects greater in the treatments with greater biochar and straw application rates (Fig. 3b). However, at the equivalent C addition rate, biochar addition had a much greater effect on suppressing N_2O emission rates than did the straw treatments, with the B1 and B2 treatments reducing the mean N_2O emission rates by 55 and 96 % as compared with the respective straw treatment or by 66 and 99 % as compared with the CK.

Enzyme activities

Biochar applications had no effect on dehydrogenase activities as compared to the CK; however, straw additions significantly increased dehydrogenase activities relative to biochar additions and the CK ($P < 0.01$), and the greater the

Fig. 2 The effects of straw and its biochar application on **a** the dynamics of CH_4 emission (mean \pm SD) and **b** mean CH_4 emission rates during a 100-day incubation experiment. The *insert* plots the data from the first 10 days of the incubation. Treatment codes are CK control, no biochar or straw application; B1 biochar application at a rate equivalent of 10 t ha^{-1} ; B2 biochar application at a rate equivalent of 25 t ha^{-1} ; S1 straw application at a rate equivalent of 15 t ha^{-1} ; and S2 straw application at a rate equivalent of 37.5 t ha^{-1}

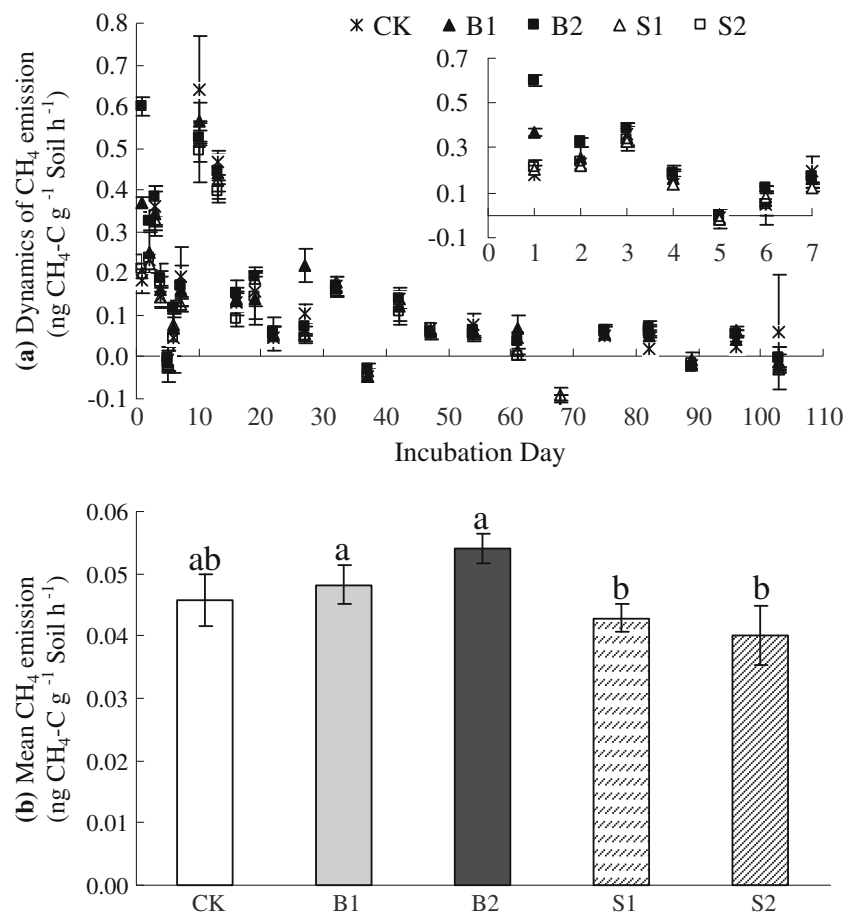
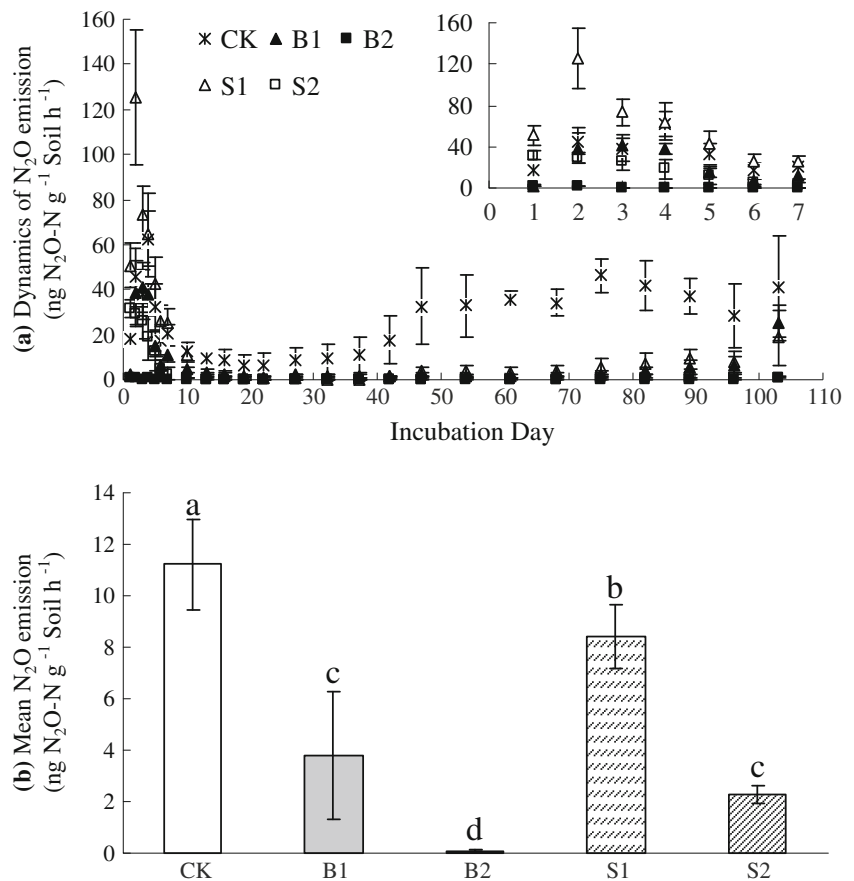


Fig. 3 The effects of straw and its biochar application on **a** the dynamics of N₂O emission (mean±SD) and **b** mean N₂O emission rates during a 100-day incubation experiment. The *insert* plots the data from the first 10 days of the incubation. Treatment codes are *CK* control, no biochar or straw application; *B1* biochar application at a rate equivalent of 10 t ha⁻¹; *B2* biochar application at a rate equivalent of 25 t ha⁻¹; *S1* straw application at a rate equivalent of 15 t ha⁻¹; and *S2* straw application at a rate equivalent of 37.5 t ha⁻¹



straw addition rate, the greater the dehydrogenase activity (Fig. 4a). Activities of β-glucosidase increased with the increasing rate of straw addition. Biochar (B1 and B2) treatments reduced β-glucosidase activities by 28 and 34 %, respectively, as compared with the straw treatments (S1 and S2) (Fig. 4b). Both biochar and straw treatments reduced urease activities as compared to the CK (Fig. 4c). Straw additions significantly decreased urease activities in comparison to biochar additions and CK. Urease activities decreased with the increasing rate of biochar and straw additions.

Relationships among greenhouse gas emissions and enzyme activities

Mean CO₂ production was found to be related to all three enzyme activities, among which positive correlations were observed with dehydrogenase ($r_s=0.44$, $P<0.05$; data not shown, same below) and β-glucosidase activities ($r_s=0.85$, $P<0.01$), while a negative relationship was found with urease activities ($r_s=-0.82$, $P<0.01$). There was a negative correlation between mean production of CH₄ and β-glucosidase activities ($r_s=-0.45$, $P<0.05$). Mean production of N₂O was positively correlated with urease activities ($r_s=0.57$, $P<0.05$). A positive correlation was found between β-glucosidase and

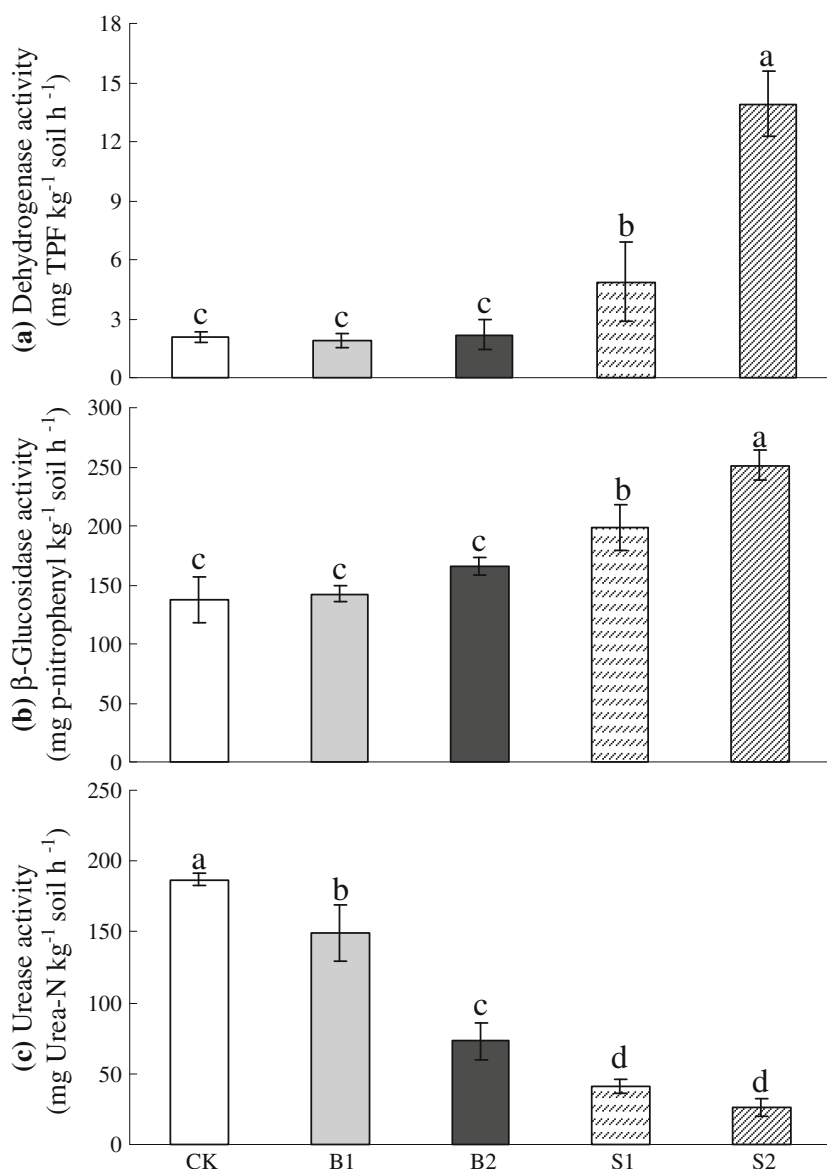
dehydrogenase activities ($r_s=0.67$, $P<0.01$). No significant correlations were found among the rates of the three GHG emissions.

Discussion

Biochar addition did not affect soil CO₂ emissions as compared to the CK (Fig. 1b), indicating that probably biochar had no effect on microbial activities and that little biochar decomposition occurred during the incubation period (Jones et al. 2011; Spokas et al. 2009). However, an increasing CO₂ emission was observed in the straw treatments, and approximately 77 % of straw C was respired over the incubation period (data not shown), indicating increased microbial activities due to the relatively high amounts of easily decomposable organic matter in the straw (Singh et al. 2010). Those results are consistent with another study that used the same biochar and straw on a different soil and with a much shorter incubation period of 12 days (Cheng et al. 2012).

Biological oxidation of organic compounds is generally a dehydrogenation process (Tabatabai 1994), and thus, dehydrogenases are important enzymes during the biological oxidation of organic compounds. The products of hydrolysis involving the enzyme β-glucosidase are believed to be

Fig. 4 The effects of straw and its biochar application on **a** soil dehydrogenase (mean±SD), **b** β -glucosidase, and **c** urease activities after an 100-day incubation. Treatment codes are CK control, no biochar or straw application; B1 biochar application at a rate equivalent of 10 tha^{-1} ; B2 biochar application at a rate equivalent of 25 tha^{-1} ; S1 straw application at a rate equivalent of 15 tha^{-1} ; and S2 straw application at a rate equivalent of 37.5 tha^{-1}



important energy sources for microorganisms in soils which make β -glucosidase an indicator of changes of soil organic matter (Bell et al. 2010; Garcia and Hernandez 1994). The fact that the activities of those two enzymes were highly correlated ($P < 0.01$) and that both enzyme activities were correlated with the production of CO_2 ($P < 0.05$) in our study was in agreement with the role of these two enzymes in the soil (Gärdenäs et al. 2011). Our results also showed that straw additions significantly increased dehydrogenase and β -glucosidase activities as compared to biochar additions and the CK (Fig. 4a, b). These results indicate that when the form of C added was biochar (relative to straw), the C was more recalcitrant and did not stimulate soil microbial or enzyme (dehydrogenase and β -glucosidase) activities.

There have been reports of reduction of CH_4 emissions from soils after biochar addition (Rondon et al. 2005, 2006; Spokas et al. 2009). However, CH_4 production also occurs

under anaerobic conditions (Fenchel et al. 1998). In our research, biochar addition did not affect the CH_4 production rate as compared to the CK (Fig. 2b). The effects of straw application on CH_4 emission have been studied mostly in rice paddy systems and showed that CH_4 emissions increased due to straw application (Bossio et al. 1999; Ma et al. 2008). However, we found a significant reduction in CH_4 production rate (Fig. 2) by straw addition, indicating that under aerobic conditions, which are similar to upland conditions, straw application increased the soil's ability to take up CH_4 (Tate et al. 2007).

Emissions of N_2O from soils are primarily from microbially driven nitrification and denitrification processes. In the latter case, oxygen is limiting and anaerobic (mainly bacteria) reduction of nitrate occurs where nitrate becomes the electron acceptor. Results from our study (Fig. 3a) demonstrate that biochar additions were effective in reducing

overall emissions of N_2O as compared to straw additions and the CK. The effect on the reduction of N_2O emission was better by the application of biochar than that of straw residual was similar to the finding of Van Zwieten et al. (2010b). This means that organic materials such as straw when converted into biochar will not only provide energy but will also reduce emissions of soil N_2O , a potent greenhouse gas (Clough et al. 2010; Singh et al. 2010). The suppression of N_2O emissions may be related to the alkali (liming effects resulting from the addition of ash that had a pH of 10) added to the soil that had the potential to increase the N_2O -reducing activity of denitrifying communities which shifted the main microbial source of N_2O from ammonia oxidation to denitrification (Baggs et al. 2010; Cavigelli and Robertson 2000, 2001; Clough et al. 2004; Van Zwieten et al. 2010a; Yanai et al. 2007).

The decomposition of straw and thus its ability to immobilize N may be the cause for the lower rates of N_2O emissions from straw added soils (Cheng et al. 2012; Ryszkowski and Kędziora 2007). The process of straw decomposition is influenced by enzymes such as urease and the activity of urease in the soil seems to be mainly the result of its release from decaying microbial and plant cells which were primarily associated with soil organic matter and clay minerals (Geisseler et al. 2010; Kandeler et al. 1999; Reynolds et al. 1985). In our study, urease activities were reduced by both biochar and straw treatments as compared to the CK. Our results of reduced N_2O emission and urease activity by the biochar and straw addition treatments are consistent with reports that soil urease activity is closely connected with N_2O emissions (Bai et al. 2002, 2003). The abnormally low N_2O emissions with straw addition were due to its high rate of addition without any additional inorganic N. The low and high rates of straw addition were equivalent to an addition of 15 and 37.5 Mg ha^{-1} of straw, compared to typical straw yields in Alberta of less than 5 Mg ha^{-1} . The amount of C added at the high rate of straw (1,500 mg per jar) would immobilize about 100–200 mg of N, but initial soil $\text{NO}_3\text{-N}$ was only 2 mgN per jar and the added straw only contained about 38 mgN per jar. High N immobilization in straw-amended treatments thus explains the reduction of N_2O emissions from straw addition. The implication is, however, the effectiveness of biochar addition for reducing N_2O emissions may be greater if more available N were present in the soil.

Overall, straw applications to the soil increased CO_2 production but reduced N_2O production, while biochar amendments had no effect on CO_2 emission and almost completely suppressed N_2O emission when the high biochar application rate was used. The lack of biochar application effect on CH_4 production was in contrast with the depressed CH_4 emission after straw application. The global warming potential of CH_4 and N_2O are 23 and 296

times greater than that of CO_2 in a 100-year period (Muñoz et al. 2010). Therefore, the benefit for reducing the greenhouse effect from the substantial reduction of N_2O emissions after biochar application outweighs that of the reduction in CH_4 emission after straw application. In addition, toxins produced when straw residue break down can inhibit plant seed germination and growth (Ma et al. 2008; Procházková et al. 2003; Thomsen and Christensen 1998). Straw incorporation can also increase disease transfer from previous crops (Janya et al. 2010). Pyrolysis of straw would resolve all these issues while contributing to C sequestration, soil amelioration, and reduction of GHG emissions. Further research is needed to gain more information about the environmental vs. economic benefits of biochar vs. straw application.

Although extrapolation of the findings from this short-term laboratory study to long-term field results should be conducted with caution, field applications of biochar could possibly be used to suppress GHG emissions from arable soils, depending on the moisture content and aeration status of the soil. Further research is needed to broaden our understanding of the effectiveness of biochar application on reducing GHG emissions from different soils in Alberta under field conditions.

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