

Manuscript prepared for SOIL Discuss.

with version 2015/04/24 7.83 Copernicus papers of the L^AT_EX class copernicus.cls.

Date: 3 December 2015

Effect of biochar and liming on soil nitrous oxide emissions from a temperate maize cropping system

R. Hüppi^{1,2}, R. Felber¹, A. Neftel¹, J. Six², and J. Leifeld¹

¹Climate and Air Pollution Group, Agroscope Research Station Zurich, Zürich, Switzerland

²Department of Environmental Science, Institute of Agricultural Sciences, ETH Zurich, Zürich, Switzerland

Correspondence to: R. Hüppi (hueppir@ethz.ch)

Abstract

Biochar, a carbon-rich, porous pyrolysis product of organic residues may positively affect plant yield and can, owing to its inherent stability, promote soil carbon sequestration when amended to agricultural soils. Another possible effect of biochar is the reduction in emissions of nitrous oxide (N_2O). A number of laboratory incubations have shown significantly reduced N_2O emissions from soil when mixed with biochar. Emission measurements under field conditions however are more scarce and show weaker or no reductions, or even increases in N_2O emissions. One of the hypothesized mechanisms for reduced N_2O emissions from soil is owing to the increase in soil pH following the application of alkaline biochar. To test the effect of biochar on N_2O emissions in a temperate maize cropping system, we set up a field trial with a 20 t ha^{-1} biochar treatment, a limestone treatment adjusted to the same pH as the biochar treatment (pH 6.5), and a control treatment without any addition (pH 6.1). An automated static chamber system measured N_2O emissions for each replicate plot ($n = 3$) every 3.6 h over the course of 8 months. The field was conventionally fertilised at a rate of 160 kg N ha^{-1} in 3 applications of 40, 80 and 40 kg N ha^{-1} as ammonium nitrate.

Cumulative N_2O emissions were 52% smaller in the biochar compared to the control treatment. However, the effect of the treatments overall was not statistically significant ($p = 0.27$) because of the large variability in the dataset. Limed soils emitted similar mean cumulative amounts of N_2O as the control. There is no evidence that reduced N_2O emissions with biochar relative to the control is solely caused by a higher soil pH.

1 Introduction

Agriculture faces major challenges regarding world food security because of climate change, continued population growth and resource-depleting practises (IAASTD, 2009). Accounting for roughly 12% of anthropogenic greenhouse gas (GHG) emissions per year, agriculture is a sector with a considerable mitigation potential and, at the same time, is highly vulnerable to the consequences of a changing climate (IPCC, 2014). With its 300 fold warming

potential compared to CO₂, nitrous oxide (N₂O) from soil is a downside of the large productivity increase in agriculture, mostly due to synthetic nitrogen fertiliser application. Reducing agricultural N₂O emissions would reduce the GHG induced radiative forcing (IPCC, 2014), improve the stability of the stratospheric ozone layer (Ravishankara et al., 2009) and reduce agriculture's energy intensity when achieved with a lower nitrogen fertiliser use (IAASTD, 2009).

Biochar is produced by thermal decomposition of organic material in a low-oxygen environment, called pyrolysis. This stable charcoal-like material has the potential to contribute to the mitigation of climate change by increasing soil carbon (C) (Lehmann, 2007; Woolf et al., 2010; Lal et al., 2011). In addition, biochar can increase crop yields (Jeffery et al., 2011; Biederman and Harpole, 2013; Crane-Droesch et al., 2013) and reduce water stress, which helps to adapt to climate change (Mulcahy et al., 2013). Its application to soils that have a small cation exchange capacity and low organic carbon content is associated with higher crop yields (Crane-Droesch et al., 2013) with an overall mean response of 10 % (Jeffery et al., 2011). For fertile, temperate soils improvement of soil quality is not key to biochar application. Rather, biochar effects on soil-borne GHG emissions, N₂O in particular, has become a strong argument for its amendment.

Biochar also controls nitrogen (N) cycling (Clough et al., 2013). Biochar can reduce N leaching (Steiner et al., 2008; Güereña et al., 2013) and soil-borne N-containing GHG (Van Zwieten et al., 2015). Especially N₂O emissions from soil are reduced on average by 54 % in lab studies and 28 % in field measurements (Cayuela et al., 2015). In field situations, N₂O reduction effects are typically difficult to verify because of less uniform conditions and a large spatial and temporal variability of fluxes (Felber et al., 2013; Schimmelpfennig et al., 2014). A few field experiments indicated an increase in N₂O (e.g., Verhoeven and Six, 2014; Liu et al., 2014), many showed no significant effects (Karhu et al., 2011; Scheer et al., 2011; Suddick and Six, 2013; Anderson et al., 2014; Angst et al., 2014) while other studies indicated decreasing N₂O emissions (e.g., Van Zwieten et al., 2010; Zhang et al., 2010; Taghizadeh-Toosi et al., 2011; Felber et al., 2013; Case et al., 2014). Only few studies

with biochar have looked at N₂O emissions beyond 120 days (Verhoeven and Six, 2014), hence there is a large uncertainty about longer term effects of biochar addition.

Biochars are often alkaline and therefore increase soil pH after application (Joseph et al., 2010). Denitrifying bacterial communities have the potential to increase their N₂O-reducing activity with increasing pH, which may reduce N₂O emissions from soils (Cavigelli and Robertson, 2001; Simek and Cooper, 2002; Čuhel et al., 2010). Low pH possibly impedes the synthesis of a functional N₂O reductase enzyme (Bakken et al., 2012). Some authors suggest that the elevated soil pH is responsible for reduced N₂O emissions following biochar application through increased activity of N₂O reducing bacteria (Van Zwieten et al., 2010; Zheng et al., 2012). In contrast, Yanai et al. (2007) argue that the suppression of N₂O emissions by biochar is not through increased N₂O reduction activity because biochar ash also increases soil pH but does not reduce N₂O emissions. Cayuela et al. (2013) showed that biochar's acid buffer capacity was a more important factor in denitrification than the pH shift in soil. There are indications that biochar enhances nosZ expression, the gene responsible for the transcription of the N₂O reductase in denitrifying microorganisms (Harter et al., 2014; Van Zwieten et al., 2014). This could be a mechanistic link to the observed reduction in N₂O emissions through biochar increasing soil pH and microbial activity. In contrast, under conditions favouring nitrification and not being as sensitive to pH as total denitrification, biochar addition increased N₂O emissions in the lab (Sánchez-García et al., 2014) and possibly in the field (Verhoeven and Six, 2014).

In this study, we test (i) whether N₂O emissions are reduced following the application of biochar to soil of a temperate maize cropping system and (ii) whether this possible reduction in N₂O emissions is similar when soil pH is increased by other means. The latter was tested by a treatment where limestone was added to increase soil pH to the same level as that from the addition of 20 t ha⁻¹ biochar. N₂O emissions and maize yield were quantified during one growing season in the field.

2 Method

2.1 Field site

The experiment was established on a cropland field near the Agroscope research station in Zurich, Switzerland (47.427° N, 8.522° E, 437 m a.s.l.). The climate is temperate with a mean annual air temperature of 9.4 °C and mean annual rainfall of 1054 mm (Climate data 1981–2010, Meteoswiss, 2013 from the MeteoSwiss station Zurich Affoltern 500 m from the experimental site). The field was under conventional management with maize in 2013, the year prior to the experiment.

The soil is a clay loam with a particle size distribution of 37 % sand, 27 % silt and 36 % clay. The soil is a Eutric Mollic Gleysol (Drainic) (IUSS Working Group WRB, 2014). The untreated soil has a pH of 6.3 in water (1 : 2.5 *w/v*), total organic carbon content of 26.2 g kg⁻¹, total N of 2.9 g kg⁻¹ and bulk density of 1.3 g cm⁻³.

2.2 Biochar

Several biochars were screened in advance to pick one with a high liming capacity and with properties in agreement to the guidelines for contents of polycyclic aromatic hydrocarbons (PAHs), C and N of the European Biochar Certificate (EBC, 2012). The chosen biochar was produced in a Pyreg reactor (Pyreg GmbH, Dörth, Germany) by Verora in Edlibach ZG, Switzerland in late 2013 (see chapter 30, case study 2 in Lehmann and Joseph, 2015). Pyreg reactors use slow pyrolysis in a continuous system with an average residence time of circa 25 min and a peak temperature of approximately 650 °C. The feedstock was green waste mainly from tree pruning. The biochar has the following properties: 64.9 % total C; 62.1 % C_{org}, pH 9.8 (1 : 10 in water); liming capacity 17.2 % CaCO₃, 148 m² g⁻¹ BET surface area and ash content 20 %. Elemental ratios are 0.11 O / C and 0.33 H / C molar and 94 C / N by mass. Moisture content at the time of application was 12 %. Biochar was sieved < 3 mm shortly before it was spread on the field.

2.3 Experimental setup

Three different treatments were introduced; 20 t ha⁻¹ biochar, control without additions and a limestone treatment to increase the soil pH to the same level as with biochar. The field was split into 3 × 3 plots with a size of 2 by 3 m (6 m² per plot and 3 replicates for each treatment). One meter buffer zones were established between plots on all sides. The 3 different treatments were arranged in a randomized complete block design with the 3 × 3 grid accounting for spatial variability. The whole field, including the buffer zones, were planted with maize (*zea mays*). Initial pH values were not different among treatment plots (see pH measurement from January 2014 in Fig. 2).

2.4 Field management

The field was ploughed in autumn 2013 after the maize harvest. In January 2014, 20 t ha⁻¹ biochar and 2 t ha⁻¹ limestone, respectively, were spread on the wet, ploughed field surface. Freshly applied biochar was gently mixed with the first 1–3 cm of soil by hand at the same time. In mid-February 2014, the automated GHG chamber system was installed and in March the field was harrowed by a rototiller to a depth of circa 15 cm. The chamber frames were reset into the soil again and Decagon TE5 temperature and humidity sensors (Decagon Devices Inc., Pullman, WA, USA) were placed at a depth of 8 cm in the centre of each plot. The TE5 sensor measures the volumetric water content in soil by time domain reflectometry (TDR) at 70 MHz.

In May, potassium (K) and phosphorus (P) fertiliser was applied at a rate of 41.4 kg P ha⁻¹ and 132 kg K ha⁻¹. Nitrogen was applied in 3 portions of 40, 80 and 40 kg N ha⁻¹ on the 26 May, 16 June and 16 July, respectively, as ammonium nitrate (LONZA-Ammonsalpeter 27.5 % N). At each event fertiliser was spread on each plot of 6 m² and chamber frame of 0.03 m² separately to ensure equal distribution. On the 5 May, two of the three lime replicates were treated with another 1 t ha⁻¹ of limestone because the pH was not in the same range as the biochar plots. Maize (Padrino from KWS SAAT AG, Einbeck, Germany) was sown on the 8 May with 0.14 m distance within rows that were 0.6 m apart from each

other. For plant protection only one herbicide application was conducted on the 19 June with 1 L ha⁻¹ Dasul (Syngenta, Basel, Switzerland), 1 L ha⁻¹ Mikado (Bayer CropScience, Germany) and 1 kg ha⁻¹ Andil (Omya AG, Switzerland). Despite manual weeding and herbicides a considerable amount of weeds emerged. Plots were harvested on the 13 October.

2.5 Nitrous oxide measurement

N₂O and CO₂ emissions were measured with static chambers of a fully automated measurement system (Flechard et al., 2005; Felber et al., 2013) consisting of nine stainless steel chambers (30 × 30 × 25 cm). These chambers were placed on PVC frames inserted 3 cm deep into soil. The frame positions were moved three times during the growing season to obtain a better spatial representation of each plot. After maize had been sown, the chamber positions were between rows and no vegetation was grown within the chamber frame. Each of the 9 chamber lids were automatically closed and opened sequentially (over a period of 3.6 h) allowing N₂O and CO₂ to accumulate in the chamber headspace for 15 min. Chamber headspace air was circulated (1 L min⁻¹ air flow) through an inlet and outlet line from each chamber through polyamide tubes (4 mm I.D.) to the analytical system and back to the chamber headspace after sample analysis. The analytical and chamber control instruments were installed in a nearby field cabin under temperature controlled air conditioning. N₂O concentrations were continuously measured and stored every minute using a gas filter correlation analyser (TEI Model 46c, Thermo Fisher Scientific, Waltham, MA, USA). The gas stream is exposed to infrared light from specific bands (filtered), both from N₂O absorbing and non absorbing bands. From this difference a gas specific and concentration sensitive signal is retrieved. The instruments linearity is described with ± 2% with negligible interference of H₂O, CO₂ or CO. CO₂ was measured with an infrared sensor from Liston Scientific Corp. (Irvine, CA, USA). The system was calibrated every 11 h with three different concentrations from certified gas standards (Carbagas, Rümlang, Switzerland). The N₂O analyser showed a drift with room temperature variations that the air conditioning could not avoid completely. Hence a temperature correction factor was applied to the raw data from a regression of the device temperature with data during calibrations in May. The temperature

correction factor used was about 9.1 ppm per °C temperature change from the 37 °C device reference temperature. The mean N₂O analyser device temperature in June–July was 37.4 ± 2 °C (± 1 sd).

N₂O and CO₂ fluxes from soil were calculated from the continuous concentration measurement (resolution 1 per min) when chamber lids were closed. Data from the first 3 min of the total 15 min closure time were omitted from the flux calculation to remove signal noise due to gas exchange from the system during chamber switching and closing (Felber et al., 2013). The same flux estimation procedure (R-script by R. Fuss on bitbucket.org, see Fuss, 2015) was used as in Leiber-Sauheitl et al. (2014). It is a modification of the HMR package (Pedersen et al., 2010) that chooses between exponential curvature for non-linear chamber behaviour (Hutchinson-Mosier regression) and robust linear regression (Huber and Ronchetti, 1981). The exponential HMR scheme considers non-linear concentration increase in the chamber due to a possibly decreasing concentration gradient, chamber leakage and lateral gas transport. Robust linear regressions provide a more reliable flux estimate for low fluxes when there is a lot of variation due to limited measurement precision and outliers. Following the flux script's recommendation, non-linear HMR was used for 1034 fluxes, whereas for all the other 13 034 fluxes the robust linear regression was chosen. The resulting flux estimates from this procedure were then filtered for implausible large N₂O uptake by soil (i.e. when the ambient N₂O concentration suddenly drops with increased mixing in the boundary layer). N₂O fluxes smaller than -10 ng N₂O m⁻² s⁻¹ (Neftel et al., 2010) were removed as well as data associated with a likely invalid chamber functioning (i.e. frozen lids) indicated by CO₂ fluxes < -0.5 μmol m⁻² s⁻¹ (Felber et al., 2013). From the entire dataset of 14 068 fluxes, 302 were rejected due to the CO₂ flux threshold and additional 49 fluxes due to N₂O (2.5 % of the total number of fluxes removed). Considering a cumulative sum of all fluxes in the dataset, filtering reduced this number by 0.61 %.

2.6 Yield

The harvest (above-ground biomass) was separated into grain yield (kernels) and by-product (stems, leaves). Cobs were threshed and dried whereas the by-product was weighed freshly

on the field, chaffed and a sub-sample was then dried to measure water content and for further plant nutrient analysis. From both grains and by-product, dry matter total N, P, K, Ca and Mg content were measured (FAL, 1996). For yield based N_2O emissions, cumulative N_2O emissions in $kg N_2O-N ha^{-1}$ were related to total above-ground biomass dry matter (DM) yield in $t ha^{-1}$ (see Table 3) and to total above-ground N uptake in $kg N ha^{-1}$ (see discussion).

2.7 Soil sampling and analysis

Soil samples for pH, ammonium (NH_4^+) and nitrate (NO_3^-) measurements were taken on the 31 January, 31 March, 26 May, 16 June and 4 September 2014. At each sampling, five randomly distributed soil cores per plot were taken (0–10 cm) and pooled. Soil pH was determined in moist soil samples using water at a ratio of 1 : 2.5 w/v and measured with a PH100 ExStik pH meter (Extech Instruments Corp., Nashua, NH, USA). Soil bulk density was measured on the 27 June at a depth of 3–8 cm using $100 cm^3$ steel cores, 3 per plot.

For soil NO_3^- and NH_4^+ concentrations, 20 g of moist soil were mixed with 100 mL 0.01 M $CaCl_2$ solution. The suspension was shaken for 30 min, filtered and then analysed by segmented flow injection analysis on a SKALAR SANplus analyser (Skalar Analytical B.V., Breda, Netherlands).

2.8 Statistical analysis

The obtained fluxes from the automated chamber system were aggregated to 6 h means producing a regular, smoothed dataset. The system was able to measure each chamber three times for every 11 h calibration cycle during regular operations, hence on average 1.6 measurements for each chamber were included in each a 6 h mean. Still missing values after this aggregation step were linearly interpolated for each chamber. Treatment averages and standard errors were calculated from the 3 chambers on the replicated plots. If not indicated otherwise, treatment means are shown with ± 1 standard error.

Statistical analyses were performed with R (version 3.0.1, The R Project, 2014). Significance level was chosen at $p < 0.05$ for all procedures, unless indicated otherwise. Significant treatment effects for cumulated fluxes were determined using ANOVA from rbase package (treatments: control, biochar and lime; $n = 3$). Bartlett test of homogeneity of variances showed conflicting ANOVA assumptions for the cumulative fluxes. This could be improved by log transformation of the flux data.

3 Results

3.1 Environmental field conditions

The year started with above average temperatures and low rainfall (Fig. 1). End of May to June was dry with high temperatures being on average for Switzerland 1.5°C above the 1981–2010 norm (Meteoswiss, 2015). The soil's volumetric water content fell to circa 20%, inducing high water stress on the young maize seedlings. The lack of soil moisture presumably hampered the dilution of the first application of 40 kg N ha^{-1} in the soil solution. Along with the 2nd N fertilisation the field was therefore irrigated with 33 mm water (shown as green bar in Fig. 1). The summer months July and August were rather cold and wet with daily mean air temperatures below 20°C (Meteoswiss, 2015).

Soil volumetric water content tended to be higher in biochar plots (Fig. 1) with 37 out of 423 (8.7%) half-daily means showing a statistically significant treatment effect.

3.2 Soil pH and nitrogen

Soil pH increased with limestone and biochar addition by circa 0.4 pH units (Fig. 2). During the time with major emissions in June, the pH between control and biochar/lime soils significantly ($p < 0.001$) increased from 6.1 to 6.5 with. The initial soil pH was on average 6.3 and not different among treatments. Following biochar application soil pH increased to up to 7.4 whereas with addition of limestone soil pH increased to up to 6.9 (averages across replicates). The pH sharply decreased after the initial peak, especially in those two liming

plots, which were treated subsequently with another 1 t ha^{-1} in May. Soil pH of biochar and lime treatments were not significantly different at any sampling time, whereas soil pH of the control treatment was systematically below that of the amended soils.

Mean soil bulk density was not statistically different between treatments ($1.31 \pm 0.03 \text{ g cm}^{-3}$ in the control, $1.29 \pm 0.07 \text{ g cm}^{-3}$ in biochar and $1.36 \pm 0.04 \text{ g cm}^{-3}$ in the liming treatment).

Soil mineral N was not statistically different between treatments at any sampling date (Tables 1 and 2).

3.3 N₂O fluxes

Emissions were characterized by peak events, particularly in summer, and by background emissions in spring and autumn (Fig. 3). Main emissions occurred after the second fertilisation event with the highest application rate around early August. Afterwards, there were only emissions from one of the lime plots but almost none until the end of October from all the other plots. This also corresponds to the low amounts of available soil N, indicating that the plants had taken up most of it. All treatments revealed similar temporal N₂O emission dynamics but the height of the peaks differed. During peak events emissions from the biochar treatment were often lower than those from the other treatments, especially compared to the control. This resulted in an increasing difference in cumulative fluxes (Fig. 4) between control and biochar. Mean cumulative emissions for the entire growing season were 170 ± 16.5 , 353 ± 31.7 and $359 \pm 164 \text{ mg N}_2\text{O-N m}^{-2}$ for biochar, control and lime treatments, respectively (see Table 3 for plotwise results). Relative to the control, mean cumulative N₂O emissions were 52 % smaller in the biochar treatment. The whole treatment effect was, however, not statistically significant ($p = 0.26$) due to the large variability in the dataset. Emission means from control and lime were very similar. With lime, N₂O emissions were highly variable and this treatment included both the chamber with the highest and also the one with the lowest cumulative emission. Alternatively, we also calculated p -values comparing only biochar and control treatments with a Welch Two-Sample t test. This resulted in a significant difference ($p = 0.022$). All p -values have to be treated with caution because

they were produced with a minimal number of replicates. Furthermore a large treatment effect size is not reflected in the p value.

N_2O emissions per unit N applied calculated from the 160 kg N ha^{-1} with the mean cumulative emissions during the growing season, resulted in 1.06 % for biochar, 2.21 % for control and 2.25 % for the lime treatment. In analogy to cumulated emissions these values were not significantly different among treatments and have the same variance and p -values.

3.4 Maize yields and plant growth

Maize yields were not significantly different between treatments, for both grains (product) and by-product (i.e. stems, leaves) (Fig. 5). Nitrogen uptake by maize did not differ among treatments (Fig. 6, Table 3). Table 3 shows cumulated N_2O emissions for each plot and per area as well as per DM yield. Yield based emissions (Table 3) resulted in $0.128 \pm 0.010 \text{ kg N}_2\text{O-N per t-DM}$, for biochar, $0.319 \pm 0.036 \text{ kg N}_2\text{O-N per t-DM}$ for control and $0.306 \pm 0.148 \text{ kg N}_2\text{O-N per t-DM}$ for the liming treatment. Although the yield based emission with biochar is 60 % lower compared to the control, overall there is no significant treatment effect ($p = 0.19$). There was no difference between treatments for any of the measured nutrients in the yield (data not shown).

4 Discussion

4.1 N_2O emissions

Our high-frequency automated N_2O chamber measurements give a detailed picture of the emissions from a biochar and lime field trial. Neither soil NO_3^- nor NH_4^+ concentrations can explain N_2O emission patterns at any point in time. Although cumulative N_2O emissions were not significantly different among the three treatments, emissions with added biochar were 52 % below the control treatment. The magnitude of reduction is in agreement with the meta-analysis of Cayuela et al. (2015) who showed a general reduction of N_2O emissions by biochar of $49 \pm 5 \%$ (lab and field experiments) but it is larger than the reduction found

by the same authors under field conditions ($28 \pm 16\%$). In our maize field in the temperate zone, N_2O emissions can thus decrease with biochar addition as much as they have been shown to be reduced under controlled lab conditions.

Our results show no decrease in N_2O emissions when limestone is used to increase the soil pH to the same level as that with biochar. This finding does not support the hypothesis that biochar's N_2O reduction effect is similar to a geochemical adjustment of soil pH. However, it must be considered that the large variability among the three replicates hampers the power of this conclusion. A post-hoc power analysis showed a 23.4% probability of accepting a true alternative hypothesis considering the obtained results in cumulative N_2O emission. To have at least a power of 80% we would have needed 10 replicates for each treatment. The high variability solely in the liming treatment might be due to additional lime application to the field in May 2014 and the high spatial-temporal variability of that soil property in general. The two replicates that received additional limestone were the ones that emitted more N_2O than the other plot. Hence, instead of reducing emissions by increasing the pH, the additional limestone application could have provoked local arbitrary disturbance to soil chemistry leading to emission hotspots. To determine the biochar effect on N_2O emissions, we therefore also compared only the biochar and control treatments (see results); according to the analysis of that reduced dataset, the cumulative emissions in the biochar amended plots were significantly lower (by 52%) than in the control treatment.

Using the same measurement technique, application rate and similar biochar properties Felber et al. (2013) also reported N_2O emission reductions, but smaller as compared to the difference we saw between biochar and control. In line with our results other field studies have shown significant reductions in N_2O emissions following biochar amendment (Taghizadeh-Toosi et al., 2011; Liu et al., 2012). A number of studies found no significant effect of biochar addition in the field (Schimmelpfennig et al., 2014; Angst et al., 2014; Scheer et al., 2011; Karhu et al., 2011; Anderson et al., 2014). Often the much higher variability in the field and the low number of replications make it difficult to reproduce reduction effects observed in laboratory studies. In particular, Angst et al. (2014) found no significant difference but there was a tendency for lower emissions with biochar addition, suggesting

that the variability in the field was too high to get significant effects. However there are also studies that showed increased emissions from biochar application in the field (Verhoeven and Six, 2014; Shen et al., 2014). There is a large variability of biochar properties and effect size between these field studies. Since the driving mechanism of how biochar reduces N₂O emissions from soil are still unknown, it can only be shown by meta-analysis that a low H : C_{org} ratio seems to be beneficial for N₂O suppression (Cayuela et al., 2015).

Biochar has been shown to increase water-holding capacity and reduce bulk density (Peake et al., 2014). Mukherjee et al. (2014) showed that 92 % decrease in N₂O emissions by biochar coincided with reduced bulk density by 13 % and increased soil nanopore surface area by 12 % relative to the control. In our experiment there are some situations where increased volumetric water content with biochar coincide with reduced N₂O emissions (Fig. 1 and 2). Although there was no significant difference in bulk density, supposed increase in nanopore surface provides both suitable pores for water retention and oxygen air. Overall the improved soil aeration by biochar dominates the effect of increased water content and hence does not favour denitrification (Van Zwieten et al., 2010).

Sánchez-García et al. (2014) found that biochar increases soil N₂O emissions produced by nitrification-mediated pathways. In our study, the water content (Fig. 1) was high during periods of high emissions, suggesting that during periods of high water content denitrification dominates the N₂O production in soil. The high emissions were thus often triggered by large precipitation events. There are many indications from lab experiments that biochar can reduce N₂O emissions in denitrifying conditions at high water content (Yanai et al., 2007; Singh et al., 2010; Felber et al., 2013; Harter et al., 2014). Under denitrification conditions, the pH between 6 and 8 exerts control over the N₂O : N₂ ratio (Stevens et al., 1998), especially with a pH of the soil below 7, when the reduction of N₂O to N₂ is inhibited by acid conditions (Simek and Cooper, 2002). Various studies have suggested that an elevated soil pH is responsible for reduced N₂O emissions following biochar application through increased activity of N₂O reducing bacteria (Van Zwieten et al., 2010; Zheng et al., 2012). In contrast, Yanai et al. (2007) argued that the suppression of N₂O emissions by charcoal is not due to increased N₂O reduction activity with increased soil pH because biochar ash

increased the pH to the same degree as biochar, but did not reduce N₂O emissions. In the lab, Cayuela et al. (2013) found no N₂O mitigation when soil pH was increased to the same level as biochar did but with CaCO₃ addition. They also showed that biochar's buffer capacity but not biochar pH was highly correlated with lower N₂O emissions compared to pH-adjusted biochars (Cayuela et al., 2013). In our case, we used a biochar with rather high liming capacity (17.2% CaCO₃) and pH (9.8). We can confirm that with this kind of biochar N₂O emissions can effectively be reduced also in real field conditions, although the high variability in the limed treatments does not allow us to reject the hypothesis of soil pH being the major driver of N₂O emission reductions.

More recent studies show that biochar enhances nosZ abundance in soil bacteria, which can lead to lower N₂O emissions (Harter et al., 2014; Van Zwieten et al., 2014). Some authors relate this enhancement of N₂O reducing bacteria to biochar's redox activity that facilitates electron shuttling for the sensitive process of N₂O reduction (Kappler et al., 2014; Cayuela et al., 2013). This shuttling might be the connection between reduced N₂O emissions and low H : C_{org} ratios (Cayuela et al., 2015) in biochar that refers to condensed aromatic structures and its quinone/hydroquinone moieties being electro-active by allowing electron transfer across conjugated pi-electron systems (Klöpffel et al., 2014). Such high electro-catalytic activity has also been shown in N-doped C nanotube arrays (Gong et al., 2009). Hence, in contrast to a promotion of microbial N₂O reduction, there is also the possibility that biochar abiotically reduces N₂O through its electrocatalytic abilities represented by a high aromaticity with low H : C_{org} ratios. Indeed, this is one of the various abiotic mechanisms that reduce N₂O emissions suggested by Van Zwieten et al. (2015).

4.2 Yield and nutrients

In our experiment, grain and by-product biomass production were not increased by biochar application to soil. There is large uncertainty around the yield effect of biochar but meta-analyses reported an average increase of 10 % (Jeffery et al., 2011; Liu et al., 2013). Crane-Droesch et al. (2013) described a more detailed global response of biochar on yields. They identified a substantial and specific agroecological niche for biochar in soils with low organic

C content and low cation exchange capacity, typical for highly-weathered tropical or sandy soils. Given these findings, we would not expect a large increase in productivity at our site which is rich in soil C and clay. Positive yield response could however increase with time (Crane-Droesch et al., 2013) and might not show clear effects within the first year of the biochar application yet. Our data is also in agreement with Jay et al. (2015) who showed that biochar had no effect on the yield of different crops after a single rotational application (20 and 50 t ha⁻¹) in a sandy loam under intensive management.

Nitrogen uptake was not changed by biochar or liming. Although there was no significant difference in P uptake between the treatments, by-product material from biochar-treated plots tended to have higher P uptake than the control (+100 % increase, data not shown). Vanek and Lehmann (2014) showed significant increase in P availability through enhanced interactions between biochar and arbuscular mycorrhizas.

Liu et al. (2012) reported a biochar application rate dependent decrease in emission intensity per yield, from 0.17 kg N₂O-N t⁻¹ in the control to 0.10 and 0.07 kg N₂O-N t⁻¹ with 20 and 40 t ha⁻¹ biochar applied. For an agronomic assessment of N₂O emissions it is most relevant to relate the cumulative emissions to the yield (Van Groenigen et al., 2010). Emissions of the control per above-ground N uptake (29.6 kg N₂O-N (kg N)⁻¹) are much higher than the reported mean of 8.4 kg N₂O-N (kg N)⁻¹ at fertilisation rates between 180 and 190 kg N ha⁻¹ (Van Groenigen et al., 2010). With biochar however, this number decreases by 60 %, whereas with lime it remains at the level of the control ($p = 0.21$). Yield based emissions are a good way to express biochars effects both on N₂O emissions and yield, but the experimental uncertainties of each dataset are also cumulated within this number.

5 Conclusions

We found a 52 % reduction in N₂O soil emissions from biochar compared to control treatment in a maize field trial. This shows that also in temperate, intensive maize cropping systems under real field conditions, N₂O emissions can be reduced substantially by biochar.

There is no evidence that the reduction with biochar, relative to control, is solely induced by a higher soil pH. The pH hypothesis is thus not supported by our data.

Acknowledgements. We would like to thank Markus Jocher for support with the chamber measurement technique, Martin Zuber and Rob!n Giger for chemical analysis in the laboratory, Sarah Grimm (ETHZ) for statistical consulting as well as Philipp Walter and Fritz Käser for agricultural field support.

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Table 1. Nitrate content ($\text{mg NO}_3^- \text{-N kg}^{-1}$) in soil during the experiment. Standard error is indicated in brackets.

date	biochar	control	lime
2014-01-31	2.77 (0.41)	2.92 (0.13)	3.12 (0.25)
2014-03-31	6.26 (0.98)	8.57 (0.77)	8.40 (0.76)
2014-05-26	3.13 (0.36)	7.54 (1.18)	5.86 (1.45)
2014-06-16	9.19 (1.66)	9.38 (3.69)	11.65 (1.24)
2014-09-04	1.30 (0.15)	1.09 (0.21)	1.33 (0.26)

Table 2. Ammonium content ($\text{mg NH}_4^+\text{-N kg}^{-1}$) in soil during the experiment. Standard error is indicated in brackets.

date	biochar	control	lime
2014-01-31	1.11 (0.07)	1.00 (0.12)	0.68 (0.05)
2014-03-31	0.42 (0.24)	0.36 (0.21)	0.25 (0.21)
2014-05-26	0.11 (0.08)	0.12 (0.07)	0.47 (0.40)
2014-06-16	0.45 (0.13)	2.48 (1.80)	1.67 (0.36)
2014-09-04	0.38 (0.33)	0.39 (0.14)	0.16 (0.06)

Table 3. Cumulated N₂O emission per area, above-ground dry matter yield and above-ground plant N uptake for each plot (grains, stems and leaves).

treatment	block	N ₂ O per area [kg N ₂ O-N/ha]	N ₂ O per dry matter yield [kg N ₂ O-N/t-DM]	above-ground plant N uptake [kg-N/ha]
biochar	1	1.63	0.112	162
biochar	2	1.99	0.145	142
biochar	3	1.48	0.126	123
control	1	3.06	0.255	143
control	2	3.39	0.325	109
control	3	4.26	0.378	118
lime	1	6.76	0.591	121
lime	2	1.24	0.097	135
lime	3	2.80	0.230	131

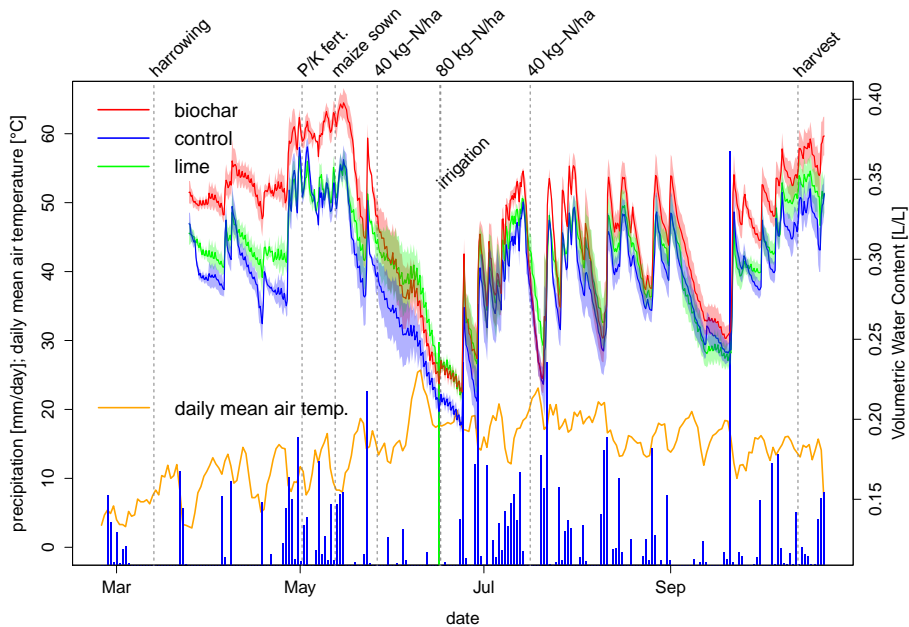


Figure 1. Soil moisture means for each treatment are shown in red, blue and green solid lines with 1 s.e. as shaded area. Blue bars show the rainfall in mm d^{-1} and the orange line is daily mean air temperature. The green bar indicates the irrigation of 33 mm with the second N fertilisation.

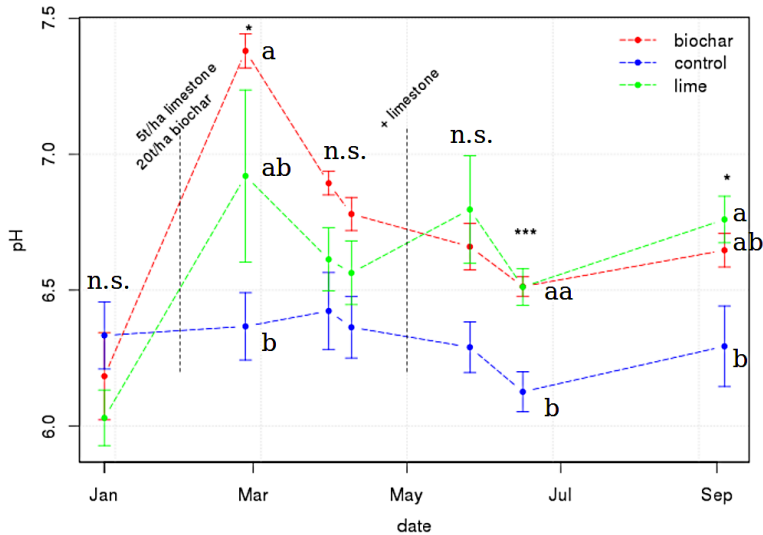


Figure 2. Soil pH (mean with 1 s.e. bars) during the time of the experiment. Significant differences ($p < 0.05$) are indicated with stars according ANOVA test and Tukey Honest Significant Differences (TukeyHSD) are indicated by different letters, n.s. = not significant.

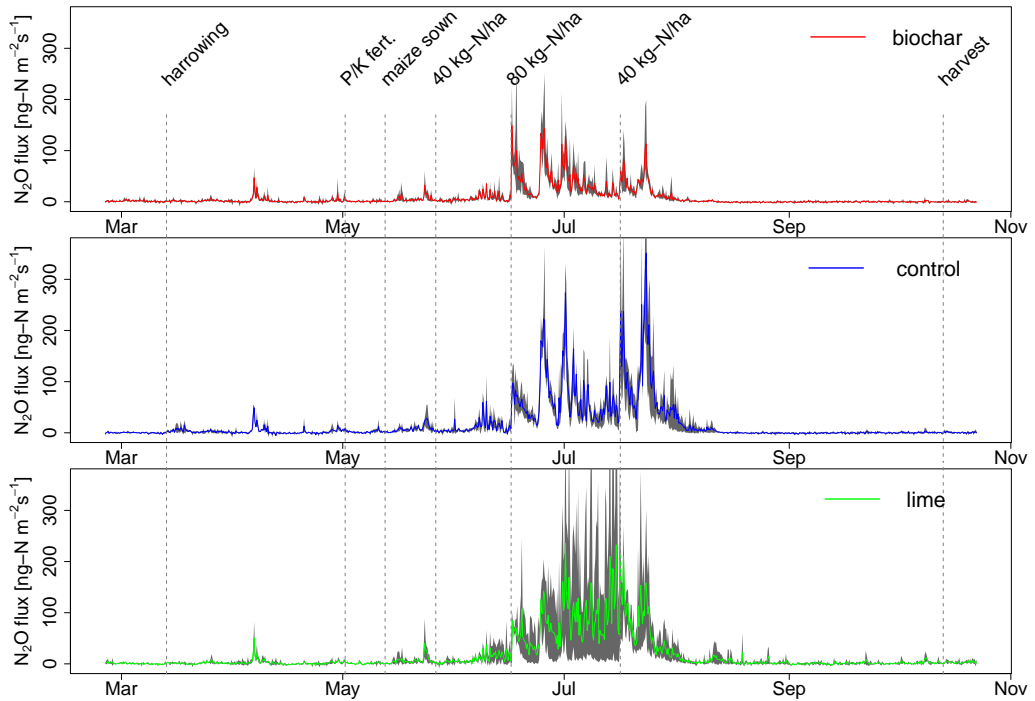


Figure 3. Mean N_2O emissions for each treatment (coloured line) with highest and lowest replicate in grey.

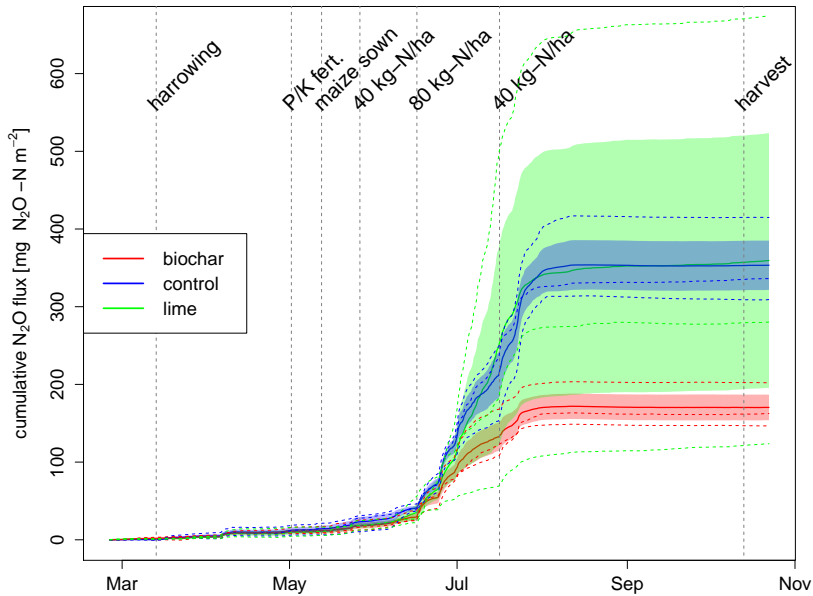


Figure 4. Mean cumulative N₂O fluxes as solid lines. Shaded areas represent the standard error of the mean from the 3 replicates (dashed lines) per treatment.

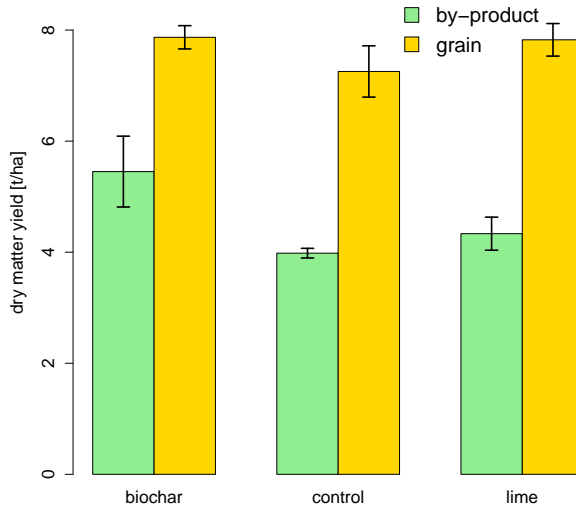


Figure 5. Grain yield and by-product biomass production (dry matter yield). Error bars show one standard error ($n = 3$).

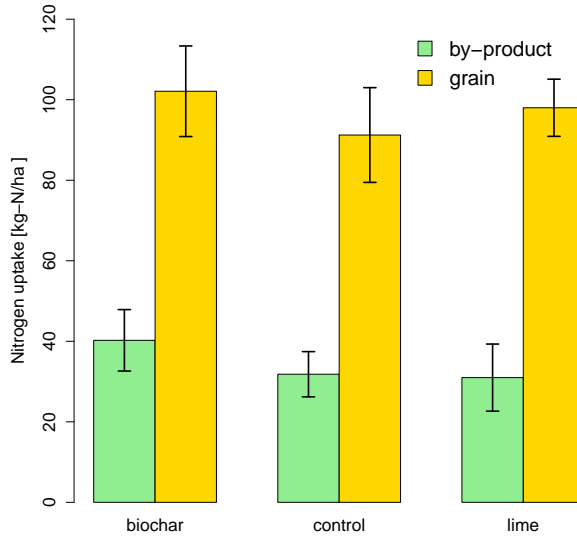


Figure 6. N uptake by grains and by-product (stem, leaves). Error bars show one standard error ($n = 3$).