Biochar and short-term $\text{N}_2\text{O}$ and $\text{CO}_2$ emission from plant residue-amended soil with different fertilisation history

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Abstract
The effect of biochar application on nitrous oxide ($\text{N}_2\text{O}$) and carbon dioxide ($\text{CO}_2$) 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$_{\text{slow}}$) and in high temperature fast (BC$_{\text{fast}}$) 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$_{\text{slow}}$ but not BC$_{\text{fast}}$ application on $\text{N}_2\text{O}$ emissions was found for maize leaves-amended soil. The short-term effect of residue application on $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ emissions than biochar application in layers. Neither of the studied ways of biochar application to the soils systematically reduced $\text{CO}_2$ emissions. Compared to BC$_{\text{slow}}$ application of thermally more labile BC$_{\text{fast}}$ with wider oxygen and carbon (O:C) and hydrogen and carbon (H:C) ratios did not systematically reduce $\text{N}_2\text{O}$ emissions and increased $\text{CO}_2$ 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 ($\text{N}_2\text{O}$) and carbon dioxide ($\text{CO}_2$) 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 $\text{N}_2\text{O}$ and $\text{CO}_2$ emissions from the soils. Mogge et al. (1999) measured $\text{N}_2\text{O}$ emissions from sandy soils fertilised with farmyard manure for 30 years and found that annual gaseous $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ emissions at a soil moisture content of 60% water-holding capacity, but had no influence on $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ and $\text{CO}_2$ emissions (Baggs et al., 2000; Huang et al., 2004; Toma,
Hatano, 2007; Rizhiya et al., 2011). The effect usually is short-lived. Most of the N\textsubscript{2}O emissions after plant residue incorporation occur during the first two weeks (Baggs et al., 2000; Rizhiya et al., 2011), and the highest CO\textsubscript{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\textsubscript{2} and N\textsubscript{2}O production. Biochar may enhance soil CO\textsubscript{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\textsubscript{2}O emission: some studies have found up to 70% reduction of soil N\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{org} ratio reduced soil N\textsubscript{2}O emission more effectively.

According to Mosier (2001), two thirds of the N\textsubscript{2}O emissions in agriculture are related to N-fertiliser / manure / plant residue use. Can we reduce short-term but very high N\textsubscript{2}O and CO\textsubscript{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°25ʹ36ʺ N, 8°31ʹ7ʺ E) in Zurich, Switzerland the effect of farmyard manure and mineral fertilisers (in 5 replicates) on the Haplic Luvisol (FUha) (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\textsuperscript{-1} (FYM) applied every second year, and mineral fertiliser 140 N, 38 P, 167 K and 56 Mg kg ha\textsuperscript{-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\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} in a 0.01 M CaCl\textsubscript{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\textsubscript{slow} and BC\textsubscript{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\textsubscript{slow} was produced in a Pyreg reactor designed for biochar production. BC\textsubscript{fast} was from a Spanner Re2 wood power plant designed to produce electrical power and heat. The pyrolysis process of BC\textsubscript{slow} (about 500–600°C) represents low temperature slow pyrolysis, whereas BC\textsubscript{fast} represents high temperature (about 900°C) fast pyrolysis in sensor Bruen 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\textsubscript{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\textsuperscript{-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\textsuperscript{-1} N and 84 kg ha\textsuperscript{-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\textsuperscript{-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\textsubscript{2}O 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\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+}) 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\textsubscript{2}-solution (FAL, 1998), clay 14%) properties and crop yields was measured in the 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\textsubscript{2}O and CO\textsubscript{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\textsubscript{2}O and CO\textsubscript{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\textsubscript{2}O and CO\textsubscript{2} in these gas samples was measured with a gas chromatograph (GC, SRI 8610C with nitrogen, and N\textsubscript{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 CO₂ and N₂O. Concentrations of N₂O and CO₂ in the laboratory air were also measured and controlled during the measurements. Daily and cumulative N₂O and CO₂ fluxes were calculated.

The Shapiro–Wilks 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) N₂O and CO₂ 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 N₉₅ soil).

<table>
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<tr>
<th>Table 1. Initial properties of the soil and maize leaves (with standard error of mean) used in the experiment</th>
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<tr>
<td><strong>CONT</strong></td>
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<tr>
<td>Total carbon (C) %</td>
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<tr>
<td>Total nitrogen (N) %</td>
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<td>Carbon and nitrogen ratio (C:N)</td>
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<td>Plant-available N-NO₃⁻, mg kg⁻¹ soil</td>
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<tr>
<td>Plant-available N-NH₄⁺, mg kg⁻¹ soil</td>
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<td>Field water content %</td>
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<td>pHH₂O</td>
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CONT – plot with no fertilizer 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) with concentrations of NO₃⁻-N slightly higher (p < 0.05) in the FYM and NPKMg treatments. Application of the biochars to the soil increased its pHH₂O values by 0.3–0.4 with no significant difference related to the biochars or the field soil treatments.

The two biochars studied in the experiment differed in chemical and physical properties (Table 2). The specific surface area of BCfast was double that of BCslow. At the same time BCfast 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 BCfast as a fast pyrolysis biochar and BCslow as a slow pyrolysis biochar. In agreement with a higher contribution from O and H containing molecules BCfast was thermally less stable (maximum heat flow 2.6 W g⁻¹ at 400°C) than BCslow (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 BCfast compared to better pyrolysed biochars such as BCslow.

<table>
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<th>Table 2. Properties of the two biochars used in the laboratory experiment</th>
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<td><strong>Biochar</strong></td>
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<td>Fast pyrolysis</td>
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<td>Slow pyrolysis</td>
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Nitrous oxide (N₂O) emission. In the unamended soil N₂O emissions during the entire period of the experiment varied between 0.05 and 0.74 mg N₂O-N m⁻² h⁻¹ with no significant difference related to the field soil management. Application of BCslow to the unamended soil did not change N₂O emission, while application of BCfast significantly (p < 0.05) increased N₂O 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 N₂O emission (to 0.07–6.66 mg N₂O-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 BCslow in the soil amended with maize leaves resulted in a significant reduction of the N₂O flux (to 0.09–0.89 mg N₂O-N m⁻² h⁻¹, p < 0.05) from the soil with all the three field treatments, while mixing BCfast with the maize leaves-amended soil significantly reduced N₂O emission (to 0.09–3.29 mg N₂O-N m⁻² h⁻¹, p < 0.05) from the CONT and FYM treatments soil but not from the NPKMg soil.

**Cumulative N₂O fluxes.** The cumulative N₂O 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 N₂O-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 N₂O 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 N₂O flux which, for these treatments, varied between 24.8 and 132.9 mg m⁻² N₂O-N (Fig. 1A, B). A significant (p < 0.01) systematic reduction (over 60%) of the cumulative N₂O flux from the maize leaves-amended soil with all the three field treatments was found only when BCslow was mixed with the soil. In this case the cumulative N₂O 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 N₂O-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 BCfast near the bottom of the cores with the maize leaves-amended soil had no significant effect on the N₂O cumulative flux independent of the
field soil management, while application of the BCslow near the surface of the soil core significantly ($p < 0.01$) reduced N$_2$O cumulative flux only from the CONT treatment soil. Unlike BCslow, BCfast never systematically changed cumulative N$_2$O fluxes from the maize leaves-amended soil. The only significant reduction ($p < 0.01$) of the cumulative N$_2$O flux was measured when BCfast 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$_2$O cumulative fluxes from the maize leaves-amended soil with BCfast were significantly higher than those with BCslow 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 BCslow 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 BCfast resulted in a significant ($p < 0.05$) increase of CO$_2$ emission from the unamended soil with all the NPKMg treatments soil, but not for the CONT treatment. Application of BCfast at the bottom of the soil core significantly ($p < 0.05$) increased the cumulative CO$_2$ flux from the soil with all the three field treatments compared to the CONT soil. Application of the BCfast to the maize leaves-amended soil also resulted in a cumulative CO$_2$ flux increase (39–292%) with no difference related to the field soil management. Mixing BCfast 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 BCslow at the bottom of the soil core significantly ($p < 0.05$) increased the cumulative CO$_2$ flux only from NPKMg treatment. Application of the BCfast 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 BCslow to the maize leaves-amended soil 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 BCslow 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 BCslow 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 BCslow 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 BCfast at the bottom of the soil core significantly ($p < 0.05$) increased the cumulative CO$_2$ flux only from NPKMg treatment. Application of the BCfast 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 BCslow 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 BCfast 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.
CO₂ cumulative fluxes from the maize leaves-amended soil with BC\text{fast} were significantly higher ($p < 0.0005$) than those with BC\text{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\text{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\text{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\text{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\text{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\text{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\text{slow} is mixed with the soil and for NPKMg soil also when BC\text{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.
Discussion

Nitrous oxide (N\textsubscript{2}O) 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\textsubscript{2}O emissions from the unamended soil with or without biochar were low (24–124 mg m\textsuperscript{-2} N\textsubscript{2}O-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\textsubscript{2}O fluxes exceeded 10 g ha\textsuperscript{-1} N\textsubscript{2}O-N only when the available nitrogen in the soil was greater than 10 mg kg\textsuperscript{-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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O emissions, but high daily N\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{slow} and 181–875% – for BC\textsubscript{fast} compared to the soil without maize leaves. Still, the addition of BC\textsubscript{slow} to the maize leaves-amended soil significantly reduced the N\textsubscript{2}O emissions.

The reduction of N\textsubscript{2}O emission after BC\textsubscript{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\textsubscript{2}O emission after biochar application was always lower for biochars with higher molar H:C\textsubscript{org} ratio. In our experiment BC\textsubscript{fast} was characterized by narrower O:C and H:C ratio and higher thermal stability, both indicating a more elaborated aromatic structures than BC\textsubscript{fast}. The highest reduction effects of BC\textsubscript{slow} on the cumulative N\textsubscript{2}O flux from the maize leaves-amended soil were observed when BC\textsubscript{slow} was mixed with the soil. Felber et al. (2014) showed the importance of proper mixing of biochar with soil for N\textsubscript{2}O flux reduction. Most of the proposed hypothesis how biochar can reduce N\textsubscript{2}O emissions (Clough et al., 2013) rely on a high contact surface between biochar and soil. However, application of BC\textsubscript{slow} near the CONT treatment soil surface also resulted in a statistically significant decrease of the cumulative N\textsubscript{2}O flux from maize leaves-amended soil suggesting that some of the N\textsubscript{2}O produced in the soil could also be absorbed on the biochar surface.

Carbon dioxide (CO\textsubscript{2}) emission. Cumulative CO\textsubscript{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\textsubscript{2} emissions from the unamended soil were systematically higher for BC\textsubscript{fast} than for BC\textsubscript{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\textsubscript{fast} is distinctly below that of BC\textsubscript{slow}. Together these data indicate that BC\textsubscript{fast} is more labile which may have contributed to enhanced CO\textsubscript{2} emissions from the studied soil. When maize leaves were applied, the effect of BC\textsubscript{slow} addition was less pronounced than that of BC\textsubscript{fast} and the bulk CO\textsubscript{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\textsubscript{fast}. In contrast to N\textsubscript{2}O emissions, CO\textsubscript{2} emissions were hardly affected by the placement of the biochar in the soil column. For the more labile BC\textsubscript{fast} emissions were high.

Figure 4. Plant-available nitrogen (NH\textsubscript{4}+\textsubscript{-N} + NO\textsubscript{3}–-N, mg kg\textsuperscript{-1} soil with standard deviations) with no (A, B, C) and with (D, E, F) maize leaves (ML) in the soil during the experiment
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 placement near the soil surface. Sixty years difference et al., 2017). Based on the soil N

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 NO$_3$ 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 NO$_3$ 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$_2$O) 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$_2$O 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$_2$O 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$_2$O 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$_2$O 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$_2$O 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$_2$O flux reduction compared to applying biochars in layers.

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References


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with different fertilisation history


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Medžio anglies įtaka trumpalaikieji N\textsubscript{2}O ir CO\textsubscript{2} emisijai iš augalų liekanomis papildyto skirtingai tręšti dirvožemio

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Santrauka

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Tręšimo medžio anglimi įtaka azoto suboksido (dioksido) (N\textsubscript{2}O) ir angles dioksido (CO\textsubscript{2}) emisijai iš dirvožemio, į jį įterpus kukurūzų lapus, buvo tirta laboratoriniame eksperimente, dirvožemio mėginiuose su skirtingais tręšimo variantais. Įtaka medžio anglių įterpimą įdirvožemio dirvožemyje buvo nustatyta skirtumai per 60-ies metų dirvožemio tręšimo laikotarpį. Mažinant CO\textsubscript{2} emisijos sisteminai nesumazino, bet išaugo dirvožės ginkluotumai ir skirtingių tręšimo variantų gentys ginkluotumai buvo mažiausiausia. 

Reikšminiai žodžiai: dirbama žemė, greita pirolizė, kukurūzų lapai, laboratorinis bandymas, šiltnamio efekto priklausomybė nuo dirvų kasmenų.