



Effect of six engineered biochars on greenhouse gas emissions from a loamy sand and a silt loam

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ABSTRACT Biochar produced from the pyrolysis of agricultural and forest biomasses have the potential to sequester carbon in soil and to reduce greenhouse gas (GHG) emissions. The goal of this research study was to evaluate the effect of engineered biochars produced from the pyrolysis of agricultural and forest biomasses on soil properties and GHG emissions. A 45-days incubation study was carried out, in which two types of soil (loamy sand and silt loam) were mixed with six different engineered biochars at a dose of 2% in 1 liter jars. The engineered biochars were produced from woody biomass, switchgrass and the solid fraction of pig manure (SFPM) in a vertical auger reactor using different pyrolysis operating parameters determined in previous experiments. At the beginning of the incubation, soil moisture content was adjusted at 80% WFPS (water-filled pore space) with a solution of ammonium nitrate that corresponds to a dose of 170 kg of nitrogen per hectare. Gas samples were taken to monitor N₂O and CO₂ emissions on the first three days, and then weekly. When compared to control (soil without biochar), N₂O emissions decreased only in the silt loam amended with wood and switchgrass biochar; these four biochar treatment showed a high C/N ratio (> 30). Biochar produced from wood at high temperature (644°C), with low O/C_{org} and H/C_{org} ratios (0.13 and 0.58, respectively), did not increase CO₂ emissions in both soils, indicating high biochar carbon stability. Results of this study demonstrated that both biochar and soil properties have an impact on N₂O and CO₂ emissions.

Keywords: Auger Pyrolysis, Biochar, Bio-oil, Biomass

INTRODUCTION The use of negative emission technologies for the permanent removal of carbon dioxide (CO₂) 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. The production of biochar and its amendment to soil was identified as a method to 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). Recently it was identified among the most promising negative emission technologies (UNEP, 2016), having a useful negative emission potential (0.7 Gt C_{eq.} yr⁻¹), and potentially have the lower impact on land, water use, nutrients, albedo, energy requirement and cost (Smith, 2016). Biochar is produced from the thermochemical conversion of biomass in an oxygen-limited environment, i.e. pyrolysis. 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; Sun et al., 2014). Thus, not all biochars are valuable for the improvement of soil properties and as a negative emission technology. In fact, biochar can have 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 its C content (C_{biochar}) will be sequestered (i.e. retained) in soils for more than 1000 years (Brassard et al., 2016). Moreover, many research studies demonstrated that biochar can reduce soil greenhouse gas (GHG) emissions when its C/N ratio is higher than 30 (Cayueta et al., 2014). The liming effect of biochar (Sohi et al., 2010; Sun et al., 2014), 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 adsorption of NO₃⁻ and NH₄⁺ on biochar (Kettunen & Saarnio, 2013; van Zwieten et al., 2010) and an enhance soil aeration (Augustenborg et al., 2012; Rogovska et al., 2011) are the mechanisms so far identified that can be responsible for a decrease of N₂O emissions after soil biochar amendment. In addition, the effect of a specific biochar on GHG emissions and on its stability will also depend on the environmental factors, i.e. soil properties, temperature and moisture (Bai et al., 2014).

The aim of this research project was to validate the hypothesis that production of engineered biochars with specific requirements for soil amendment can be a negative emission technology, reducing soil GHG emissions. Thus, six engineered biochars were amended in two types of soils in an incubation study, and emissions of CO₂ and N₂O were measured over a 45-days period. In addition, the relationships between soil GHG emissions and the chemical properties were studied.

MATERIALS AND METHODS

Biochar production and characterization Six engineered biochars were produced using a vertical auger pyrolysis reactor as described by Brassard et al. (2017). Pyrolysis operating parameters and biochar properties are presented in Table 1. Two biochars were produced from wood (B1 and B2), two from switchgrass (SG; B3 and B4), and two from the solid fraction of pig manure (SFPM; B5 and B6). B2, B4, and B6 were produced at higher temperature with longer biomass residence time in the reactor and have optimal properties in order to maximize the C_{biochar} sequestration potential (low O/C_{org} and H/C_{org} ratios). B1, B3, and B5 were produced with lower temperature and shorter residence time and have the opposite characteristics (high O/C_{org} and H/C_{org} ratios). Biochars produced from wood and switchgrass are expected to reduce soil GHG emissions since their C/N ratio is higher than 30.

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 (2011) standard. The C, hydrogen (H) and nitrogen (N) contents were evaluated by dry combustion (Leco TruSpec, St. Joseph, MI, USA). The oxygen (O) content was calculated by subtracting the C, H, N, and ash contents from 100 wt. %. Inorganic C was analysed as outlined in the ASTM D 4373-02 standard (ASTM, 2002). Organic C was calculated as total C –

inorganic C. The specific surface area of biochar was determined by gas (CO₂) 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 (Figure 1) 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	B1	B2	B3	B4	B5	B6
Pyrolysis parameters							
Biomass		Wood	Wood	SG	SG	SFPM	SFPM
Temperature	°C	516	644	459	591	526	630
Res. Time ¹	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	% (w.b.)	26.4	18.5	26.9	18.9	18.6	46.4
Bio-oil	% (w.b.)	58.2	51.5	60.2	49.4	49.0	37.9
Biochar properties							
C _{total}	% (w.b.)	71.6	80.0	67.1	79.9	51.5	49.2
C _{org}	% (w.b.)	70.7	76.0	64.9	79.5	47.4	45.2
H	% (w.b.)	4.8	3.73	4.85	3.36	3.73	3.36
O	% (w.b.)	21.6	13.4	22.9	9.8	15.6	13.7
N	% (w.b.)	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	% (w.b.)	0.9	1.2	1.5	1.4	0.9	0.9
Ash (750 °C)	% (d.b.)	1.4	2.1	4.1	5.5	23.6	28.1
O.M.	% (d.b.)	98.6	97.9	95.9	94.5	76.4	71.9
O.M./C _{total}	Mass ratio	1.38	1.22	1.43	1.19	1.48	1.46
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

¹ Residence time of biomass in the reaction chamber

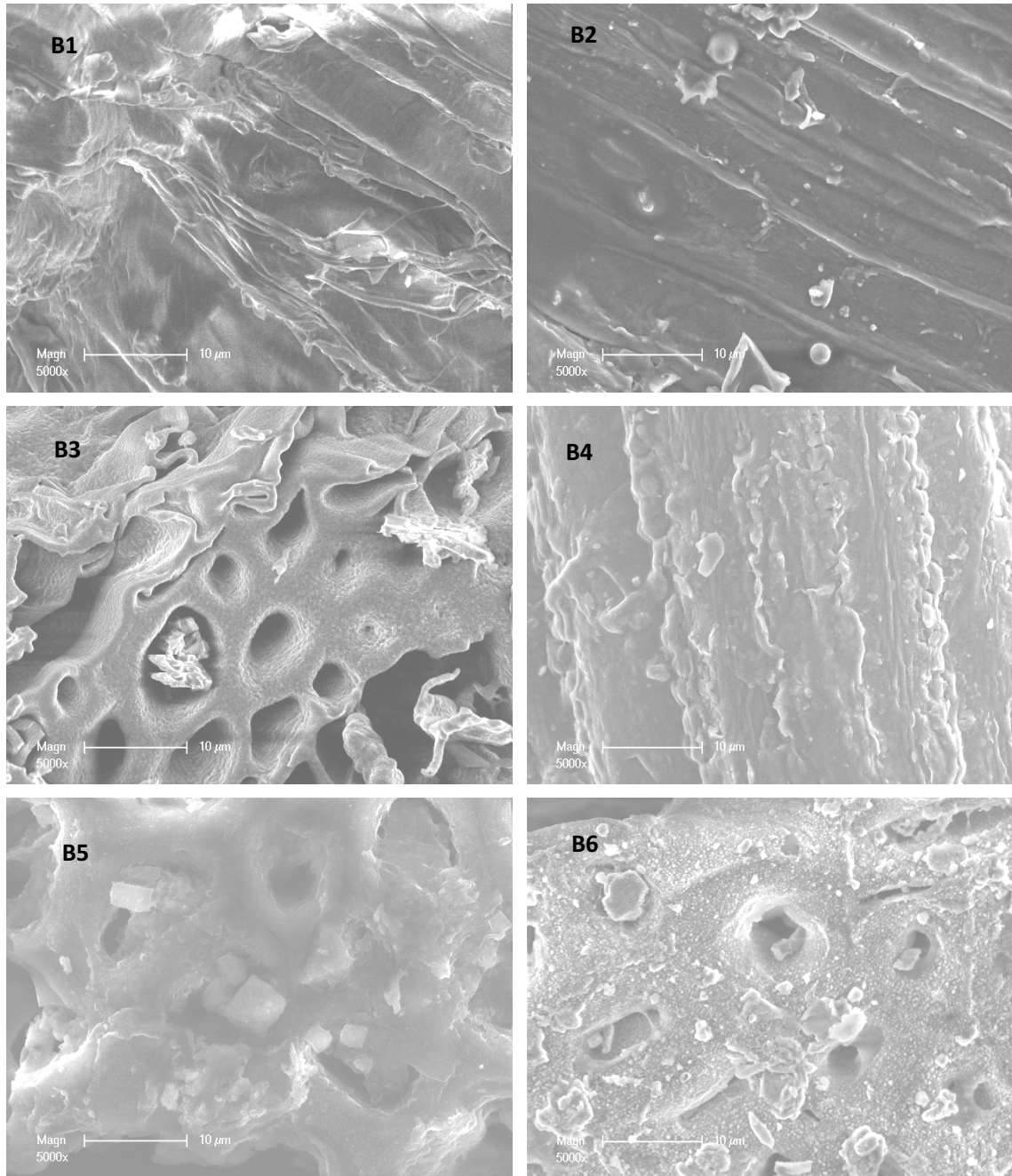


Figure 1. SEM/EDX pictures of biochars (B1, B2, B3, B4, B5 and B6)

Soil sampling and characterization Surface soil samples (0-15 cm) were collected from two agricultural regions in the province of Quebec (Canada): a silt loam in St-Lambert de Lauzon (46°36' N and 71°10' W) and a loamy sand in Deschambault (46°40' N and 71°55' W). Soils were air-dried and ground to obtain < 2 mm fraction. Total carbon (C) and nitrogen (N) were analyzed by dry combustion (Leco TruSpec, St. Joseph, MI, USA). N-NH₄ and N-NO₃ were extracted from 5 g sample in 25 g of KCl (2M) following 1 h stirring. Phosphorus (P), Potassium (K), aluminium (Al) and Magnesium (Mg) were measured with the Mehlich-3 method. Moreover, soluble P (P_{sol}) was measured using the Sissingh method (Sissingh, 1971). Water-soluble organic C (WSOC) and water-soluble inorganic C (WSIC) were measured from water extraction. Organic matter content was

measured at 375 °C, pH was measured in water, and water content was determined by gravimetric method. Particle size was analyzed and soils were classified according to the USDA classification.

Incubation experiment A 45-days incubation study was carried out in a plant growth chamber (Conviron, Controlled Environments Ltd., Winnipeg, Canada) in order to evaluate the effect of the six engineered biochars on the emissions of CO₂ and N₂O from soil samples. In order to mimic the environmental conditions during summer in Quebec (Canada), the growth chamber was lightened for 15 hours per day while the temperature was adjusted to 22 °C and to 18 °C for the night time period (9 hours).

A total of 14 treatments in three replicates (six biochars amended to two types of soil, and two control treatments without biochar) were evaluated. The biochars were added to the soil at a dose of 2% (w/w) and mixed thoroughly. Then, 747 g (d.b.) of each soil and biochar mixture was added in four jars of 1 liter capacity. The bulk density (d.b.) of the silt loam and the loamy sand without biochar was adjusted to 1.20 and 1.39 g cm⁻³, and was slightly decreased with biochar addition to 1.19 and 1.37 g cm⁻³, respectively. At the beginning of the incubation period, all treatments were fertilized with a solution of NH₄NO₃ at a dose of 75.6 mg N kg⁻¹, which corresponds to 170 kg N ha⁻¹. In order to favor N₂O emissions, water was added to fill 80% of pore space (80% WFPS). In fact, according to Ussiri and Lal (2013), denitrification becomes the main source of N₂O when water content is between 70 and 80% WFPS. Water content was adjusted again to 80% WFPS on days 23, 37 and 44, i.e. 24 hours before three of nine gas samplings.

Gas sampling and analysis The N₂O and CO₂ fluxes from soil samples were measured at days 1, 2, 3, 10, 17, 24, 31, 38 and 45 after the addition of the fertilizing solution. At the moments of sampling, the jars were closed tightly and gas samples were taken from the three replicates of each treatment after 30 minutes (t₃₀) using a 60-mL gas-tight syringe inserted through septa in a through-wall connector. Then, the gas sample was injected into air pre-evacuated 20-mL vials with septa. In order to calculate the flux according to the linear regression scheme (Hutchinson & Mosier, 1981), additional samples were taken over the soil surface in ten random jars before they were closed, representing the initial concentration (t₀), and a gas sample was taken from a fourth jar of each treatment after 15 minutes (t₁₅). Samples at t₁₅ were not taken from the same jars than at t₃₀ in order to keep the pressure constant during the period of operation when jars were closed. On the same day, gas N₂O and CO₂ concentrations (in ppm_v) were analysed with a gas chromatography-mass spectroscopy (GC-MS; Varian 3600). Gas concentrations were converted into mg m⁻³ using the ideal gas law and the flux (mg kg⁻¹ h⁻¹) was calculated by linear regression (Hutchinson & Mosier, 1981). Cumulative emissions of N₂O and CO₂ over the 45-days incubation period were calculated by linear integration of hourly fluxes starting on day one.

Analysis of soil after incubation After the incubation period, the content of each jar was put in a plastic bag, mixed thoroughly, and kept refrigerated before the chemical analyses were performed on soil samples. The analyses that were carried out on soil samples before incubation were repeated on the soil and biochar mixtures after incubation. In addition, P_{soluble} was measured in soil mixtures with biochar produced from the SFPM (B5 and B6) due to the high P content of these biochars.

Statistical analysis Analysis of variance was performed using the mixed procedure of SAS (Little et al., 2006) in order to determine significant differences in N₂O and CO₂ emissions among treatments. The fixed variables of the mixed model include the treatment, the date and the interaction date x treatment. The random variables were the replicates, the interaction treatment x replicate, and the experimental error. The date was a factor of repeated measurements with a variance covariance matrix which has been modeled to fit the correlations among the sampling on the same experimental unit. Fixed variables were all significant. The two-by-two differences among treatments were determined by the date of the sampling. The same analysis was performed for soils chemical properties.

RESULTS

The effect of biochar on N₂O emissions The cumulative N₂O emissions during the 45 days incubation averaged from the three replicates are presented in Table 2. In the loamy sand, biochar addition always increased cumulative N₂O emissions when compared to the control soil without biochar, and the difference was significant with biochars made from wood (B1 and B2) and SFPM (B5 and B6). In the silt loam, the cumulative N₂O emissions were also significantly increased with the biochar made from the SFPM (B5 and B6). However, biochars made from wood and switchgrass decreased the N₂O emissions by 53% (B1), 42% (B2), 90% (B3) and 58% (B4). However, the difference was only significant with B3 made from switchgrass at lower temperature. These results are similar to those reported in a meta-analysis study carried out by Cayuela et al. (2015). The authors found that the average reduction in N₂O emissions in controlled laboratory studies was of $54 \pm 3\%$. Fig. 2 and Fig. 3 illustrate the cumulative emissions at each day of sampling. N₂O flux is always higher in the silt loam (Fig. 3) than in the loamy sand (Fig. 2). The hourly flux is high on day 1 and day 2, decreased on day 3 and reach out very low values near zero on days 10 and 17. On day 24, the next day after the soils were rewetted, N₂O hourly flux slightly increased in all treatments, particularly in treatments with B5 and B6, these biochars having a high N content. For example, in the silt loam with B5, the hourly flux increased from $0.04 \mu\text{g N}_2\text{O-N kg}^{-1} \text{h}^{-1}$ on day 17 to $45.33 \mu\text{g N}_2\text{O-N kg}^{-1} \text{h}^{-1}$ on day 24, and it increased from $0.14 \mu\text{g N}_2\text{O-N kg}^{-1} \text{h}^{-1}$ on day 17 to $21.36 \mu\text{g N}_2\text{O-N kg}^{-1} \text{h}^{-1}$ on day 24 with B6. Thereafter, hourly fluxes decreased and were very low, even on the next day after the subsequent rewetting of samples on days 37 and 44.

Table 2. Cumulative emissions of N₂O (mg N-N₂O kg⁻¹_{soil}) and CO₂ (mg C-CO₂ kg⁻¹_{soil}) from day 2 to day 45 (mean value of three replicates \pm standard error)

	N ₂ O emissions		CO ₂ emissions	
	Loamy sand	Silt loam	Loamy sand	Silt loam
B1	0.426 \pm 0.143*	0.909 \pm 0.238	62.3 \pm 7.7*	122 \pm 5.5
B2	1.25 \pm 0.56*	0.740 \pm 0.285	38.7 \pm 3.8	126 \pm 8.9
B3	0.216 \pm 0.085	0.162 \pm 0.014*	184 \pm 20.5*	196 \pm 17.6*
B4	0.144 \pm 0.083	0.655 \pm 0.244	81.3 \pm 9.0*	130 \pm 4.4
B5	1.14 \pm 0.31*	6.08* ¹	223 \pm 19.9*	273 \pm 13.7*
B6	0.451 \pm 0.039*	2.71 \pm 0.549*	157 \pm 9.4*	213 \pm 3.7*
Control	0.054 \pm 0.032	1.57 \pm 0.186	10.2 \pm 3.2	94.5 \pm 7.5

*Significant difference (P < 0.05) when compared to control; ¹ Missing data in 2 replicates.

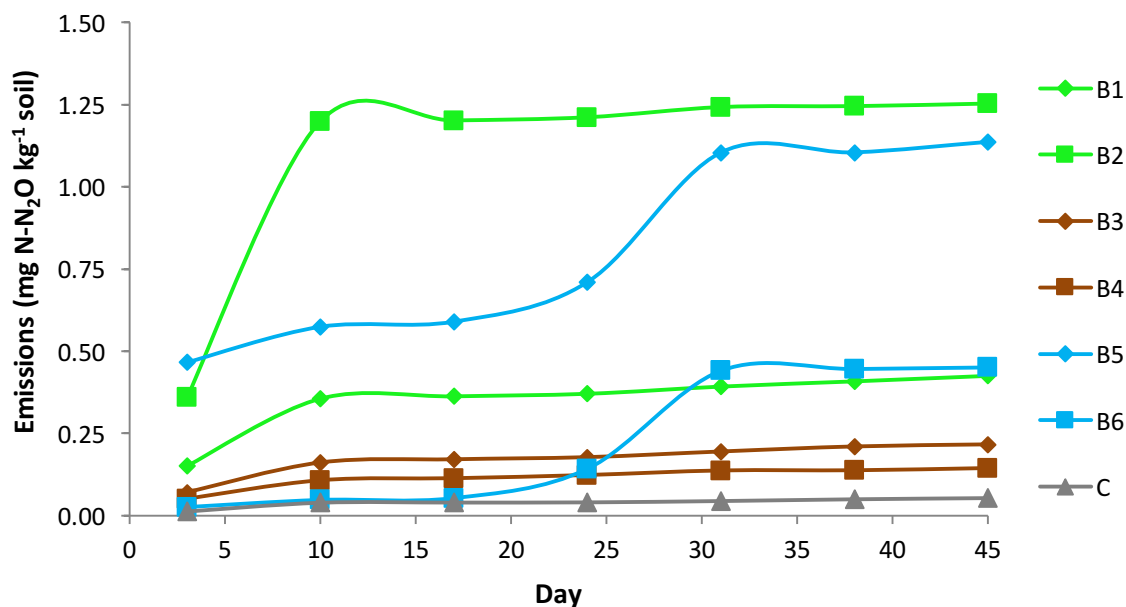


Figure 2. Cumulative emissions of N₂O (mg N-N₂O kg⁻¹ soil) after the 45-days incubation period in the loamy sand – Mean value of three replicates

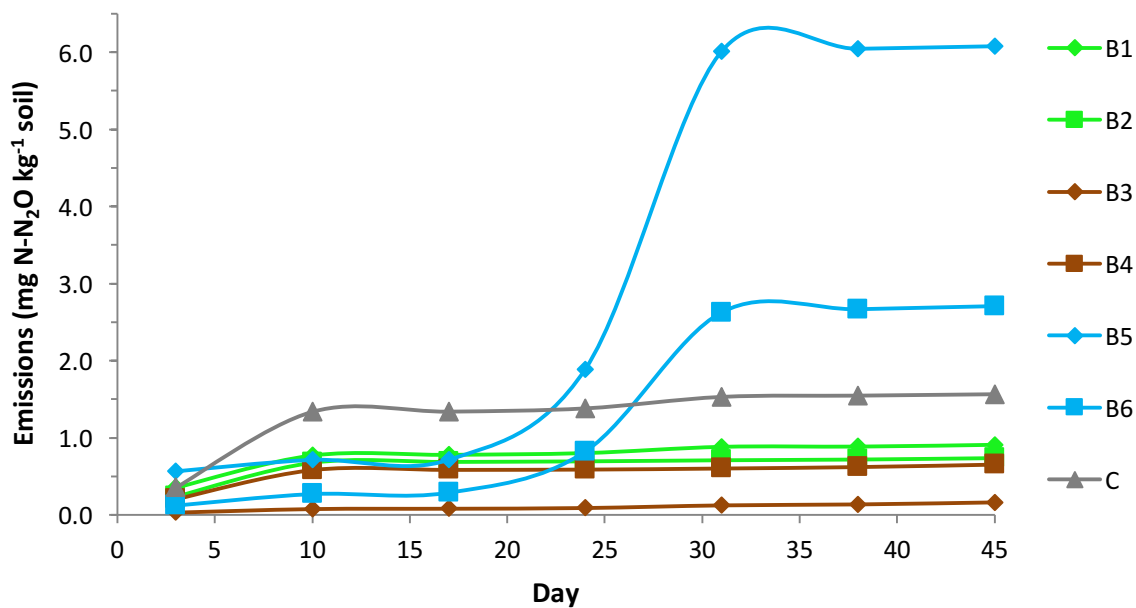


Figure 3. Cumulative emissions of N₂O (mg N-N₂O kg⁻¹ soil) after the 45-days incubation period in the silt loam – Mean value of three replicates

The effect of biochar on CO₂ emissions The average cumulative soil CO₂ emissions from the three replicates after the incubation period of 45 days are presented in Table 2. CO₂ flux was always increased in soil treated with biochar as compared to the control soil without biochar. In the loamy sand, the increase was significant with all biochars (P < 0.01), except with B2 made from wood at

high temperature. The hypothesis is that this biochar resists decomposition better with low H/C_{org} and O/C_{org} ratios of 0.54 and 0.13, respectively (Table 1). The same tendency was observed in the silt loam with B1, B2 and B4, as CO_2 emissions were not significantly increased. However, CO_2 emissions from soil amended with biochars made from SFPM (B5 and B6) and from switchgrass at low temperature (B3) were significantly higher ($P < 0.01$), these biochars having H/C_{org} and O/C_{org} ratios higher than 0.7 and 0.2, respectively. Fig. 4 and Fig. 5 show a similar trend for CO_2 emissions in both soils, but silt loam emits more CO_2 than sandy loam. For all treatments, the hourly fluxes were the highest on the first days and decreased constantly until day 17 where they stabilized, as cumulative emissions continue to increase constantly. By day 24, the hourly fluxes in the loamy sand without biochar (control) and with B1 and B2 were reduced to near zero.

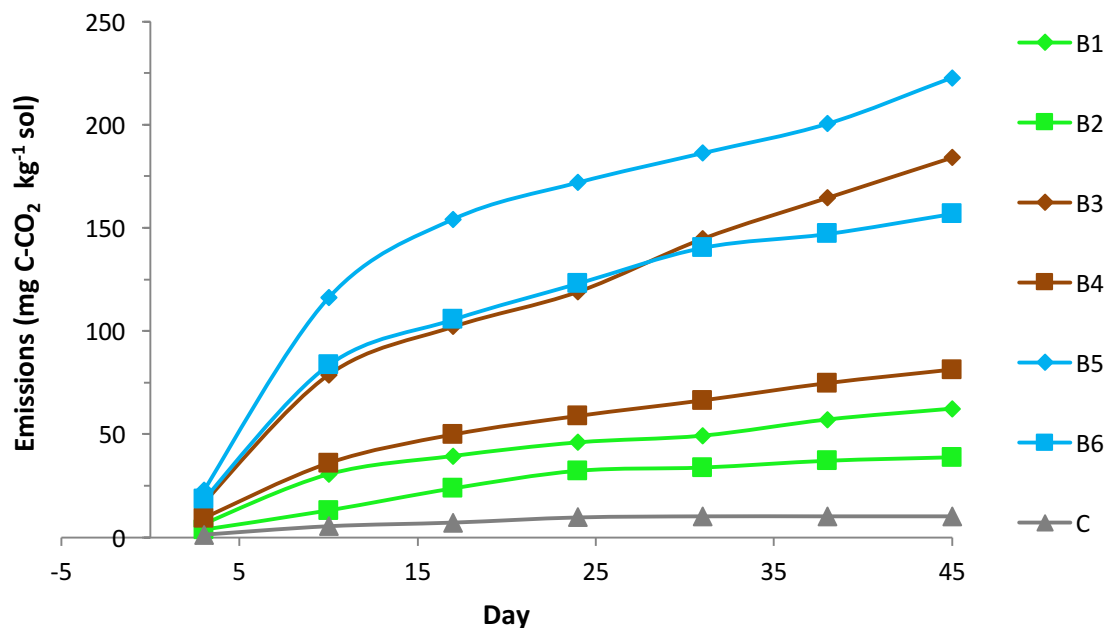


Figure 4. Cumulative emissions of CO_2 (mg C- CO_2 kg⁻¹ soil) after the 45-days incubation period in the loamy sand - Average of three replicates

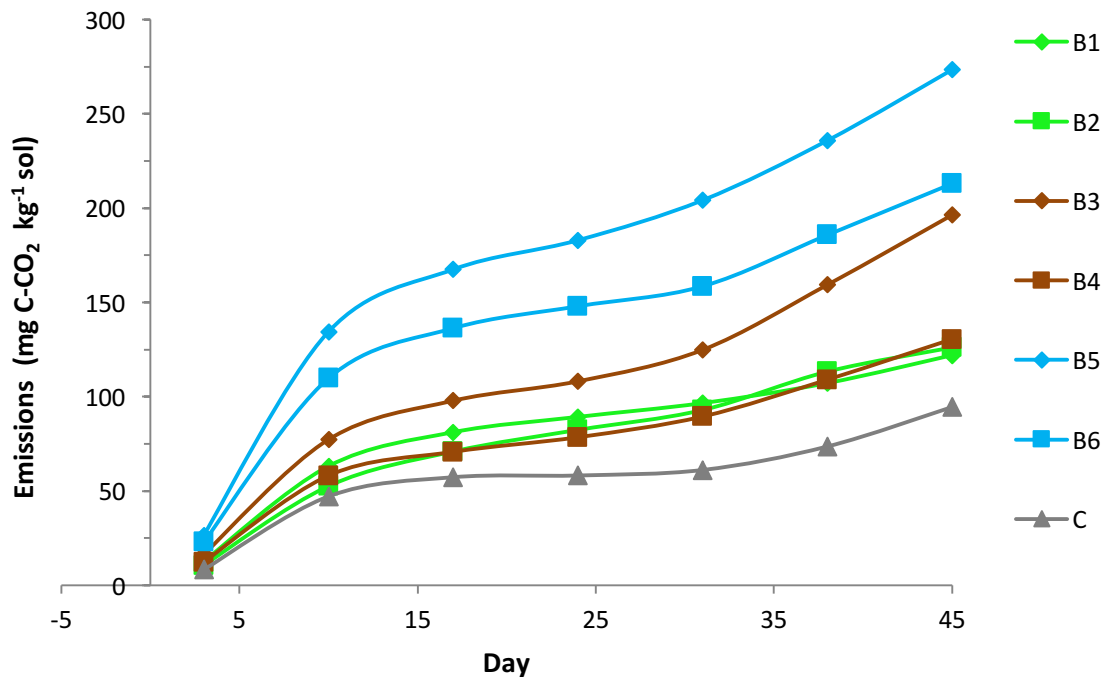


Figure 5 – Cumulative emissions of CO₂ (mg C-CO₂ kg⁻¹soil) after the 45-days incubation period in the silt loam – Mean value of three replicates

The effect of biochar on soil chemical properties The chemical analysis of the untreated soils and of all treatments after incubation are presented in Table 3 (loamy sand) and Table 4 (silt loam). The water content in the loamy sand treatments varied from 15.3 to 16.8% and from 23.2 to 26.4% in the silt loam, while it is slightly higher in biochar treatments than in the control soil. After the incubation, both control soils were acidic, with a pH 5.4 and 4.9 in the silt loam and the loamy sand, respectively. Biochar amendment resulted to increased pH for both soil types as compared to the treatment without biochar, the difference being significant ($P < 0.05$) in all treatments except for B1 and B2 of the loamy sand. The increase was particularly high in soil amended with biochar made from the SFPM (B5 and B6; Tables 3 and 4).

Following the incubation period, biochar increased the consumption of NH₄⁺ in the silt loam when compared to the control soil, which could be explained by an increase of nitrification efficiency. The same tendency was observed in the loamy sand with B1, B2, B3 and B4; however, NH₄⁺ concentration was increased with biochar made from the SFPM (B5 and B6). More N was nitrified to NO₃⁻ in the silt loam with B5 and B6 which could have caused an increased denitrification. In the other treatments, biochar caused the immobilization of NO₃⁻, the concentration of NO₃⁻ being lower than in the control soil. As stated by Burger and Jackson (2003), C inputs often increase NO₃⁻ immobilization. In fact, biochar amendment increased C_{tot} in all treatments when compared to control. As expected, water-soluble C (WSC) concentration after incubation was lower in the treatments with biochars made from wood and switchgrass (B1, B2, B3 and B4) than in the control treatments. Only biochars made from SFPM (B5 and B6) allowed a significant increase of water-soluble organic C (WSOC) ($P < 0.05$), which was 61 and 72 mg kg⁻¹ in the loamy sand and in the silt loam, respectively. Water-soluble inorganic C (WSIC) was also higher in treatments with SFPM biochars when compared to control. The other biochars also increased inorganic soluble C concentration in the silt loam, but it was decreased in the loamy sand.

Biochar produced from the SFPM contributed to increase the available P and P_{soluble} concentration in both soils. However, only 21.8 to 28.1% of the P added from biochar that became available. The percentage of P_{soluble} vs $P_{\text{available}}$ in treatments with B5 and B6 varied between 7.5 and 7.8%, which is higher than in the control soils in which that percentage was 2.2% and 1.7% in the loamy sand and in the silt loam, respectively.

Other elements (K, Ca, Mg and Al) were similar in both soils amended with biochar produced from wood and switchgrass and in the control soils without biochar. However, biochar produced from SFPM increased the concentration of K, Ca and Mg.

Table 3. Chemical properties of the loamy sand and of the soil and biochar mixture after the incubation period (average value of three replicates)

Properties	Unit	Soil mixtures after the incubation period							
		Initial C	SB1	SB2	SB3	SB4	SB5	SB6	C
Humidity	% (w.b.)	1.24	16.3	16.1	16.6	16.8	16.7	16.7	15.3
pH		6.2	5.5	5.5	5.8	5.7	6.5	6.9	5.4
C_{total}	% (d.b.)	0.675	1.170	1.127	1.247	1.193	1.153	1.051	0.611
WSC	mg kg ⁻¹	88.0	50.9	51.1	63.7	59.4	145	166	68.6
WSOC	mg kg ⁻¹	62.4	39.6	41.1	50.7	46.4	107.6	107.4	46.6
WSIC	mg kg ⁻¹	25.6	11.4	10.0	13.1	12.9	36.8	58.8	22.0
N	% (w.b.)	0.052	0.056	0.049	0.060	0.058	0.095	0.079	0.047
N-NH ₄ ⁺	mg kg ⁻¹	0.871	0.513	0.573	0.515	0.542	1.09	0.953	0.602
N-NO ₃ ⁻	mg kg ⁻¹	5.41	70.6	70.9	65.8	61.9	76.5	66.6	77.4
P	mg kg ⁻¹	145	152	147	155	152	273	288	149
P_{soluble}	mg kg ⁻¹	4.13	--	--	--	--	21.4	22.6	3.2
K	mg kg ⁻¹	31.4	49.0	41.7	82.1	75.2	426	520	33.4
Ca	mg kg ⁻¹	615	620	599	649	620	797	852	616
Mg	mg kg ⁻¹	13.9	15.7	14.8	29.0	19.3	135	149	14.7
Al	mg kg ⁻¹	1261	1288	1266	1261	1262	1224	1201	1305

SB1 to SB6 : mixtures of loamy sand with biochars 1 to 6; C: Control soil without biochar

Table 4. Chemical properties of the silt loam and of the soil and biochar mixtures after incubation (average value of three replicates)

Properties	Unit	Soil mixtures after the incubation period							
		Initial C	LB1	LB2	LB3	LB4	LB5	LB6	C
Humidity	% (w.b.)	3.19	23.8	23.7	23.2	25.3	25.6	26.4	23.5
pH		5.4	5.2	5.0	5.2	5.1	5.6	6.0	4.9
C_{total}	% (d.b.)	1.730	2.92	2.777	2.833	2.923	2.543	2.630	1.677
WSC	mg kg ⁻¹	156.1	129	113.1	139.0	140.3	207.0	215.7	124.8
WSOC	mg kg ⁻¹	111.1	94.9	81.0	98.4	92.4	171.9	172.0	100.6
WSIC	mg kg ⁻¹	45.0	34.4	32.0	40.7	48.1	35.2	43.7	24.3
N	% (w.b.)	0.145	0.147	0.137	0.158	0.157	0.209	0.215	0.152
N-NH ₄ ⁺	mg kg ⁻¹	5.70	1.58	1.53	1.27	1.27	2.51	1.54	2.78
N-NO ₃ ⁻	mg kg ⁻¹	42.2	140.7	133.3	140.3	134.0	200.3	156.7	152.7
P	mg kg ⁻¹	30.3	32.0	31.1	35.7	32.5	133.3	176.0	30.9
P_{soluble}	mg kg ⁻¹	0.942	--	--	--	--	10	13.7	0.5
K	mg kg ⁻¹	51.7	67.7	62.6	93.2	100.8	352.7	504.3	53.8
Ca	mg kg ⁻¹	950	950	971.0	1019	992.3	1171	1314	976.0
Mg	mg kg ⁻¹	115	119	117.7	132.3	114.3	234.7	276.3	112.7
Al	mg kg ⁻¹	1192	1270	1275	1244	1249	1187	1164	1269

LB1 to LB6 : mixtures of silt loam with biochars 1 to 6; C: Control soil without biochar

DISCUSSION

Selection of engineered biochars to decrease soil N₂O emissions N₂O release by soils is driven by nitrification (oxidation of NH₄⁺ to NO₃⁻ via NO₂⁻) under aerobic conditions, and by denitrification (reduction of NO₃⁻ to N₂O and N₂) under anaerobic conditions (Oertel et al., 2016). The results of this short-term incubation study provided evidence that N₂O mitigation depends on the biochar and soil characteristics, and also on their impact on physico-chemical factors and soil N cycling. Only biochars made from wood and switchgrass (C/N ratio > 30) resulted to a decrease of N₂O emissions when added to soil, and the effect was observed only in the silt loam, as cumulative N₂O emissions in the control loamy sand was already low. The decrease was particularly pronounced with biochars made from switchgrass at the lowest temperature (B3). It could be explained by the lower N content in B3 as compared to B4 produced at a higher temperature. Biochars made from the SFPM, having a high N content and thus a low C/N ratio (< 30), increased significantly the N₂O emissions in both soils. This could be due to enhanced N content in these soils. Feng and Zhu (2017) reported that soil N₂O emission was affected by the ratio of biochar to N fertilizer. The authors found a negative linear relationship between the increase in N₂O emission and soil TC/IN (total carbon / inorganic nitrogen) after biochar application. High TC/IN ratio (> 60) was associated to the suppression of N₂O emissions, and low TC/IN ratio (< 45) to the promotion of N₂O emission. In the present study, a similar conclusion can be drawn but with higher ratios, as significant increase of N₂O emission was found in treatments with a TC/IN ratio < 170. In a study carried out by Sarkhot et al. (2012), the addition of biochar to soil led to significant reductions in net ammonification, nitrification, and mineralization. A combination of different factors could have affected the N cycle in soil, and thus the N₂O production. For example, one important environmental factor responsible for the reduced N₂O emission from biochar-amended soil could be limited bioavailability of electron donors and acceptors (DOC, NH₄⁺ and NO₃⁻) for microbial nitrification and denitrification due to sorption/immobilization onto biochar particles. In a study by Harter et al. (2014), as DOC, NH₄⁺ and NO₃⁻ concentrations decreased, N₂O fluxes declined. The hypothesis formulated by the author was that electron donors and acceptors for microbial N₂O formation became limiting. This hypothesis could be confirmed in the silt loam in the present study. As the N₂O emission was decreased in the soils amended with B1, B2, B3 and B4 as compared to the control soil without biochar, N-NH₄⁺ content was significantly lower and N-NO₃⁻ content was lower, the difference being significant with B2 and B4. It means that N could have been immobilised in those treatments. On the contrary, as N-NO₃⁻ concentration in the silt loam amended with B5 and B6 was increased (N mineralization), N₂O emission was increased. Similarly, after a 126-days incubation study, Case et al. (2012) hypothesised that the lower extractable N-NO₃⁻ content in biochar amended soil than in the control soil could explain the N₂O suppression with increasing biochar amendment. NO₃⁻ could have been either immobilised within microbial biomass, or adsorbed onto the biochar surface.

According to Castaldi et al. (2011), an increased activity of N₂O-reducing bacteria due to an elevated soil pH could decrease the N₂O/N₂ ratio. In the present study, pH was increased with biochar amendment, especially B5 and B6 mixtures, thus this effect alone could not explain the reduction of N₂O emissions in the silt loam. Improved soil aeration through biochar addition and consequently reduced denitrification is another mechanism proposed by Augustenborg et al. (2012). The SEM-EDX pictures show that B3 has a larger porosity, which could have a positive impact on soil porosity, and thus could be linked to the significant decrease of N₂O emissions in the silt loam.

Biochar stability in soil In the present research study, soil CO₂ emission was considered as an indicator of biochar stability. CO₂ emissions were always higher in soils amended with biochar than in control soils, and the CO₂ release was particularly high in the first 10 days. According to Ameloot et al. (2013), enhanced release of CO₂ after biochar addition to soil, which occurs mainly in the first days, may result from priming of native soil organic carbon (SOC) pools, biodegradation of biochar components from stimulation of soil organisms by biochar, or abiotic release of biochar-C. In the

context of the present study, it was not possible to confirm whether biochar caused a positive or negative priming effect on SOC mineralization because biochar C was not labeled. However, the hypothesis is that the degradation of the labile C in biochar caused the increased CO₂ emissions, as reported by Troy et al. (2013) and Spokas et al. (2009). The fast mineralization of fresh biochar has previously been attributed to the decomposition of labile organic C due to their lower masses and simpler structures. After mineralization of the labile biochar-C pool, mineralization rates in amended soils decrease and become nearly equal to rates in control treatments.

Despite the higher C-CO₂ emissions from the biochar treatments, C-CO₂ emitted represent a small proportion of biochar-C and does not compromise its potential to sequester C in soil (Jones et al., 2011). The quantity of C mineralized from biochar was estimated by subtracting the cumulative C-CO₂ emitted by the control soils from the cumulative C-CO₂ emitted by the biochar treatments. Quantities of C mineralized from biochar ranged from 39 to 273 mg C-CO₂ kg_{soil}⁻¹, which represent 0.18 to 1.68% of the total C in biochar. These values are in accordance with the results of other studies (Gascó et al., 2016; Luo et al., 2016; Steinbeiss et al., 2009; Zimmerman et al., 2011). A meta-analysis carried out by Wang et al. (2016) indicates that biochar addition can stimulate total soil CO₂ emissions by 28 to 32%. The same study revealed that the average biochar decomposition rate for studies lasting less than 6 months was 0.023% per day. For example, Bruun et al. (2012) carried out an incubation study of biochar amended in a sandy loam and reported cumulative C losses of 2.9 and 5.5% for biochar produced from slow pyrolysis and fast pyrolysis of wheat straw, respectively. Other studies have shown that biochar C mineralises at a very slow rate in soils, e.g. averaged 0.1 to 3% applied biochar-C mineralised per year (Fang et al., 2015).

The cumulative CO₂ emissions depended on soil type and on the type of biochar and pyrolysis operating parameters. For a type of biochar (wood, switchgrass or SFPM), cumulative CO₂ emissions were always lower for the biochar produced at the highest temperature, these biochars having a lower H/C_{org} and O/C_{org} ratio. This is in accordance with the conclusions of other studies in which biochars produced at different temperature were evaluated (Al-Wabel et al., 2013; Junna et al., 2014; Luo et al., 2011; Sun et al., 2014). Moreover, CO₂ emissions from B5 and B6 treatments were particularly high as compared to the other treatments. This could be due to the high N input by the biochars made from the SFPM. In fact, soil respiration generally increases with increasing soil N content (Oertel et al., 2016). The morphology of biochar can also give an indication on the C_{biochar} stability. In fact, B2 and B4 have the lowest O/C_{org} and H/C_{org} ratios (< 0.15 and < 0.55, respectively) and show the most regular patterns of asperity (Fig. 1).

CONCLUSION The results of this study demonstrated that biochar can be produced and used as a negative emission technology in order to reduce soil N₂O emission and to sequester C_{biochar} in soil. However, the benefits were specific to both soil and biochar properties. When compared to the control soil without biochar, N₂O emissions were only decreased in the silt loam amended with biochar made from wood and switchgrass. The decreased N₂O emissions could be related to reduced NH₄⁺ and NO₃⁻ concentrations in soil after biochar amendment due to an increase efficiency of nitrification, or to the increase in soil aeration due to biochar porosity. Soil CO₂ emissions were favored by biochar amendment, but emissions in soils amended with biochars produced at the highest temperature were lower, indicating a higher stability. The evaluation of soil microbial diversity and abundance will allow to evaluate other mechanisms responsible for the decrease of soil N₂O in soil. In order to validate the results of this study, long-term studies should be carried out in the field in the presence of crops.

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