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Biochar-induced N_2O emission reductions after field incorporation in a loam soil

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ABSTRACT

Biochar addition to soils is heralded to reduce N_2O emissions, but still, the explanatory mechanisms have not been resolved. Moreover, it is uncertain whether N_2O emission reductions would persist after prolonged biochar incorporation in the field. In this study, we incorporated four biochar types in a loam textured cropland field and intact soil cores were sampled to investigate the physical control of biochar on denitrification after 7 months. During a first incubation experiment, we measured N_2O emissions from undisturbed and disturbed (i.e. sieved (2 mm) and grounded) soil cores. Both in the disturbed and undisturbed soil cores biochar at water filled pore space (WFPS) of 80% reduced the N_2O emissions by 50–90%, refuting the hypothesis that biochar exerts an indirect physical control over soil denitrification several months after incorporation. Secondly, we hypothesized that biochar creates denitrification 'hotspots' in soil, where complete reduction of N_2O to N_2 is promoted compared to non-amended soil. In these hotspots biochar particles could act as microlocations with local anaerobic conditions and local higher pH, stimulating in this way complete denitrification. Via the acetylene inhibition method we did not observe a reduction in the $N_2O/(N_2O + N_2)$ ratio, which could suggest that biochar did not promote the reduction of N_2O to N_2. Manipulations likely to promote labile C bioavailability, here either by glucose addition or by soil particulate OM disclosure after disruption of soil aggregates, resulted in the most prominent biochar-induced N_2O emission reductions.

1. Introduction

Nitrous oxide (N_2O) is an important greenhouse gas (GHG), with a 265 times higher global warming potential than CO_2 over 100 years (IPCC 2013). N_2O emissions may be emitted as an intermediate during various microbial soil processes, such as denitrification, nitrification, nitrifier-denitrification and codenitrification (Butterbach-Bahl et al. 2013; Wrage et al. 2001). During denitrification, specialized microorganisms reduce nitrate (NO_3^-) via intermediates to N_2O and finally to N_2 (Dalal et al. 2003). Prerequisites for N_2O release during denitrification are oxygen-depleted conditions, high availability of NO_3^- and a C-source as an electron donor (Wrage et al. 2001). Denitrifier activity and N_2O emissions therefore increase relatively abruptly at moisture conditions of at least 70% water filled pore space (WFPS) (Bateman and Baggs 2005). As the enzyme N_2O reductase has a high sensitivity for O_2, in soils approaching full water saturation complete denitrification to N_2 occurs and the ratio of N_2O/N_2 approaches zero (Morley and Baggs 2010).

In recent years evidence has been accumulated that biochars of various types may reduce N_2O emissions from soils (Ameloot et al. 2013a; Case et al. 2012; Chintala et al. 2015; Kammann et al. 2012; Spokas and Reicosky 2009; Van Zwieten et al. 2009; Yanai et al. 2007). A number of mechanisms for this N_2O emission reduction have been proposed, such as the capacity of biochar to shuttle electrons (Cayuela et al. 2013; Kappler et al. 2014), increase the soil pH (Van Zwieten et al. 2009), adsorb denitrification substrates (Clough et al. 2013; LeCroy et al. 2013; Yao et al. 2012) and change the soil structure (Van Zwieten et al. 2009; Yanai et al. 2007), without a clear conclusion to date. The mechanisms investigated in this paper involving a control of biochar over N_2O emissions are twofold, viz. 1) biochar-induced improvements of soil aeration and 2) the stimulation of the last denitrificaiton step. It has been hypothesized that the increased porosity of biochar amended soil with consequent enhanced soil aeration and O_2 supply inhibits the denitrification process and suppresses soil N_2O and N_2 emissions (Van Zwieten et al. 2009; Yanai et al. 2007). Ample research has indeed demonstrated that biochar amendments to soils decrease soil bulk density (Abel et al. 2013; Case et al. 2012; Laird et al. 2010), however, no clear cause-and-effect relationship with decreased N_2O emissions in biochar amended soils has been identified yet. Secondly, biochar may act as denitrification 'hotspots' where complete denitrification to N_2 occurs through shuttling electrons, local pH increases around the biochar particles or partial anaerobic conditions in the biochar pores. It is clear that the processes influencing N_2O emissions in biochar amended soils are far from unraveled. Moreover, whether this N_2O emission reduction capacity is still active after incorporation in the field, and the mechanisms responsible for this remain unclear.

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In this study, a field experiment was set up in which four biochar types were incorporated in a loamy cropland soil. After seven months, undisturbed soil cores were taken from the field and incubated and N_2O emissions were monitored. The aim of this approach was to test two of the suggested structural mechanisms explaining the reduction in soil N_2O emission upon biochar amendment. First, we tested whether an altered soil structure resulting from biochar addition lessens anaerobic conditions in soil and therefore reduces soil N_2O emissions. We hypothesize that such emission reduction should then not occur in physically disrupted soil cores. Secondly, we quantified N_2O emissions from undisturbed soil cores with and without acetylene. We hypothesized that biochar creates denitrification 'hotspots' in soil, where complete reduction of N_2O to N_2 is promoted compared to non-amended soil. In these 'hotspots' biochar particles could act as microlocations with local anaerobic conditions and local higher pH, stimulating in this way complete denitrification.

2. Material and methods

2.1. Biochar production and characterization

The production process of the biochars used was previously described by Ameloot et al. (2013a). Briefly, biochars were produced via slow pyrolysis from two feedstocks, namely swine manure digestate (D) and willow wood (W), at two different pyrolysis temperatures, 350 °C and 700 °C. In this way four biochar types were produced: D350, D700, W350 and W700. The pH_{H2O} was determined by weighing 1 g of biochar and adding 10 ml of H_2O, the slurry was well mixed and pH was measured after 18 h with a pH electrode (Thermo Orion, 420A plus). All samples were analyzed for total C and N contents by catalytic combustion (Variomax CNS analyzer, Elementar, Germany). Potassium, Mg, P, Al, Ca, Fe, Na, B and Mn contents were determined with an ICP-OES (ICAP 6000 series, Thermo scientific) after microwave destruction (Milestone Ethos One, Milestone, Italy) with 7 ml HNO_3 (65%) and 2 ml H_2O_2. All analyses were carried out in duplicate or triplicate.

2.2. Soil sampling

A small-scale field experiment with biochar was set up in previous *Miscanthus* field in Beitem, Flanders (50°53′N, 3°6′E) on an Alfisol with a loam texture (USDA; 13.7% clay, 44.2% silt and 42.1% sand). The organic C content of the soil was 12.2 g kg^{-1} and the N content was 0.86 g kg^{-1}. On April the 23rd of 2012 the four biochars were incorporated in the soil at an application rate of 10 t ha^{-1} in small plots of 20 cm × 60 cm to a depth of 10 cm, corresponding to an addition of 120 g biochar per plot. The soil from the plots was excavated until a depth of 10 cm, and biochar was mixed with the soil on a plastic sheet after which the soil + biochar mixture was put back. The small plot sizes allowed for a very accurate and homogeneous addition of the biochar. A control plot received the same type of physical disturbance but without biochar addition. On 11 December of 2012 twelve undisturbed soil cores were collected from each plot using steel rings (diameter 5 cm, height 5 cm). Thereafter the soil cores were left to dry to the air. In addition the soil density was determined on an intact soil core from each plot. The overall density was 1.57 ± 0.04 Mg m^{-3}. All the soil within a plot was removed until a depth of 10 cm, dried to the air for several weeks and slightly grounded with a pestle and mortar to disrupt macro aggregates and sieved on a 2 mm mesh. After sampling all soils were kept in the dark at a constant temperature of 15 °C until February 2013 when the incubation experiments were set-up.

2.3. Soil incubation experiment 1

In a first incubation experiment we investigated the impact of physical disruption of the soil structure on the emissions of N_2O from biochar amended soils. For this, three of the undisturbed soil cores were used. Additionally, three disturbed soil cores were prepared from the soil removed from each plot. To this end, 154.1 g of the ground and air-dried soil was filled into steel rings (diameter 5 cm, height 5 cm) and compacted to obtain the same bulk density of 1.57 g cm^{-3} as in the field. A diluted KNO_3 solution was added to all soil cores in order to obtain a uniform nitrate concentration of 31 μg NO_3^--N g^{-1} dry soil and to bring the soil moisture level to an equivalent of 70% water filled pore space (WFPS). The soil cores were individually put into an airtight container with a volume of 1125 ml and incubated in the dark at an ambient temperature of 17.7 °C. N_2O emissions were measured twice a day for six days and after each sampling the containers were left open for 10 min to replenish oxygen. Since N_2O emissions remained generally very low after six days of incubation (see below), we increased the soil moisture content to 80% WFPS and added an external C-source, namely a dilute glucose solution at a rate of 0.5 mg glucose-C g^{-1} soil. Thereafter soil N_2O emissions were measured again twice a day for six days.

2.4. Soil incubation experiment 2

In a second incubation experiment, we investigated whether the addition of biochar to soil would enhance further reduction of N_2O to N_2, possibly by formation of anaerobic denitrification hotspots. Per treatment six undisturbed soil cores were incubated in closed containers at a moisture content of 70%WFPS, with again addition of 31 μg NO_3^--N g^{-1} dry soil and 0.5 mg glucose-C g^{-1} soil. In three containers 10 vol% acetylene was added. Acetylene inhibits the last step of denitrification, i.e. formation of N_2 from N_2O (Qin et al. 2012) and may also inhibit nitrification. After each sampling event the jars were left open and the acetylene was replenished. The total amount of N_2 emitted was estimated as the difference between the N_2O emissions with acetylene and the N_2O emissions without acetylene. N_2O emissions were measured until the concentration in the headspace of the closed containers were below the detection limit which occurred after 67 h.

2.5. Chemical analysis and gas sampling

Soil pH_{H_2O} was determined by weighing 10 g of soil and adding 50 ml of deionized H_2O, the slurry was well mixed and pH was measured after 18 h with a pH electrode (Thermo Orion, 420A plus). The mineral N content was determined by extracting 40 g of soil with 200 ml of 1 M KCl and these extracts were analyzed for NO_3^- content with a continuous flow auto-analyzer (San++, Skalar Anaytical, Breda, The Netherlands). For N_2O measurements 12 ml glass exetainers® (Labco Limited, Ceredigon, UK) were pre-evacuated three times consecutively by means of a vacuum pump and flushed with He. Finally, a vacuum of 0.04 mbar was established in the extainers. Headspace gas samples were collected from the closed containers using an air-tight syringe (venoject multi-sample needle, Terumo, Heverlee, Belgium) and stored in the pre-evacuated extainers until measurement. The N_2O concentration of the headspace gas samples was measured by manual injection into a Thermo Electron Trace GC Ultra gas chromatograph equipped with a split injector, an electron capture detector (ECD) and two capillary columns of Porabond Q (15 and 10 m) (Interscience, Breda, The Netherlands). The operating conditions were a carrier gas N_2 flow of 29.9 ml min^{-1}, an injector temperature of 200 °C and a column and oven temperature of 30 °C and detector temperature of 310 °C. Calibration curves for each treatment were obtained before each measurement by injecting 200, 400, 600, 800 and 1000 μl of the N_2O standard gas (23 ± 1.5 μl N_2O-N l^{-1} He).

2.6. Data analysis

For each repetition the cumulative N_2O-N or N_2–N emission was calculated. Significant differences ($P < 0.05$) in cumulative N_2O or N_2 emissions at the last sampling date between control treatments and biochar amended treatments were identified on the cumulative values by one-