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Biochar's effect on soil nitrous oxide emissions from a maize field with lime-adjusted pH treatment

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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 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, and a control treatment without any addition. 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}.

Cumulative N_2O emissions were 53 % smaller in the biochar compared to the control treatment. However, the effect of the treatments overall was not statistically significant ($p = 0.26$) because of the large variability in the dataset. Limed soils emitted similar mean cumulative amounts of N_2O as the control. This indicates that the observed N_2O reduction effect of biochar was not caused by a pH effect.

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 CO_2, nitrous oxide (N_2O) from soil is a downside of the large productivity increase in agriculture, due to synthetic nitrogen fertiliser application. Reducing agricultural N_2O 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).

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 nitrous oxide (N_2O) emissions from soil are reduced on average by 54 % in lab studies and 28 % in field measurements (Cayuela et al., 2015). In field situations, N_2O 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 N_2O (e.g., Verhoeven and Six, 2014; Liu et al., 2014), many showed no significant effects (Angst et al., 2014; Karhu et al., 2011; Scheer et al., 2011; Suddick and Six, 2013; Anderson et al., 2014) while other studies indicated decreasing N_2O emissions (e.g., Felber et al., 2013; van Zwieten et al., 2010; Taghizadeh-Toosi et al., 2011; Zhang et al., 2010; Case et al., 2014). Only few studies with biochar have looked

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at N_2O 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 N_2O-reducing activity with increasing pH, which may reduce N_2O emissions from soils (Cavigelli and Robertson, 2001; Simek and Cooper, 2002; Čuhel et al., 2010). Some authors suggest that the elevated soil pH is responsible for reduced N_2O emissions following biochar application through increased activity of N_2O reducing bacteria (van Zwieten et al., 2010; Zheng et al., 2012). In contrast, Yanai et al. (2007) argue that the suppression of N_2O emissions by biochar is not through increased N_2O reduction activity because biochar ash also increases soil pH but does not reduce N_2O 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 N_2O reductase in denitrifying microorganisms (Harter et al., 2014; Van Zwieten et al., 2014). This could be a mechanistic link to the observed reduction in N_2O 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 N_2O 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 N_2O emissions are reduced following the application of biochar to soil of a temperate maize cropping system and (ii) whether this possible reduction in N_2O emissions is due to an increase in pH. 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. N_2O 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. According to the world reference base for soil resources (IUSS Working Group WRB, 2006) it is a Eutric Mollic Gleysol (Drainic). 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 0.29 $g\,kg^{-1}$ 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 polycyclic aromatic hydrocarbons (PAHs), C- and N-content 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 % Corg, pH 9.8 (1 : 10 in water); liming capacity 17.2 %$CaCO_3$, 148 $m^2\,g^{-1}$ 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 m^2 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 in January on 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 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.

In May, potassium (K) and phosphorus (P) fertiliser was applied at a rate of 41.4 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). The fertiliser doses were spread on each plot of 6 m^2 and chamber frame of 0.03 m^2 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

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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 13th of October.

2.5 Nitrous oxide measurement

N_2O and CO_2 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. Two frames were placed on each plot at a similar distance to the plot borders. These 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 3.5 h) allowing N_2O and CO_2 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 continuously after sample analysis. The analytical and chamber control instruments were installed in a nearby field cabin under temperature controlled air conditioning. N_2O concentrations were continuously measured and stored every minute using a gas filter correlation technique (TEI Model 46C, Thermo Environmental Instruments Inc., Sunnyvale, CA, USA). CO_2 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 N_2O analyser showed a drift with temperature variations that the air conditioning could not avoid completely.

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Hence a temperature correction factor was applied to the raw data from a regression of the device temperature with data during calibrations in May.

N_2O and CO_2 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. The resulting flux estimates from this procedure were then filtered for implausible large N_2O uptake by soil. N_2O fluxes smaller than $-50\,\text{ng-}N_2O\,m^{-2}\,s^{-1}$ (Neftel et al., 2010) were removed as well as data associated with a likely invalid chamber functioning (i.e. frozen lids) when CO_2 flux $< -0.5\,\mu mol\,m^{-2}\,s^{-1}$ (Felber et al., 2013). In total 302 CO_2 and 351 N_2O data points from the entire dataset (14 068 points) were rejected.

2.6 Yield

The yield was separated into grain (kernels) and plant material. Cobs were threshed and dried whereas the plants were weighed freshly on the field, chaffed and a subsample was then dried to measure water content and for further plant nutrient analysis. From both plant and grain, dry matter total N and P were measured (FAL, 1996).

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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, the Netherlands).

2.8 Statistical analysis

The obtained fluxes from the automated chamber system were aggregated to 8 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 2.2 measurements for each chamber were included in each a 8 h mean. Still missing values after this aggregation step were linearly interpolated for each chamber. Treatment averages and standard deviations were calculated from the 3 chambers on the replicated plots.

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 solved by log transformation of the flux data.

In addition, a generalized least squares model (GLS) was constructed with weekly cumulated N_2O emissions as dependent variable, and weekly averages of soil volumetric water content (VWC) and the treatments (control, biochar, lime) as explanatory variables. A restricted maximum likelihood generalised linear model from nlme R package was used to calculate the GLS.

3 Results

3.1 Meteorological data on the field

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 ha^{-1} N in the soil solution. Along with the 2nd N fertilisation the field was therefore irrigated with 33 mm water (shown as green bar in the precipitation dataset). The summer months following (July and August) were rather cold and wet with daily mean air temperatures below 20 °C (Meteoswiss, 2015).

The GLS model indicated a significant, treatment specific ($p = 0.0202$) effect of weekly mean soil VWC on weekly cumulated N_2O fluxes ($p = 0.0034$). Biochar plots had significantly higher soil water content than lime and control plots ($p < 0.001$). However, there is no interaction between treatment and VWC on a weekly basis ($p = 0.542$).

3.2 Soil pH and nitrogen

Soil pH increased with limestone and biochar addition in medium terms by circa 0.4 pH units (Fig. 2). 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

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decreased after the initial peak, especially in those two liming plots, which were treated 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 $g\,cm^{-3}$ in the control, 1.29 $g\,cm^{-3}$ in biochar and 1.36 $g\,cm^{-3}$ in the liming treatment).

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

3.3 N_2O 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 of 80 kg-N ha^{-1} 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 N_2O 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, 357 and 360 mg-$N_2O\,m^{-2}$ for biochar, control and lime treatments, respectively. Relative to the control, mean cumulative N_2O emissions were 53 % 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 are very similar. With lime, N_2O emissions were highly variable and this treatment included both the chamber with the highest and also the one with the lowest cumulative emission. We therefore also calculated p values for biochar and control treatments only with a Welch Two-Sample t test resulting in a significant difference with $p = 0.022$.

Emission factors calculated from the 160 kg-N ha^{-1} applied with the mean cumulative emissions during the growing season, resulted in 0.67 % for biochar, 1.42 % for control and 1.43 % for the lime treatment, but these values were not significantly different. For comparison with with IPCC emission factors, background emissions need to be subtracted. We estimated background emissions by cumulating only N_2O emissions that were directly influenced by the N-fertiliser applied (between 26 May and 13 August = approx. 3 months) and subtract half of the cumulative emissions from the residual period measured (approx. 6 months). This resulted in IPCC emission factors of 0.58 % for biochar, 1.28 % for control and 1.25 % for the lime treatment.

3.4 Maize yields and plant growth

Maize yields were not significantly different between treatments, for both grain and plant dry matter (Fig. 5). Nitrogen and P uptake did not differ among treatments (Figs. 6 and 7).

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-lime field trial. Neither soil NO_3^- nor NH_4^+ concentrations can explain N_2O emission patterns at any point in time. Estimated IPCC emission factors are at the lower end of the range of the IPCC guidelines for cropland soils of 0.3–3 % (IPCC, 2006). Although cumulative N_2O emissions were not significantly different among the three treatments, emissions with added biochar were 53 % 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 ± 5 % (lab and field experiments) but it is larger than the reduction found by the same authors under field conditions (28 ± 16 %). In our temperate maize field, N_2O emissions thus decreased with biochar addition as much as they have been shown to be reduced under controlled lab conditions.

Our results show no a 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 solely due to a geochemical manipulation of soil pH. However, it must be considered that the large variability among the three replicates hampers the power of this conclusion. 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; the cumulative emissions in the biochar amended plots are significantly lower (by 53 %) than in the control treatment.

The GLS model shows that not only treatment but also water content affects soil N_2O emissions. However, the mechanism behind the overall negative feedback of VWC on N_2O emissions (i.e. higher VWC leads to lower emissions) can not be derived from our data. Biochar effects on soil physical properties have been shown to increase water-holding capacity, reduce bulk density and increase soil sub-nanopore surface together with a 92 % decrease in N_2O emissions (Peake et al., 2014; Mukherjee et al., 2014). This suggests that increased soil aeration by biochar dominates the effect of increased water content and hence does not favour denitrification (van Zwieten et al., 2010).

Using the same measurement technique, application rate and similar biochar properties we find much higher emission reductions in cropland than Felber et al. (2013) in a grassland field. In line with our results other field studies have also shown significant reductions in N_2O emissions following biochar amendment (van Zwieten et al., 2010;

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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. However there are also studies that showed increased emissions from biochar application in the field (Verhoeven and Six, 2014; Shen et al., 2014).

Sánchez-García et al. (2014) found that biochar increases soil N_2O emissions produced by nitrification-mediated pathways. In our study, the water content (Fig. 1) was high during periods of high emissions and suggesting that during periods of high water content denitrification dominates the N_2O 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 N_2O emissions in denitrifying conditions at high water content (Felber et al., 2013; Harter et al., 2014; Singh et al., 2010; Yanai et al., 2007). Under denitrification conditions, the pH exerts control over the $N_2O:N_2$ ratio (Simek and Cooper, 2002). Various studies have suggested that an elevated soil pH is responsible for reduced N_2O emissions following biochar application through increased activity of N_2O reducing bacteria (van Zwieten et al., 2010; Zheng et al., 2012). In contrast, Yanai et al. (2007) argued that the suppression of N_2O emissions by charcoal is not due to increased N_2O reduction activity because biochar ash increased pH to the same degree as biochar but did not reduce N_2O emissions. Also Cayuela et al. (2013) found no N_2O mitigation when soil pH was increased to the same level as biochar did but with $CaCO_3$ addition. They also showed that biochar's buffer capacity but not biochar pH was highly correlated with lower N_2O emissions compared to pH-adjusted biochars (Cayuela et al., 2013). In our case, we used a biochar with rather high liming capacity (17.2 % $CaCO_3$) and pH (9.8). We can confirm that with this kind of biochar N_2O emissions can effectively be reduced also in real field conditions, although the high variability in the pH adjusted control does not allow us to reject the hypothesis of

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soil pH being the major driver of N_2O emission reductions. 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 need 10 replicates for each treatment.

More recent studies show that biochar enhances nosZ abundance in soil bacteria, which can lead to lower N_2O emissions (Harter et al., 2014; Van Zwieten et al., 2014). Some authors relate this enhancement of N_2O reducing bacteria to biochar's redox activity that facilitates electron shuttling for the sensitive process of N_2O reduction (Kappler et al., 2014; Cayuela et al., 2013). This shuttling might be the connection between reduced N_2O emissions and low H : Corg 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 (Klüpfel 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 N_2O reduction, there is also the possibility that biochar abiotically reduces N_2O through its electrocatalytic abilities represented by a high aromaticity with low H : Corg ratios. Indeed, this is one of the various abiotic mechanisms that reduce N_2O emissions suggested by Van Zwieten et al. (2015).

4.2 Yield and nutrients

In our experiment, grain yield and plant 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

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show clear effects within the first year of application yet. Our data is also in agreement with Jay et al. (2015) who showed that biochar had no effect on harvest 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, green plant material from biochar-treated plots tended to have higher uptake then the control (+100 % increase). Vanek and Lehmann (2014) showed significant increase in P availability through enhanced interactions between biochar and arbuscular mycorrhizas.

5 Conclusions

We found a 53 % reduction in N_2O soil emissions from biochar compared to control treatment. This shows that also in temperate intensive maize cropping systems under real field conditions, N_2O 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.

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Table 1. Nitrate content (mg NO_3^--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)

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Table 2. Ammonium content (mg NH_4^+-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)

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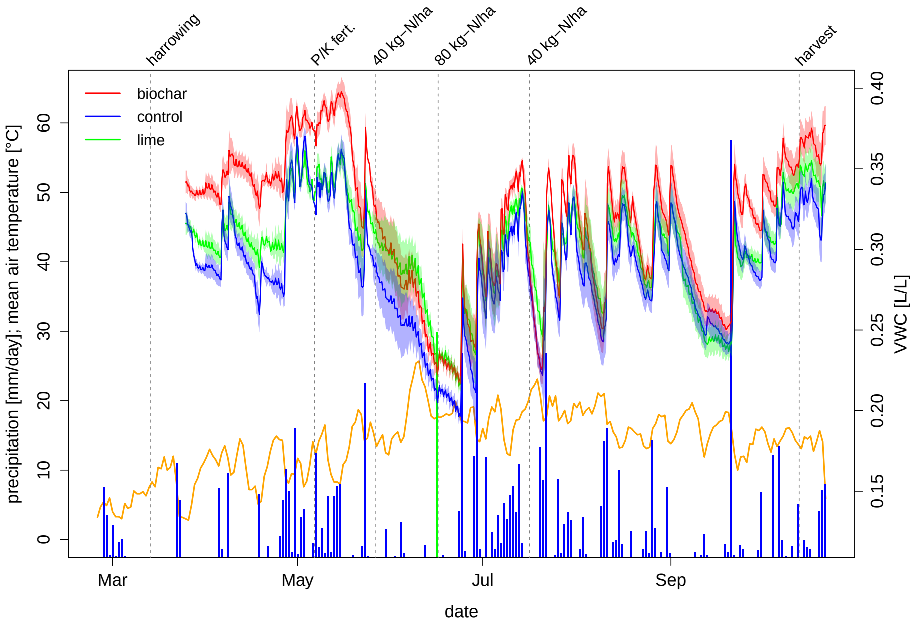

Figure 1. Soil moisture means for each treatment are shown in red, blue and green solid lines with 1 s.e. as shaded area. Blue bars show the rainfall in $mm\,d^{-1}$ and the orange line is daily mean air temperature. The green bar indicates the irrigation of 33 mm with the second N fertilisation.

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Biochar's impact on soil nitrous oxide emissions

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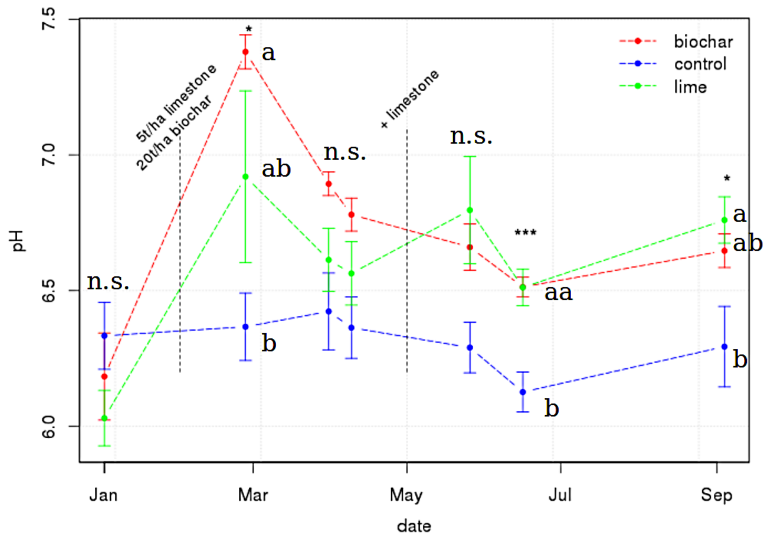

Figure 2. Soil pH (mean with 1 s.e. bars) during the time of the experiment. Significant differences ($p < 0.05$) are indicated with stars according ANOVA test and Tukey Honest Significant Differences (TukeyHSD), n.s. = not significant.

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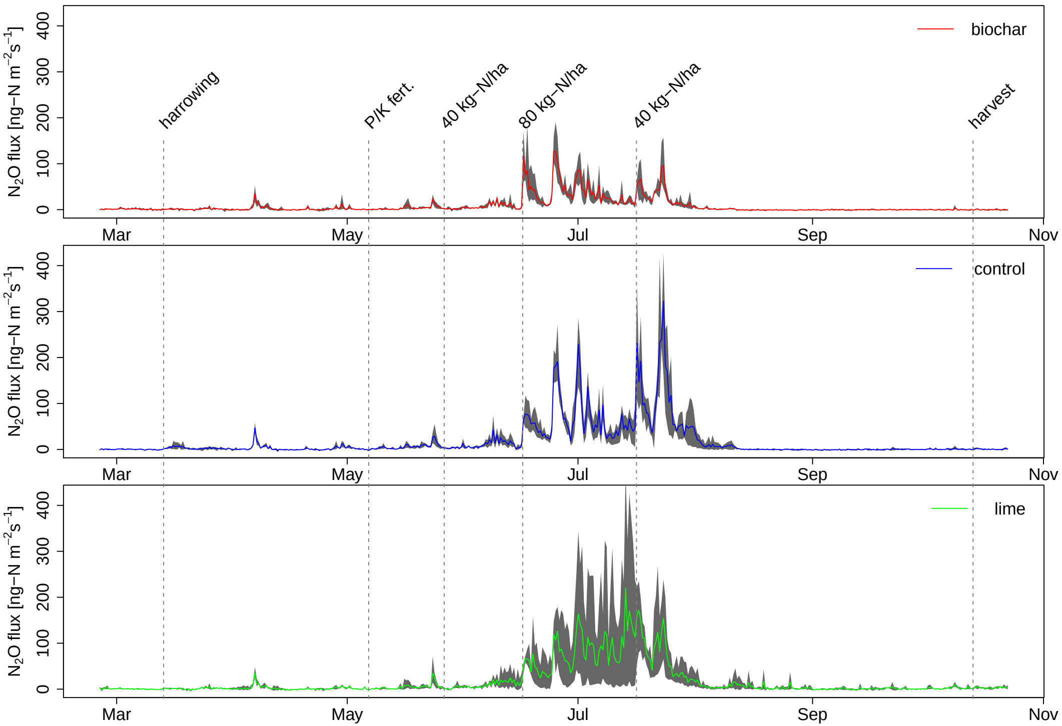

Figure 3. Mean N_2O emissions for each treatment (coloured line) with highest and lowest replicate in grey.

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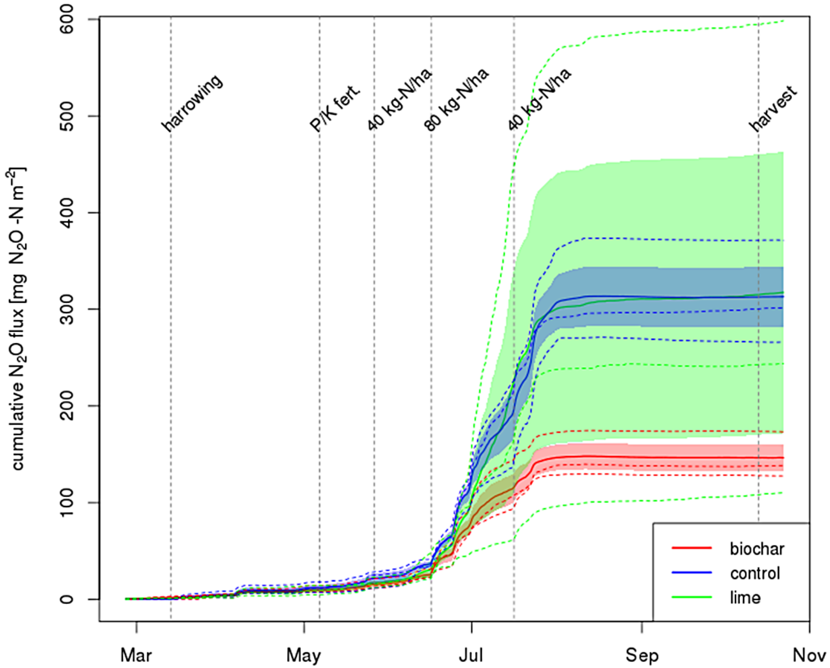

Figure 4. Mean cumulative N_2O fluxes as solid lines. Shaded areas represent the standard error of the mean from the 3 replicates (dashed lines) per treatment.

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Biochar's impact on soil nitrous oxide emissions

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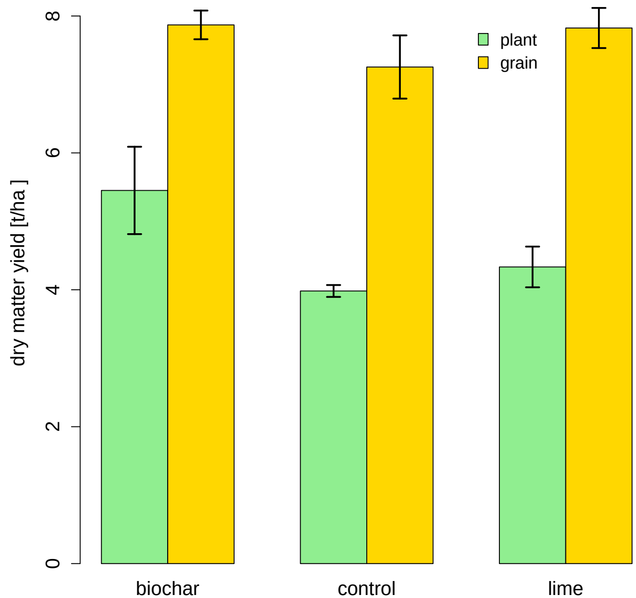

Figure 5. Yield and plant biomass production. Error bars show one standard error ($n = 3$).

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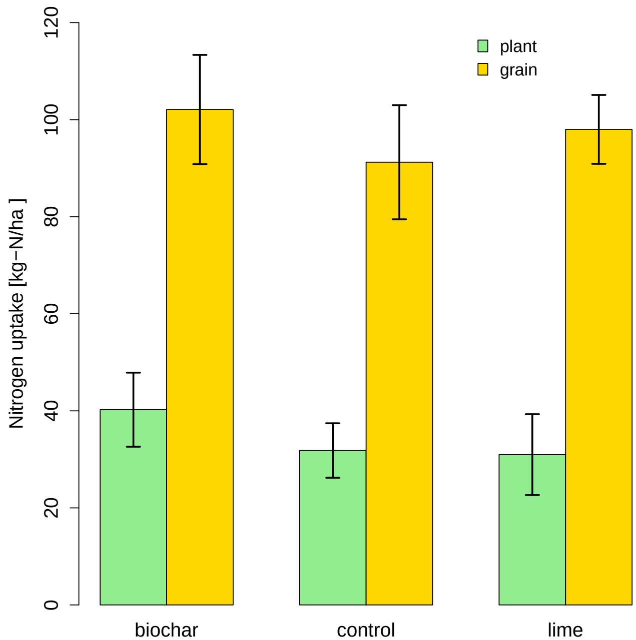

Figure 6. N uptake by plant and grain. Error bars show one standard error (n = 3).

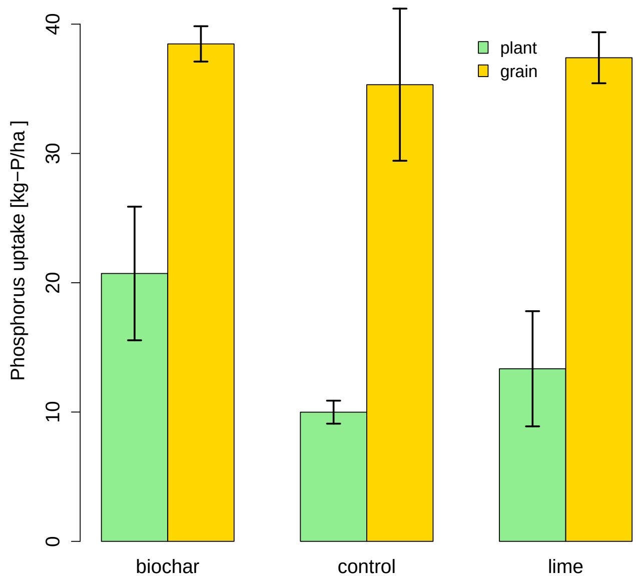

Figure 7. P uptake by plant and grain. Error bars show one standard error ($n = 3$).

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