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Biochar and short-term N_2O and CO_2 emission from plant residue-amended soil with different fertilisation history

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Abstract

The effect of biochar application on nitrous oxide (N_2O) and carbon dioxide (CO_2) emissions from an arable soil amended with maize leaves was studied in a laboratory experiment using soil samples collected from plots with three different fertiliser treatments: no fertilisation (CONT), mineral fertiliser (NPKMg) and farmyard manure (FYM), of a well characterized agricultural experiment established in 1949. Two biochars (BC) used in the experiment were produced in low temperature slow (BC_{slow}) and in high temperature fast (BC_{fast}) pyrolysis, and applied at a rate of 10 t ha^{-1}. Different fertilisation strategies induced significant differences in the soil total carbon (C) and nitrogen (N) contents (CONT < NPKMg < FYM), but at the time of the soil sample collection the soil contained low levels of plant-available nitrogen (<10 mg kg^{-1} N soil) independent of the fertilisation treatment. A stable suppressive effect of BC_{slow}, but not BC_{fast} application on N_2O emissions was found for maize leaves-amended soil. The short-term effect of residue application on N_2O emission was much stronger than the 60-year difference in the soil fertilisation strategy. Mixing of biochar with maize leaves and the soil was in general more efficient in reducing N_2O emissions than biochar application in layers. Neither of the studied ways of biochar application to the soils systematically reduced CO_2 emissions. Compared to BC_{slow}, application of thermally more labile BC_{fast} with wider oxygen and carbon (O:C) and hydrogen and carbon (H:C) ratios did not systematically reduce N_2O emissions and increased CO_2 fluxes from the soils, underpinning the role of biochar stability and composition for controlling plant residue-related greenhouse gas (GHG) emissions.

Key words: arable soil, greenhouse gases, fast pyrolysis, laboratory experiment, maize leaves, slow pyrolysis.

Introduction

Nitrous oxide (N_2O) and carbon dioxide (CO_2) fluxes from agricultural soils depend on a complex interaction between climate parameters, soil properties and soil management. Different long-term soil fertilisation strategies can lead to significant changes in the soils' physical, chemical and biochemical properties and, as a result, in direct N_2O and CO_2 emissions from the soils. Mogge et al. (1999) measured N_2O emissions from sandy soils fertilised with farmyard manure for 30 years and found that annual gaseous N_2O losses from this soil were twice higher than those from a grassland receiving nitrogen (N) with mineral fertilisers. Jäger et al. (2011; 2013) have found that increased soil organic carbon (C) stocks related to long-term (over 27 years) farmyard manure application to sandy arable soils resulted in increased N_2O emissions at a soil moisture content of 60% water-holding capacity, but had no influence on N_2O emission rates in the short-term laboratory experiment after the application of different N-fertilisers. Buchkina et al. (2010) have shown that high inputs of farmyard manure (FYM) resulted in an increase in soil organic carbon, water-soluble carbon and N_2O emissions from the soil a year later, even during the relatively dry growing season. Clark et al. (2012) have shown that after 160 years of different fertiliser treatments the soil with high rates of N-fertiliser and with farmyard manure application emitted significantly more N_2O than the unamended soil or the soil with lower rate of mineral N-fertiliser.

The same soil after being under long-term contrasting management might respond differently to the same impacts including application of plant residues. Rizhiya et al. (2011) have shown that application of plant residues with different carbon and nitrogen (C:N) ratio to the loamy sand soddy-podzolic soil with high level of productivity (resulting from regular application of high rates of farmyard manure) led to higher N_2O emissions than application of the plant residues to the same soil but with low level of productivity (without farmyard manure application).

Plant residue application to soils is very common in arable soil management. Apart from positive effect on soil organic matter and soil nutrients this practice can result in a temporal increase of soil N_2O and CO_2 emissions (Baggs et al., 2000; Huang et al., 2004; Toma,

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Hatano, 2007; Rizhiya et al., 2011). The effect usually is short-lived. Most of the N_2O emissions after plant residue incorporation occur during the first two weeks (Baggs et al., 2000; Rizhiya et al., 2011), and the highest CO_2 fluxes are also observed straight after plant residue incorporation (Toma, Hatano, 2007). It was shown that plant residue with narrow C:N ratio induced higher emissions than the plant residue with wide C:N ratio.

Biochar is a pyrogenic material produced via pyrolysis under controlled conditions. Biochar, compared to labile materials, has much wider C:N ratio and is relatively stable against microbial degradation (Harvey et al., 2012). When applied to soils it may change soil physical, biological and chemical properties (Lehmann, 2007), responsible for CO_2 and N_2O production. Biochar may enhance soil CO_2 fluxes due to either degradation of biochar carbon or by promoting soil organic matter decomposition (Wardle et al., 2008). It may also change soil N_2O emission: some studies have found up to 70% reduction of soil N_2O emission after biochar application in fertilised treatments (Case et al., 2012; Kammann et al., 2012; Felber et al., 2014; Rizhiya et al., 2015), while other studies have reported no difference or even an increase in soil N_2O emissions after biochar application (Angst et al., 2014; Verhoeven, Six, 2014). A meta-analysis by Cayuela et al. (2015) showed that biochar with low $H:C_{org}$ ratio reduced soil N_2O emission more effectively.

According to Mosier (2001), two thirds of the N_2O emissions in agriculture are related to N-fertiliser / manure / plant residue use. Can we reduce short-term but very high N_2O and CO_2 fluxes from agricultural soils resulting from the application of plant residues with narrow C:N ratio by applying biochar? What kind of biochar should we use and how should we apply it to the soil? Would the initial soil properties affect the result?

Materials and methods

In the long-term Zurich Organic Fertilization Experiment (ZOFE), established in 1949 at the Agroscope Research Station (47°25′36″ N, 8°31′7″ E) in Zurich, Switzerland the effect of farmyard manure and mineral fertilisers (in 5 replicates) on the *Haplic Luvisol* (*LVha*) (sand 58%, silt 28%, clay 14%) properties and crop yields is being studied (Oberholzer et al., 2014). Soil samples from the field trial were used in the short-term laboratory experiment. Soil material was collected in early October 2012 from the topsoil layer (0–15 cm) of 15 plots with three contrasting treatments: no fertiliser or manure (CONT), 2.5 t of farmyard manure-C ha^{-1} (FYM) applied every second year, and mineral fertiliser 140 N, 38 P, 167 K and 56 Mg kg ha^{-1} (NPKMg), annually. Eight soil sub-samples were collected from each replicate plot and mixed to make a representative plot sample. The representative plot samples from the replicate plots with the same treatment were not mixed so that each sample was representing one replicate plot from the field. All the soil samples were analysed for total carbon (C) and nitrogen (N) contents, measured in combusted samples using an analyser Hekatech Euro EA 3000 elemental (Wegberg, Germany), content of plant-available N (extraction of NO_3^- and NH_4^+ in a 0.01 M $CaCl_2$-solution) (FAL, 1998), soil water content (measured gravimetrically) and maximum water holding capacity. The soil contained no carbonates and hence the total C content was equal to organic C.

Two freshly made biochars (BC), BC_{slow} and BC_{fast}, with different chemical properties were used in the experiment. The biochars were produced from wood based feedstock (mainly old wood and branch clippings of broad-leaved trees) but differed in production reactor type. BC_{slow} was produced in a Pyreg reactor designed for biochar production. BC_{fast} was from a Spanner Re2 wood power plant designed to produce electrical power and heat. The pyrolysis process of BC_{slow} (about 500–600°C) represents low temperature slow pyrolysis, whereas BC_{fast} represents high temperature (about 900°C) fast pyrolysis *in sensu* Bruun et al. (2012). The biochars' carbon, nitrogen and hydrogen (H) contents were measured by dry combustion and the content of oxygen (O) after pyrolysis at 1000°C using an analyzer Hekatech Euro EA 3000 elemental. The thermal stability of biochar was measured by differential scanning calorimetry Q100 (TA Instruments, USA) as in Leifeld et al. (2007). The specific surface area of the biochar was measured by N_2 adsorption and applying the Brunauer-Emmett-Teller (BET) isotherm over the relative pressure range 0.1–0.3 NOVA (Quantachrome Instruments, USA).

Sieved soil (0.5-cm sieve) was packed into 100-ml (5-cm diameter and 5-cm height) metal cylinders (soil bulk density 1.5 g cm^{-3}). The soil water content was adjusted to 80% of the soil maximum water holding capacity. Maize leaves with C:N ratio of 20.4 were used in the experiment.

Unamended soil (as collected from the field) and soil with the maize leaves mixed in was used in the experiment. Soil amended with maize leaves was receiving 40 kg ha^{-1} N and 84 kg ha^{-1} C. The biochars were applied in three different ways: as a layer near the surface of the soil core (0.5 cm deep from the top), as a layer near the bottom of the soil core (4.5 cm deep from the top) and mixed with the soil. The biochars application to the soil in the experiment was equivalent to 10 t ha^{-1}. The experiment was conducted in five replicates.

The soil cylinders were incubated at 22°C for two weeks. Rizhiya et al. (2011) have shown that the highest N_2O fluxes from soils amended with plant residues with C:N ratio similar to those of maize leaves were registered during the first two weeks after the amendment. Soil water content during the measurements was adjusted regularly by weight. Plant-available N (NO_3^- and NH_4^+) was regularly measured in the incubated soil samples over the whole period of the experiment after suspending 20 g of moist soil in 80 mL of 0.01 M $CaCl_2$-solution (FAL, 1998).

Nitrous oxide (N_2O) and carbon dioxide (CO_2) fluxes from the incubated soil were measured by placing cylinders in glass jars (200 mL) fitted with gas-tight lids and sampling ports. The same jars were used for flux measurements in Felber et al. (2014). Prior to the main experiment, extra measurements with the same soil were conducted to find out whether the N_2O and CO_2 accumulation in the jars was linear. The results of this experiment have shown that the accumulation of the two gases in the jars for 25 minutes was linear for 7 treatments out of the studied 8 with an exception for "soil + maize leaves mixed" treatment for FYM and NPKMg soils where the accumulation of the gases was very close to linear (5–8% reduction of the cumulative N_2O and CO_2 fluxes, which is less than the measurement error). For this reason and also because the volume of the glass jars was too small to allow frequent sample collection, gas samples during the main experiment were collected only in 25 min after the soil cylinders were placed in the glass jars. Gas sampling was conducted every day for the first three days of the experiment and then every second day. Concentrations of N_2O and CO_2 in these gas samples was measured with a gas chromatograph (GC, SRI 8610C with nitrogen, and N_2, as a carrier gas) equipped with an electron capture detector (ECD), a pre-column (1 m × 800 Restek HayeSep-A 80/100) to separate water vapour, and the analytical column (3 m × 800 Supelco Porapak

Q 80/100) to separate CO_2 and N_2O. Concentrations of N_2O and CO_2 in the laboratory air were also measured and controlled during the measurements. Daily and cumulative N_2O and CO_2 fluxes were calculated.

The Shapiro-Wilk test was used to find out whether the obtained results for daily (1260 single measurements for each gas) and cumulative (210 values for each gas) N_2O and CO_2 fluxes were normally distributed. As the distribution was not normal the non-parametric statistics was used for the data analyses (Kruskal-Wallis test and Mann Whitney U-test).

Results

Properties of unamended soil and biochars. Despite different management over 60 years and significant differences in soil total C and N contents (CONT < NPKMg < FYM), all the soil samples contained low amounts of total C (0.78–1.03%) and total N (0.094–0.117%), and had near neutral pH values (Table 1). At the time of sample collection the soil of all the plots did not significantly differ in field water content and contained low levels of plant-available N (<10 mg kg^{-1} N_{min} soil) with concentrations of NO_3^--N slightly higher ($p < 0.05$) in the FYM and NPKMg treatments. Application of the biochars to the soil increased its pH_{H2O} values by 0.3–0.4 with no significant difference related to the biochars or the field soil treatments.

Table 1. Initial properties of the soil and maize leaves (with standard error of mean) used in the experiment

	CONT	FYM	NPKMg	Maize leaves
Total carbon (C_{tot}) %	0.778 ± 0.011	1.030 ± 0.013	0.932 ± 0.010	41.67 ± 0.013
Total nitrogen (N_{tot}) %	0.094 ± 0.001	0.117 ± 0.002	0.108 ± 0.001	2.04 ± 0.011
Carbon and nitrogen ratio (C:N)	8.3	8.8	8.6	20.4
Plant-available N-NO_3^-, mg kg^{-1} soil	4.83 ± 0.62	7.19 ± 1.69	7.97 ± 1.81	–
Plant-available N-NH_4^+, mg kg^{-1} soil	1.53 ± 0.35	2.15 ± 0.71	1.96 ± 0.49	–
Field water content %	18.96 ± 0.43	19.79 ± 0.79	19.07 ± 0.59	–
pH_{H2O}	7.1 ± 0.1	7.0 ± 0.1	6.9 ± 0.1	–

CONT – plot with no fertiliser or manure applied, FYM – plot with farmyard manure (5 t ha^{-1} applied every second year), NPKMg – plot with mineral fertilisers (140 N, 38 P, 167 K and 56 Mg kg ha^{-1}, annually)

The two biochars studied in the experiment differed in chemical and physical properties (Table 2). The specific surface area of BC_{fast} was double that of BC_{slow}. At the same time BC_{fast} had higher pH, contained more O and H, less C and N and was characterized by higher O:C, H:C and C:N ratios. All these properties, according to Bruun et al. (2012), define BC_{fast} as a fast pyrolysis biochar and BC_{slow} as a slow pyrolysis biochar. In agreement with a higher contribution from O and H containing molecules BC_{fast} was thermally less stable (maximum heat flow 2.6 W g^{-1} at 400°C) than BC_{slow} (maximum heat flow 3.1 W g^{-1} at 455°C). As it was described earlier by Bruun et al. (2012) quite a large amount of un-pyrolysed carbohydrate fraction can remain in the biochar under fast pyrolysis conditions and presumably that can explain lower thermal stability of fast pyrolysis biochars such as BC_{fast} compared to better pyrolysed biochars such as BC_{slow}.

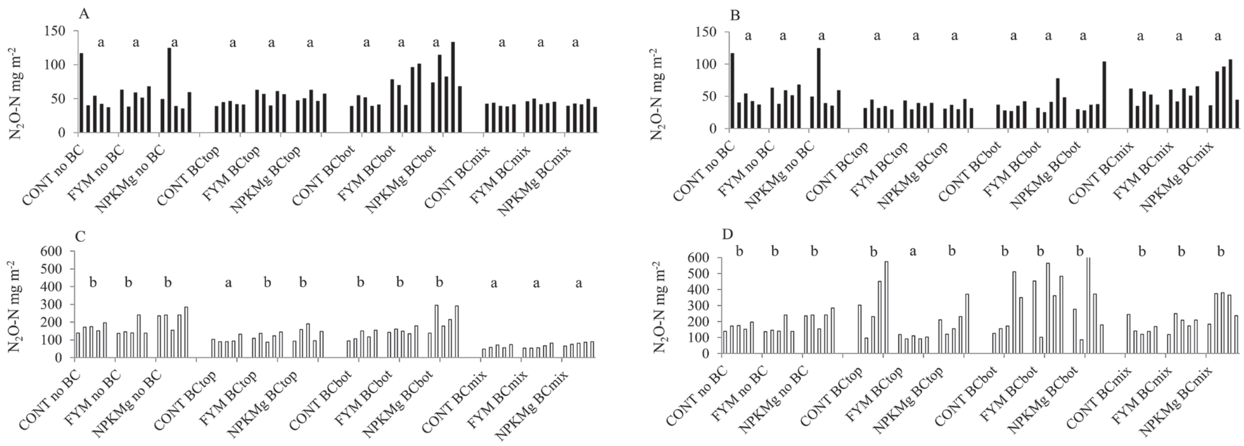
Table 2. Properties of the two biochars used in the laboratory experiment

Biochar	Specific surface area m^2 g^{-1}	Oxygen (O) % dry matter	Hydrogen (H) % dry matter	Carbon (C) % dry matter	Nitrogen (N) % dry matter	O:C molar ratio	H:C molar ratio	C:N ratio	pH_{KCl}
Fast pyrolysis	258	16.25	1.63	58.7	0.29	0.21	0.33	202	10.4
Slow pyrolysis	123	6.20	0.63	76.7	0.64	0.06	0.10	119	9.1

Nitrous oxide (N_2O) emission. In the unamended soil N_2O emissions during the entire period of the experiment varied between 0.05 and 0.74 mg N_2O-N m^2 h^{-1} with no significant difference related to the field soil management. Application of BC_{slow} to the unamended soil did not change N_2O emission, while application of BC_{fast} significantly ($p < 0.05$) increased N_2O emission but only when applied near the surface of the soil with all the studied field treatments. Application of maize leaves to the unamended soil resulted in a significant ($p < 0.0005$) increase of N_2O emission (to 0.07–6.66 mg N_2O-N m^2 h^{-1}) from the soil with all the field treatments, but in two week-time the fluxes were 5–20% of those of the first day after maize leaves application and did not differ significantly from the fluxes of the soil without maize leaves. Mixing BC_{slow} in the soil amended with maize leaves resulted in a significant reduction of the N_2O emission (to 0.09–0.89 mg N_2O-N m^2 h^{-1}, $p < 0.05$) from the soil with all the three field treatments, while mixing BC_{fast} with the maize leaves-amended soil significantly reduced N_2O emission (to 0.09–3.29 mg N_2O-N m^2 h^{-1}, $p < 0.05$) from the CONT and FYM treatments soil but not from the NPKMg soil.

Cumulative N_2O fluxes. The cumulative N_2O fluxes (Fig. 1) emitted by the unamended soil for two weeks of the laboratory experiment varied between 24.0 and 124.3 mg m^{-2} N_2O-N and had no significant difference related to the field soil management (Fig. 1A, B). Application of maize leaves to the unamended soil with all the three field treatments resulted in a significant ($p < 0.01$) three-fold and higher increase of the cumulative N_2O flux, but still with no significant difference related to the field soil management (Fig. 1C, D). Application of either biochar to the unamended soil (independent of the application method) did not result in any significant change of the cumulative N_2O flux which, for these treatments, varied between 24.8 and 132.9 mg m^{-2} N_2O-N (Fig. 1A, B). A significant ($p < 0.01$) systematic reduction (over 60%,) of the cumulative N_2O flux from the maize leaves-amended soil with all the three field treatments was found only when BC_{slow} was mixed with the soil. In this case the cumulative N_2O fluxes emitted by the maize leaves-amended soil for two weeks of the laboratory experiment varied between 48.0 and 89.4 mg m^{-2} N_2O-N with no significant difference related to the field soil management. These fluxes did not differ significantly from those measured from the unamended soil for all the three field soil treatments.

Application of BC_{slow} near the bottom of the cores with the maize leaves-amended soil had no significant effect on the N_2O cumulative flux independent of the



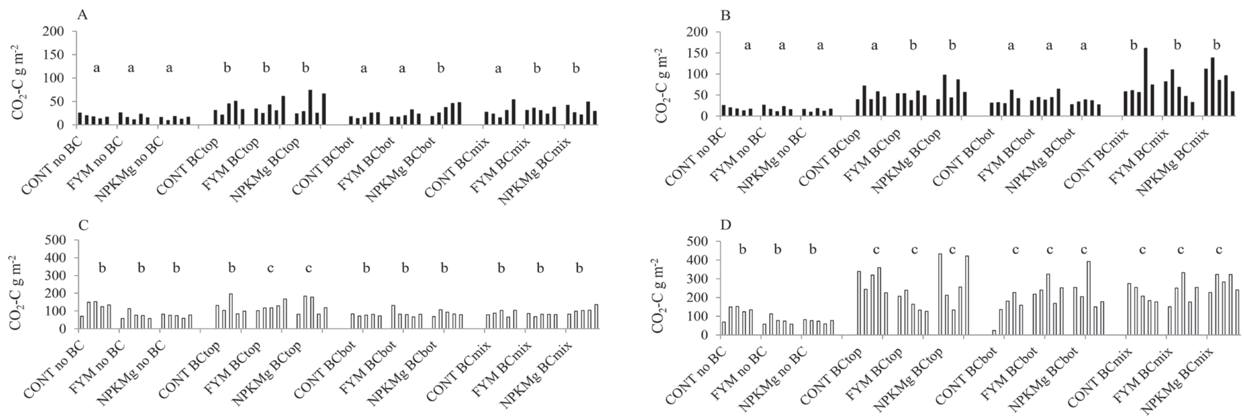
Note. BC – biochar, CONT – plot with no fertiliser or manure applied, FYM – plot with farmyard manure (5 t ha^{-1} applied every second year), NPKMg – plot with mineral fertilisers (140 N, 38 P, 167 K and 56 Mg kg ha^{-1}, annually); top – BC applied as a layer near the surface of the soil core (0.5 cm deep from the top), bot – BC applied as a layer near the bottom of the soil core (4.5 cm deep from the top), mix – BC mixed with the soil; different letters (a, b, c) above the columns indicate statistically significant differences ($p < 0.05$) between the studied parameters.

Figure 1. Cumulative nitrous oxide (N_2O-N) flux from the soil without (A, B) and with (C, D) maize leaves amended with slow (A, C) and fast (B, D) pyrolysis biochar for two weeks of the laboratory experiment

field soil management, while application of the BC_{slow} near the surface of the soil core significantly ($p < 0.01$) reduced N_2O cumulative flux only from the CONT treatment soil. Unlike BC_{slow}, BC_{fast} never systematically changed cumulative N_2O fluxes from the maize leaves-amended soil. The only significant reduction ($p < 0.01$) of the cumulative N_2O flux was measured when BC_{fast} was applied near the surface of the FYM treatment soil. In this case the cumulative flux from the maize leaves-amended soil was not significantly different from the flux of the unamended FYM soil. N_2O cumulative fluxes from the maize leaves-amended soil with BC_{fast} were significantly higher than those with BC_{slow} for all the three field treatments when the biochars were mixed with the maize leaves-amended soil ($p < 0.01$) but not when applied near the top or bottom of the soil cores.

Carbon dioxide (CO_2) emission. In the unamended soil CO_2 emissions during the period of the experiment varied between 4.42 and 207.41 mg m^2 h^{-1} and did not differ for the soil with the different field treatments. Application of BC_{slow} near the soil surface or mixing it with the soil resulted in a significant ($p < 0.0001$) increase of CO_2 emission from the unamended soil with all the studied field treatments (30.16–509.91 mg m^2 h^{-1}), while application of the biochar near the bottom of the soil core significantly ($p < 0.001$) increased CO_2 emission only from the NPKMg treatment (13.51–271.83 mg m^2 h^{-1}). Application of BC_{fast} resulted in a significant ($p < 0.05$) increase of CO_2 emission from the unamended soil with all the studied field treatments independent of the biochar placement. Application of maize leaves to the unamended soil resulted in a significant ($p < 0.001$) increase of the CO_2 emission from the soil with all the three field treatments (93.83–2344.43 mg m^2 h^{-1}). The emission from the maize leaves-amended CONT treatment soil was significantly ($p < 0.01$) higher than from the FYM and NPKMg treatments soil. Mixing BC_{slow} with the maize leaves-amended soil significantly ($p < 0.001$) increased CO_2 emission only from the NPKMg soil, while mixing BC_{fast} with the maize leaves-amended soil significantly ($p < 0.001$) increased CO_2 emission from FYM and NPKMg soils. Application of BC_{fast} near the surface of the soil amended with maize leaves significantly increased CO_2 emission form the FYM and NPKMg soils but not from the CONT treatment, while application of the BC_{slow} resulted in a significantly ($p < 0.01$) increased CO_2 emission from the soil with all the three field treatments.

Cumulative CO_2 fluxes. The unamended soil emitted between 10.8 and 46.3 g m^{-2} CO_2-C over the two weeks of the laboratory experiment without any significant difference related to the field soil management (Fig. 2A, B). Application of maize leaves resulted in a significant ($p < 0.01$) 300–600% increase of the cumulative CO_2 flux from the soil with all the three field treatments but without any significant difference related to the field soil management (Fig. 2C, D). Application of BC_{slow} to the unamended soil resulted in an 11–215% increase of the cumulative CO_2 flux, but the increase was not always significant. The highest (100–214%) and significant ($p < 0.05$) increase in the CO_2 cumulative flux from the soil with all the three field treatments was recorded when BC_{slow} was applied as a layer near the surface of the soil core. In this case there was no significant difference related to the field soil management. Mixing BC_{slow} with the unamended soil resulted in a significant ($p < 0.05$) increase of the cumulative CO_2 flux for FYM and NPKMg treatments soil, but not for the CONT treatment. Application of BC_{slow} at the bottom of the soil core significantly ($p < 0.05$) increased the cumulative CO_2 flux only from NPKMg treatment. Application of the BC_{fast} to the unamended soil also resulted in a cumulative CO_2 flux increase (39–292%) with no difference related to the field soil management. The increase was statistically significant ($p < 0.05$) for the soil with all the three field treatments only when the biochar was mixed with the soil. The other ways of the biochar placement had no significant effect on the cumulative CO_2 flux from the CONT soil, while application of the biochar near the soil core surface but not near the soil core bottom, resulted in a significant ($p < 0.05$) increase of the cumulative CO_2 flux from the FYM and NPKMg treatments soil. Application of BC_{slow} to the maize leaves-amended soil had no significant effect on the CO_2 cumulative flux from the CONT soil independent of the biochar placement, but significantly ($p < 0.05$) increased the cumulative CO_2 flux from FYM and NPKMg soils when the biochar was applied as a layer near the surface of the soil core. Application of BC_{fast} to the maize leaves-amended soil significantly increased the cumulative CO_2 flux for all the three field treatments independent of the biochar placement in the soil core.



Explanation under Figure 1

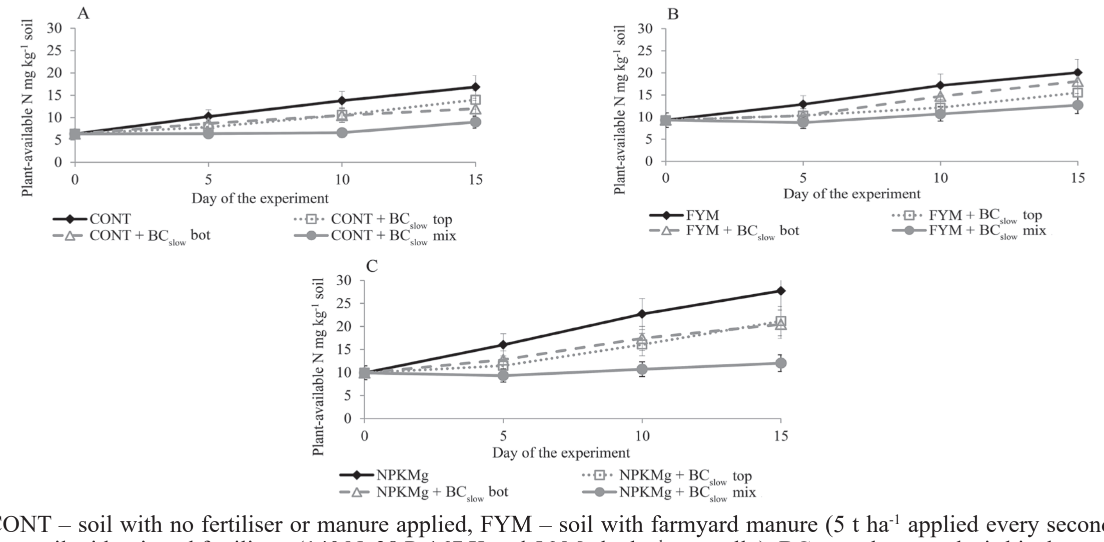
Figure 2. Cumulative carbon dioxide (CO_2-C) flux from the soil without (A, B) and with (C, D) maize leaves amended with slow (A, C) and fast (B, D) pyrolysis biochar for two weeks of the laboratory experiment

CO_2 cumulative fluxes from the maize leaves-amended soil with BC_{fast} were significantly higher ($p < 0.0005$) than those with BC_{slow} for all the studied placements of the biochars in the soil cores.

Plant-available nitrogen. Up to 80% of the plant-available N in the soil with the three field treatments was in the form of NO_3^--N. Concentration of soil plant-available NH_4^+-N was changing within 0–3 mg kg^{-1} N soil without any significant differences between the experimental treatments. Most of the changes in the soil plant-available nitrogen concentrations during the experiment were due to the changes in nitrate (NO_3-N) content, but even those were not very big. The most distinct changes in plant-available nitrogen content were measured only when BC_{slow} was applied to the unamended soil (Fig. 3). In the unamended soil plant-available nitrogen content slowly increased during the laboratory experiment showing a significant difference ($p < 0.05$) of 10–11 mg kg^{-1} N soil in the CONT and FYM treatments soil and 17–18 mg kg^{-1} N soil in the NPKMg treatment by the end of the experiment (Fig. 3). Application of BC_{slow} to the unamended soil resulted in lower plant-available N content in the soil of all the three field treatments during the whole experiment. For CONT and FYM treatments soil this decrease was significant only when BC_{slow} was mixed with the soil, while for NPKMg treatment it was significant for all the three placements of biochar in the soil core ($p < 0.05$).

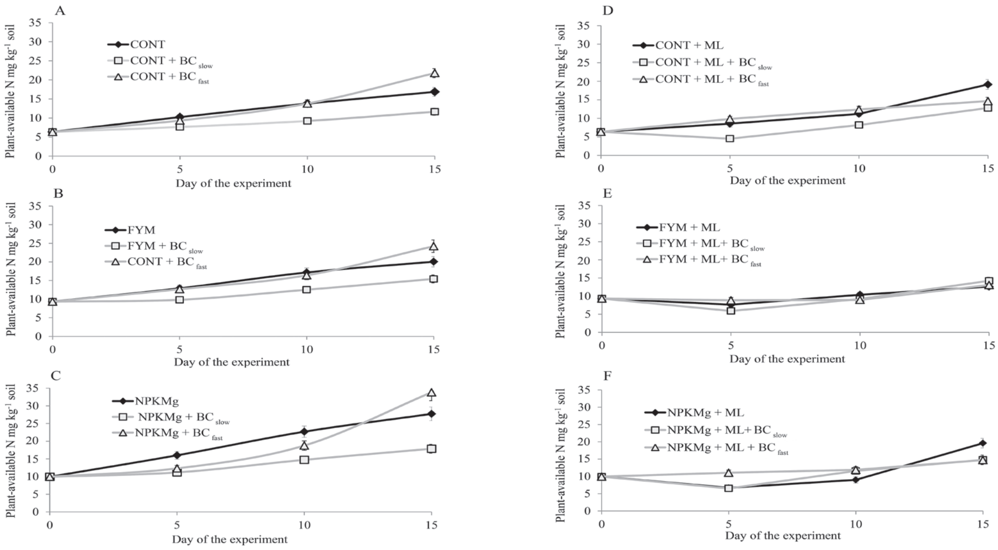
Application of BC_{fast} to the unamended soil resulted in a significant increase of soil plant-available nitrogen in the soil with all the three field treatments but only at the end of the experiment. Application of maize leaves to the soil with different field treatments resulted in lower plant-available nitrogen content in the soil from all the three field treatments throughout the whole experiment compared to the unamended soil ($p < 0.05$). Application of either biochar to the maize leaves-amended soil resulted mostly in insignificant changes in the soil plant-available nitrogen (Fig. 4).

As the placement of the biochars in most cases did not have a significant effect on the soil plant-available nitrogen concentrations of maize leaves-amended soil, Figure 4 gives average values for three different ways of biochar placements in the soil.



Note. CONT – soil with no fertiliser or manure applied, FYM – soil with farmyard manure (5 t ha^{-1} applied every second year), NPKMg – soil with mineral fertilisers (140 N, 38 P, 167 K and 56 Mg kg ha^{-1}, annually); BC_{slow} – slow pyrolysis biochar; top – BC applied as a layer near the surface of the soil core (0.5 cm deep from the top), bot – BC applied as a layer near the bottom of the soil core (4.5 cm deep from the top), mix – BC mixed with the soil; the decrease is significant for CONT, FYM and NPKMg soils when BC_{slow} is mixed with the soil and for NPKMg soil also when BC_{slow} is placed within the soil core ($p < 0.05$); error bars indicate standard error of mean.

Figure 3. Plant-available nitrogen (NH_4^+-N + NO^{3-}-N, mg kg^{-1} soil with standard deviations) in the not fertilised (CONT) (A), fertilised with farmyard manure (FYM) (B) and NPKMg (C) soils without maize leaves during the experiment



Note. CONT – soil with no fertiliser or manure applied, FYM – soil with farmyard manure (5 t ha^{-1} applied every second year), NPKMg – soil with mineral fertilisers (140 N, 38 P, 167 K and 56 Mg kg ha^{-1}, annually); BC_{slow} – slow pyrolysis biochar, BC_{fast} – fast pyrolysis biochar; the differences are significant ($p < 0.05$) at the end of the experiment, where the standard deviations show the difference; error bars indicate standard error of mean.

Figure 4. Plant-available nitrogen (NH_4^+-N + NO^{3-}-N, mg kg^{-1} soil with standard deviations) with no (A, B, C) and with (D, E, F) maize leaves (ML) in the soil during the experiment

Discussion

Nitrous oxide (N_2O) emission. The soil with different treatments used in this study had very small but statistically significant differences in total nitrogen and carbon contents, as well as in plant-available nitrogen owing to the differences in their long-term fertilisation history. Despite this, and also despite the fact that soil water content during the experiment was kept at 80% of the soil maximum water holding capacity, cumulative N_2O emissions from the unamended soil with or without biochar were low (24–124 mg m^{-2} N_2O-N). The main reason for that must have been the low level of plant-available nitrogen and carbon in the studied soil, which are both necessary components for the process of denitrification. Conen et al. (2000) found that daily N_2O fluxes exceeded 10 g ha^{-1} N_2O-N only when the available nitrogen in the soil was greater than 10 mg kg^{-1}, while Buchkina et al. (2010) showed for loamy sand soils that even in the conditions of high values of water-filled pore space soil N_2O fluxes in field experiments were never high if the soil contained low amount of available nitrogen. The results are in agreement with the studies reporting minor reductions of N_2O fluxes from soils by biochar without nitrogen fertilisation (Kammann et al., 2012) and supply of labile organic carbon (Felber et al., 2012).

The addition of maize leaves resulted in 2–10-fold increase in cumulative N_2O emissions, but high daily N_2O fluxes did not last: in two weeks they were 5–20% of those of the first day after maize leaves application and did not differ significantly from the fluxes of the soil without maize leaves which is in line with previous research (Rizhiya et al., 2011). Application of the biochars to the maize leaves-amended soil did not suppress the N_2O flux trigged by maize leaves application completely and cumulative fluxes measured from maize leaves-amended soil with different field treatments were 39–178% higher for BC_{slow} and 181–875% – for BC_{fast} compared to the soil without maize leaves. Still, the addition of BC_{slow} to the maize leaves-amended soil significantly reduced the N_2O emissions.

The reduction of N_2O emission after BC_{fast} application was mainly not significant which is in line with the meta-analysis by Cayuela et al. (2015) who found that reduction of soil N_2O emission after biochar application was always lower for biochars with higher molar H:C_{org} ratio. In our experiment BC_{slow} was characterized by narrower O:C and H:C ratio and higher thermal stability, both indicating a more elaborated aromatic structures than BC_{fast}. The highest reduction effects of BC_{slow} on the cumulative N_2O flux from the maize leaves-amended soil were observed when BC_{slow} was mixed with the soil. Felber et al. (2014) showed the importance of proper mixing of biochar with soil for N_2O flux reduction. Most of the proposed hypothesis how biochar can reduce N_2O emissions (Clough et al., 2013) rely on a high contact surface between biochar and soil. However, application of BC_{slow} near the CONT treatment soil surface also resulted in a statistically significant decrease of the cumulative N_2O flux from maize leaves-amended soil suggesting that some of the N_2O produced in the soil could also be absorbed on the biochar surface.

Carbon dioxide (CO_2) emission. Cumulative CO_2 emissions from unamended soil with all the field treatments were enhanced by biochar addition which may either indicate a stimulation of soil organic carbon decomposition, decomposition of biochar itself or a combination of both. Either process has been reported in the literature (Wardle et al., 2008; Smith et al., 2010). Cumulative CO_2 emissions from the unamended soil were systematically higher for BC_{fast} than for BC_{slow} (Fig. 2A, B). The chemical composition of the former differs from the latter in having a higher content of H and O, both indicative of a smaller degree of aromaticity (Spokas, 2010; Cross, Sohi, 2013). Also the thermal stability, which is directly related to char decomposability (Leifeld et al., 2007; Harvey et al., 2012), of BC_{fast} is distinctly below that of BC_{slow}. Together these data indicate that BC_{fast} is more labile which may have contributed to enhanced CO_2 emissions from the studied soil. When maize leaves were applied, the effect of BC_{slow} addition was less pronounced than that of BC_{fast} and the bulk CO_2 emissions from the soil with different field treatments were 2 to 7 times higher, presumably due to respiratory losses from decomposing leaves and also decomposing BC_{fast}. In contrast to N_2O emissions, CO_2 emissions were hardly affected by the placement of the biochar in the soil column. For the more labile BC_{fast} emissions were high for all the experimental treatments, whereas for the more stable BC_{slow} emissions were the highest for the biochar placement near the soil surface. Sixty years difference in soil fertilisation intensity had no systematic effect on cumulative CO_2 flux from the studied soil straight after maize leaves application.

Impact on plant-available nitrogen. The NO_3^--N concentrations in the studied soil during the laboratory experiment were low as the conditions of the experiment were more suitable for denitrification than for nitrification. Accumulation of NO_3^--N in the unamended soil at the end of the experiment in most of the treatments with both biochars indicated that nitrification was still happening, even with the soil water content kept at 80% of the soil maximum water holding capacity.

Reduction in the amount of plant-available nitrogen in the unamended soil after BC_{slow} application most likely is indicating immobilization of mineral N by C-rich material which is in line with our other work showing a decrease in the nitrification rates in a clayey loam soil after the biochars application (Buchkina et al., 2017). Based on the soil N_2O fluxes which do not significantly change after BC_{slow} application to the unamended soil, the lower NO_3^--N concentrations in the soil in this case cannot be attributed to denitrification losses of NO_3^--N being stimulated by the additional C (Clough et al., 2013). BC_{slow} effects on plant-available nitrogen in unamended soil were more pronounced in FYM and NPKMg treatments than in the CONT treatment. This indicates that BC_{slow} changes the nitrogen mineralization rates of the available substrate in the soil rather than releasing less nitrogen from the biochar itself. This is in agreement with Dempster et al. (2012) who measured a significantly decreased net N mineralization with increasing addition of biochar.

Application of maize leaves with or without the biochars to the soil leads to a significant decrease in plant-available nitrogen in the soil with all the three field treatments compared to unamended soil. In this case the decrease can be attributed not only to nitrogen immobilization, but also to higher denitrification losses stimulated by additional carbon and nitrogen added with maize leaves as N_2O fluxes from maize leaves-amended soil increase significantly compared to the unamended soil with all the three field treatments.

Conclusions

1. A suppressive effect of slow pyrolysis biochar (BC_{slow}) application on nitrous oxide (N_2O) emissions from maize leaves-amended soil was independent of the differences in the soil properties resulting from the long-term differences in fertilisation. The short-term effect of maize leaves application on N_2O emissions was much stronger than the effect of the soil properties resulting from the 60-year difference in fertilisation strategy which suggests that the biochar effects on short-term N_2O emission after plant residue incorporation are largely independent of soil management history. A proper mixing of the biochar with the soil and plant residues was in general more efficient in reducing N_2O emissions related to maize leaves application than the biochar application in layers on top or at a certain depth in the soil. Neither of the studied placements of the biochar in the soil systematically reduced carbon dioxide (CO_2) emissions.

2. Application of thermally more labile fast pyrolysis biochar (BC_{fast}) with wider oxygen and carbon (O:C) and hydrogen and carbon (H:C) ratios did not systematically reduce N_2O emissions from the studied soil either with or without plant residues despite the significantly lower content of plant-available nitrogen in the soil amended with maize leaves and BC_{fast}. BC_{fast} increased CO_2 fluxes from the soil even when no plant residues were applied to the soil, underpinning the role of biochar stability for controlling soil-related greenhouse gas (GHG) emissions.

3. Thermally more stable, BC_{slow} can be used to effectively reduce short-term N_2O but not CO_2 fluxes related to the application of plant residues with narrow carbon and nitrogen (C:N) ratio to agricultural soils. Mixing biochars with the soil and plant residues is the best way of N_2O flux reduction compared to applying biochars in layers.

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Medžio anglies įtaka trumpalaikei N_2O ir CO_2 emisijai iš augalų liekanomis papildyto skirtingai tręšto dirvožemio

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Santrauka

Tręšimo medžio anglimi įtaka azoto suboksido (dioksido) (N_2O) ir anglies dioksido (CO_2) emisijai iš dirvožemio, į jį įterpus kukurūzų lapus, buvo tirta laboratoriniame eksperimente, dirvožemio mėginius paėmus iš trijų skirtingo tręšimo variantų laukelių: netręšta (kontrolinis variantas), tręšta mineralinėmis trąšomis (NPKMg) ir mėšlu, iš lauko bandymų, vykdomų nuo 1949. Eksperimento metu naudota žemoje temperatūroje lėtos pirolizės (MALP) ir aukštoje temperatūroje greitos pirolizės (MAGP) būdu pagaminta 10 t ha^{-1} medžio anglis. Taikant skirtingas tręšimo strategijas esmingai skyrėsi suminis anglies (C) ir azoto (N) kiekis dirvožemyje (kontrolinis < NPKMg < mėšlas), bet mėginių paėmimo metu dirvožemyje buvo mažai augalų pasiekiamo N (<10 mg kg^{-1} N), nepriklausomai nuo tręšimo varianto. Kukurūzų lapais papildytame dirvožemyje patręšus MALP medžio anglimi buvo nustatytas stabilus slopinantis poveikis N_2O emisijai, tačiau jis nebuvo nustatytas patręšus MAGP medžio anglimi. N_2O emisijai trumpalaikis augalų liekanų įterpimo poveikis buvo gerokai didesnis nei skirtumai per 60-ies metų dirvožemio tręšimo laikotarpį. Mažinant N_2O emisiją medžio anglies maišymas su kukurūzų lapais ir dirvožemiu buvo efektyvesnis nei medžio anglies įterpimas į sluoksnius. CO_2 emisijos sistemingai nesumažino nė vienas iš tirtų medžio anglies įterpimo į dirvožemį būdų. Palyginus su MALP, termiškai labilesnės MAGP medžio anglies su didesniu O:C bei H:C santykiu įterpimas sistemingai nesumažino N_2O emisijos ir padidino CO_2 srautus iš dirvožemio. Tai rodo medžio anglies stabilumo ir sudėties reikšmę siekiant kontroliuoti su augalų liekanų panaudojimu susijusią šiltnamio efektą sukeliančių dujų emisiją.

Reikšminiai žodžiai: dirbama žemė, greita pirolizė, kukurūzų lapai, laboratorinis bandymas, lėta pirolizė, šiltnamio efektą sukeliančios dujos.