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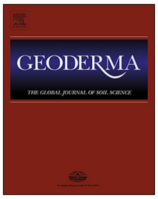

Effect of six engineered biochars on GHG emissions from two agricultural soils: A short-term incubation study

Patrick Brassard[a,b,*], Stéphane Godbout[a], Joahnn H. Palacios[a], Thomas Jeanne[a], Richard Hogue[a], Patrick Dubé[a], Lionel Limousy[c], Vijaya Raghavan[b]

[a] Research and Development Institute for the Agri-Environment (IRDA), 2700 Einstein Street, Quebec City, Quebec G1P 3W8, Canada
[b] Department of Bioresource Engineering, Macdonald Campus, McGill University, 21111 Lakeshore, Sainte-Anne-de-Bellevue, Quebec H9X 3V9, Canada
[c] Université de Haute-Alsace, Institut des Matériaux de Mulhouse (IS2M), 3 rue Alfred Werner, 28093 Mulhouse Cedex, France

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ABSTRACT

Biochar production for soil amendment was recently proposed as a tool to mitigate climate change, reducing soil greenhouse gas (GHG) emissions and sequestrating carbon (C) in soil. The aim of this research project was to test the hypothesis that only biochars with specific requirements (low H/C_{org} and O/C_{org} ratios, high C/N ratio) can reduce soil N_2O emissions without increasing CO_2 emissions in the short term. A 45-days incubation study was carried out, in which six engineered biochars made from the pyrolysis of wood, switchgrass and the solid fraction of pig manure (SFPM), were amended to two agricultural soils (loamy sand and silt loam) at a dose of 2% (w/w) in 1-liter jars. Soil moisture content was adjusted at 80% of water-filled pore space with a solution of ammonium nitrate that corresponds to 170 kg of nitrogen per hectare. N_2O and CO_2 emissions were analysed on days 2, 3, and then weekly. Soil chemical properties and bacterial richness, composition and taxonomy were analysed after the incubation period. When compared to the control soils without biochar, N_2O emissions were decreased by 42 to 90%, but only in the silt loam amended with biochars made from wood and switchgrass, these biochars having a high C/N ratio (> 30). Lower $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ concentrations were observed in these biochar treatments than in control soil. Moreover, two bacterial classes (*Deltaproteobacteria* and *Thermoleophilia*) were correlated with a decrease in N_2O emissions. For each type of biochar, those produced at the highest temperature with low O/C_{org} and H/C_{org} ratios resulted in the lowest increase in CO_2 emissions, which could indicate a higher biochar carbon stability. Overall, results of this study demonstrated that biochar can either increase or decrease soil GHG emissions depending on its properties, and that the effect can differ according to soil properties. Future long-term studies in the field in the presence of crop should be carried out in order to validate the conclusions of this study.

1. Introduction

The use of negative emission technologies for the permanent removal of carbon dioxide (CO_2) from the atmosphere was reported as a solution to limit global warming below 2 or 1.5 °C by the end of the century (UNEP, 2016), which is the objective stated in the Paris agreement in 2016. Recently, the production of biochar and its amendment to soil was identified among the most promising negative emission technologies (UNEP, 2016), having a useful negative emission potential of 0.7 Gt $C_{eq.}$ yr^{-1} (Smith, 2016). In addition, studies reported that the amendment of biochar to soil can improve soil fertility and thus increase crop yields through the improvement of soil composition, water retention, nitrification enhancement and increased nutrient uptake (He et al., 2016; Major et al., 2010; Novak et al., 2009).

Biochar is a co-product of thermochemical conversion of a biomass in an oxygen-limited environment, i.e. pyrolysis, along with syngas and the condensed bio-oil. There is a huge variability in physical and chemical properties of biochar, which depend on the feedstock and the pyrolysis operating parameters (Novak and Busscher, 2013; Y. Sun et al., 2014). Thus, not all biochars are valuable for the improvement of soil properties and as a tool to mitigate climate change.

Biochar has a high carbon (C) stability when its O/C_{org} and H/C_{org} ratios are lower than 0.2 and 0.7, respectively, and thus most of its C content ($C_{biochar}$) will be sequestered (i.e. retained) in soils for > 1000 years (Brassard et al., 2016). Moreover, many research studies demonstrated that biochars with a high C_{total}/N_{total} ratio (> 30) generally contribute to reduce soil N_2O emissions (Cayuela et al., 2014; Brassard et al., 2016). N_2O release by soils is driven by nitrification

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[*] Corresponding author at: Research and Development Institute for the Agri-Environment (IRDA), 2700 Einstein Street, Quebec City, Quebec G1P 3W8, Canada.
E-mail address: patrick.brassard@irda.qc.ca (P. Brassard).

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(oxidation of NH_4^+ to NO_3^- via NO_2^-) under aerobic conditions, and by denitrification (reduction of NO_3^- to N_2O and N_2) under anaerobic conditions (Oertel et al., 2016). Most of the mechanisms so far identified that can be responsible for a decrease of N_2O emissions after soil biochar amendment are biotic as they involve a change in microbial abundance in the soil (Bruun et al., 2011; Harter et al., 2014; He et al., 2016; Lehmann et al., 2011). The main mechanisms include: (1) the liming effect of biochar creating an optimal environment for N_2O reductase activity (Sohi et al., 2010; L. Sun et al., 2014), (2) the reduction of the availability of NO_3^- and NH_4^+ to the microorganisms involved in nitrification and/or denitrification and producing N_2O (Kettunen and Saarnio, 2013; van Zwieten et al., 2010), (3) an enhanced soil aeration which inhibits the denitrification process (Augustenborg et al., 2012; Rogovska et al., 2011) and (4) the release of toxic/inhibitory compounds like ethylene inhibiting soil biological activity (Cayuela et al., 2014). Abiotic mechanisms have also been proposed as being involved in the mitigation of N_2O emissions in biochar-amended soils. For example, Cayuela et al. (2013) proposed that biochar could act as an electron shuttle, allowing electrons to flow more easily through the soil.

In addition, the effect of a specific biochar on soil GHG emissions and on its stability will also depend on the environmental factors, i.e. soil properties, temperature and moisture (Bai et al., 2014). However, few previous studies have evaluated the effect of different biochars in a wide range of soil conditions (Fidel et al., 2017a). For example, Ameloot et al. (2013a) reported that soil texture (especially the clay content) could have an impact on the biological response to biochar addition. Moreover, Cayuela et al. (2014) found that biochar has the greatest mitigation of N_2O in fine texture soils as compared to coarse soils.

The hypothesis of this study is that only specific biochars with low H/C_{org} (< 0.7) and O/C_{org} (< 0.2) ratios can contribute to reduce soil N_2O emissions without increasing CO_2 emissions in two types of soil in the short term. To test the hypothesis, six engineered biochars with contrasting properties produced from the pyrolysis of wood, switchgrass and the solid fraction of pig manure (SFPM), were amended in two agricultural soils, incubated over a 45-days period, and emissions of CO_2 and N_2O were analysed. In addition, the relationships between soil GHG emissions and the chemical properties, microbial diversity and abundance of the soil were studied, aiming at identifying the mechanisms involved following biochar amendment to soil.

2. Materials and methods

2.1. Biochar production and characterisation

Six engineered biochars were produced using an auger pyrolysis reactor as described by Brassard et al. (2017). Three biomasses with different physico-chemical properties were selected for the pyrolysis experiments: wood pellets made from a mixture of Black Spruce (*Picea mariana*) and Jack Pine (*Pinus banksiana*), the solid fraction of pig manure (SFPM), and switchgrass (*Panicum virgatum* L.). All biomasses were ground and sieved to a particle size between 1.0 and 3.8 mm prior to pyrolysis. Two biochars were produced from wood (W1 and W2), two from switchgrass (S1 and S2), and two from the solid fraction of pig manure (SFPM; M1 and M2). Biochars W2, S2 and M2 were produced with pyrolysis operating parameters that were chosen from a response surface methodology (RSM) by Brassard et al. (2017) and are expected to have optimal properties to maximize the $C_{biochar}$ sequestration potential (low O/C_{org} and H/C_{org} ratios). Biochars W1, S1 and M1 were produced at lower temperature and during a shorter residence time (Table 1), as determine with the RSM, to have the opposite characteristics (high O/C_{org} and H/C_{org} ratios).

The chemical properties of biochars (proximate and ultimate analysis) were analysed at the IRDA laboratory (Quebec City, QC, Canada). Moisture, volatile matter and ash contents were analysed, based on the ASTM D 1762-84 standard (ASTM, 2011). The C, hydrogen (H) and nitrogen (N) contents were evaluated by dry combustion (Leco TruSpec, St. Joseph, MI, USA). The oxygen (O) content was estimated by subtracting the C, H, N, and ash contents from 100 wt%. Inorganic C was analysed by the determination of CO_2-C content with 1 M HCl, as outlined in the ASTM D 4373-02 standard (ASTM, 2002). Organic C was calculated as total C – inorganic C. Chlorine (Cl) extraction with water and dosage by titration with silver nitrate ($AgNO_3$) was used to determine the Cl content. The specific surface area of biochar was determined by gas (CO_2) adsorption according to the Brunauer, Emmett and Teller (BET) method by using a Micromeritics ASAP2020. Prior to analysis, all samples were outgassed at 300 °C for 24 h under vacuum to remove the adsorbed species from the surface of biochars. Analysis of the biochars was carried out at 0 °C, with temperature control being achieved with an ice-water bath. Finally, the morphology of biochars was analysed using Scanning Electron Microscope—Energy Dispersive X-ray Spectroscopy (SEM-EDX - Philips XL 30 FEG) at the *Institut des Matériaux de Mulhouse* (IS2M) (Mulhouse, France).

Table 1

Pyrolysis operating parameters for the production of six biochars and their physicochemical properties.

	Unit	W1	W2	S1	S2	M1	M2
Pyrolysis parameters							
Biomass		Wood	Wood	SG[b]	SG	SFPM[c]	SFPM
Temperature	°C	516	644	459	591	526	630
Res. time[a]	s	80	101	78	104	76	94
N_2 flowrate	$L\ min^{-1}$	4.0	2.9	3.4	2.6	4.0	1.7
Products yields							
Biochar	%	26.4	18.5	26.9	18.9	46.4	34.9
Bio-oil	%	58.2	51.5	60.2	49.4	37.9	41.5
Biochar properties							
C_{total}	%	71.6	80.0	67.1	79.9	51.5	49.2
C_{org}	%	70.7	76.0	64.9	79.5	47.4	45.2
H	%	4.8	3.73	4.85	3.36	3.73	3.36
O	%	21.6	13.4	22.9	9.8	15.6	13.7
N	%	0.141	0.166	0.641	0.804	4.40	4.05
C_{total}/N	Mass ratio	508	482	105	99.4	11.7	12.1
H/C_{org}	Molar ratio	0.81	0.54	0.77	0.48	0.88	0.72
O/C_{org}	Molar ratio	0.23	0.13	0.26	0.09	0.25	0.23
$P_{soluble}$	$Mg\ kg^{-1}$	13.7	7.16	109	29.4	165	55.7
Water content	%	0.9	1.2	1.5	1.4	0.9	0.9
Ash (750 °C)	%	1.4	2.1	4.1	5.5	23.6	28.1
Organic matter	%	98.6	97.9	95.9	94.5	76.4	71.9
pH		6.8	7.6	6.4	8.8	8.6	9.3
Surface area	$m^2\ g^{-1}$	94.2	138.1	108.7	133.2	70.9	65.1

[a] Residence time of biomass in the reaction chamber.
[b] Switchgrass.
[c] Solid fraction of pig manure.

2.2. Soil sampling and characterisation

Surface soil samples (0–15 cm) were collected in St-Lambert de Lauzon (46°36′ N and 71°10′ W) and in Deschambault (46°40′ N and 71°55′ W), which are two important agricultural regions in the province of Quebec (Canada). Based on the USDA textural soil classification, they were classified as a silt loam (20% sand, 55% silt and 25% clay) and a loamy sand (82% sand, 14% silt and 4% clay). Soils were stored at 4 °C for three weeks. Two days prior to the beginning of the incubation, soils were air-dried, ground and sieved to obtain < 2 mm fraction. Total carbon (C) and nitrogen (N) were analysed by dry combustion (Leco TruSpec, St. Joseph, MI, USA). N-NH_4 and N-NO_3 were extracted from 5 g sample in 25 g of KCl (2 M) following 1 h stirring. Water-soluble organic C (WSOC) was measured by a water extraction method. The pH was measured in water, and water content was determined by gravimetric method.