

How do biochar characteristics influence its capacity to mitigate N₂O emissions in agricultural soils?

Cayuela Maria L.^{1,2}, Sanchez-Monedero Miguel A.¹, Roig Asunción¹ Hanley Kelly², Enders Akio², Lehmann Johannes²

(1) Department of Soil and Water Conservation and Waste Management, CEBAS-CSIC. Campus Universitario de Espinardo. 30100 Murcia. SP

(2) Department of Crop and Soil Science. Cornell University, Ithaca NY. USA

*Corresponding author: mlcayuela@cebas.csic.es; marialuz.cayuela@gmail.com

Abstract

There is an increasing interest in the use of biochar as a strategy to mitigate nitrous oxide (N₂O) emissions from soils. Some authors have reported a substantial decrease in the N₂O emitted when biochar was applied as soil amendment. However, the mechanisms involved in this process have not been identified yet, neither the characteristics that make a biochar ideal for N₂O mitigation. In this study, an incubation experiment was performed with nine biochars that were applied at 2% (w/w) to an organic soil under optimal denitrification conditions and N₂O emissions were monitored. All biochars used in this experiment decreased N₂O emissions; however, biochar properties defined the magnitude of mitigation, which ranged between 37 and 77%. Biochar pH and ash content were identified as important characteristics imprinting biochar mitigation capacity, however no correlation was found between N₂O mitigation and C/N ratio.

Introduction

The decrease of N₂O emissions after biochar soil amendment was first reported in a greenhouse experiment by Rondon et al. (2005) [1]. They observed that N₂O emissions were reduced by up to 50% for soybean and by 80% for grass growing in a low-fertility oxisol from the Colombian savanna. Since then, the interest in biochar as a N₂O mitigation strategy in agricultural soils is continuously increasing and the number of studies evaluating N₂O emissions in biochar-treated soils has exponentially risen.

Several laboratory and field experiments reported important reductions in the N₂O emitted after biochar soil application. For instance van Zwieten et al (2010) [2] found reductions up to 85% and Stewart et al (2012) up to 92% [3]. Nonetheless, an increase in N₂O emissions in soil amended with biochar has been reported as well [4, 5] and as the number of studies increases, the responses obtained become extremely variable depending on environmental conditions, soil and biochar characteristics.

Different hypotheses have been postulated to explain why biochar might decrease N₂O emitted from soils. Biochar could enhance soil aeration, increase soil pH, favour nitrogen immobilization or it could induce a toxic effect in the soil nitrifier/denitrifier microbial communities.

To date the theorized mechanisms and the importance they might have remain controversial. Similarly, the characteristics that make a biochar suitable for N₂O mitigation are unknown. Without the basic knowledge on when, how much and why biochar modifies N₂O emissions from soil, using biochar to mitigate N₂O emissions from fertilized agro-ecosystems remains a difficult challenge.

In general, most studies reported lower mitigation capacity for low-temperature (250-400 °C) biochars [2, 6] and Kammann et al. (2012) [7] warned about the risk of increased emissions with hydrochars (by-products of hydrothermal carbonization). But there are not many studies that concentrate on the specific causes of reduction. A recent work [8] demonstrated that an increase in soil aeration makes only a minimal contribution to the suppression of N₂O emissions in a sandy-loam soil, suggesting that microbial or physical immobilization of NO₃⁻ in soil following biochar addition could be more important factors for N₂O suppression.

The focus of this study was on the denitrification pathway. The aim was to identify the physico-chemical characteristics of biochars related to their capacity to mitigate N₂O emitted from a soil exposed to optimum denitrification conditions. The effect on soil porosity was counteracted by selecting a soil where addition of biochar would not modify its water retention curves at high moisture

content. Therefore, the target variables were principally pH and C/N although other characteristics as ashes, volatiles, Fe content and biochar surface were contemplated as well.

Material and Methods

Incubation experiments.

An organic soil (cultivated histosol, USDA (1999) [9]) was selected for the experiments for two main reasons:

(i) histosols are reported to emit high fluxes of N₂O, and if biochar plays a role on N₂O emissions, it will be easier to observe the effect in a system with high emission rates;

(ii) this soil had a very low bulk density (0.65 g·cm⁻³) and biochar application at 2% (w/w) did not modify its porosity as demonstrated by its water retention curves (Table 1). 90% WFPS in this soil would correspond to 10 cm pressure, which was not significantly modified by biochar treatments.

The soil was sampled from a horticultural field in New York State (43°7'48'', -78°6'38''), sieved at <2mm and stored at 4 °C for less than one month until the beginning of the experiments.

Table 1. Water retention curves for the organic soil unamended (control) and with 2% (w/w) of four selected biochars used in the experiment.

Pressure (cm H ₂ O)	Volumetric water content (vwater:vsoil)				
	control	Grass	Brush	Manure	Woodchips
1	0.96	0.95	0.95	0.96	0.96
3.5	0.91	0.90	0.89	0.90	0.91
10	0.80	0.80	0.81	0.81	0.83
30	0.76	0.78	0.79	0.79	0.80
100	0.67	0.66	0.64	0.70	0.72
300	0.64	0.62	0.58	0.66	0.70

Nine biochars produced at 500 °C by slow pyrolysis were selected to get a wide range of pH (6.4-10.7) and C/N ratios (11-859). Biochars were thoroughly mixed with the soil at a rate of 2 % (w/w) and incubated at optimum conditions for denitrification (90% WFPS, 30 °C) during 45 days. The experiment was laid out as a randomized block design with four replicates per treatment.

Gas sampling and measurements.

Gas sampling was conducted by sealing each unit with gas-tight screw caps for 40 min and N₂O concentration was measured with gas chromatography equipped with an electron capture detector (GC-ECD). We investigated the role that certain characteristics of biochars (ash, C/N and pH) play in the control of N₂O produced through the denitrification pathway.

Results

Figure 1 shows the percentage of reduction of N₂O emissions for each of the nine tested biochars in relation to their C/N ration and their pH. All biochars used in this study decreased N₂O emissions compared to the unamended soil. The biochar leading to higher N₂O mitigation was obtained from woodchips (C/N 231, pH 6.4) and decreased by 77% the amount of N₂O emitted from soil. The biochar with lowest impact on N₂O emissions was made from grass (C/N 11; pH 9.5) and decreased emissions by 37%. The observed pattern seems to indicate that high pH biochars led to lower effect on N₂O reduction. However, no correlation was found between N₂O mitigation and biochar C/N or pH, showing that these and other factors might be interacting simultaneously.

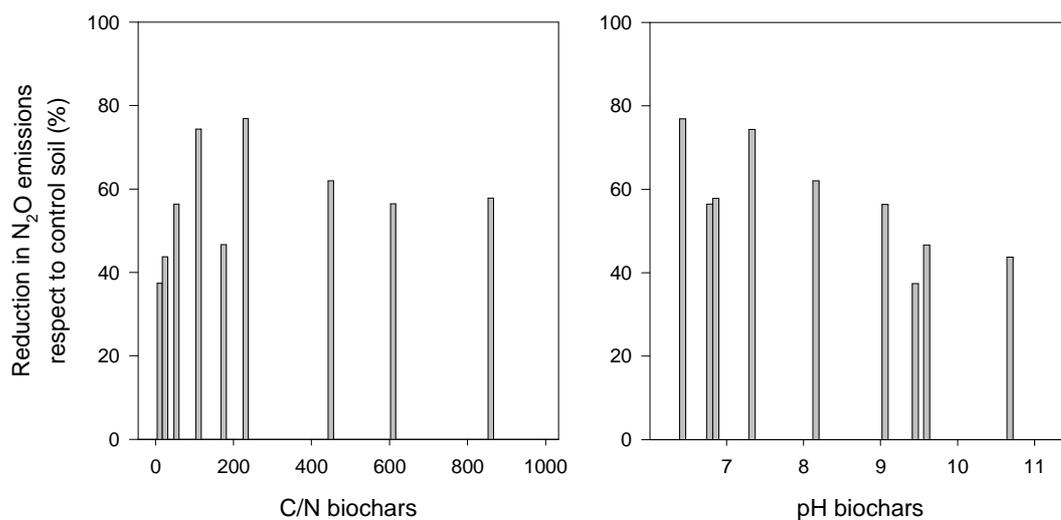


Figure 1. Percentage of reduction in N₂O emitted from soil after biochars application related to the biochars' C/N ratios (Fig 1A) and pH (Fig 1B).

After two weeks of incubation, once the peak of emissions had levelled-off, the concentration of water-extractable NO₃⁻ was determined in the control soil (12 mg N-NO₃⁻ kg⁻¹ soil) and in a treatment amended with a high C/N (C/N 609) biochar (48 mg N-NO₃⁻ kg⁻¹ soil), which suggests that N immobilization/adsorption was not the cause of N₂O reduction.

To offset the effect of pH we repeated the experiment after adjusting the pH of all biochars with hydrochloric acid to the same of the soil (pH 5.6). Figure 2 shows the results for N₂O reduction with the same biochars but when the pH had been adjusted prior to soil application.

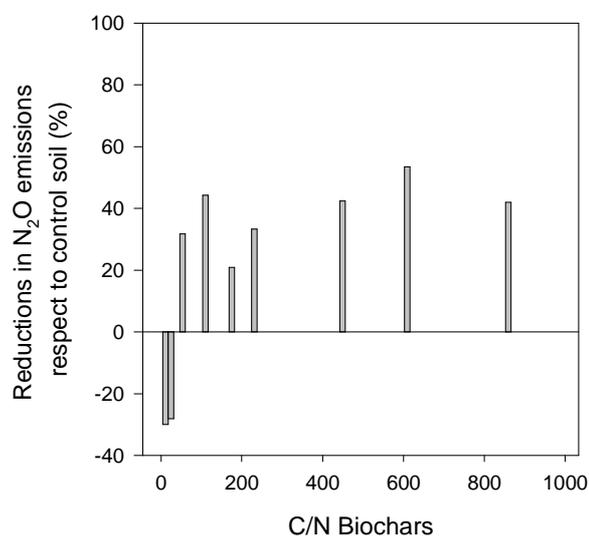


Figure 2. Percentage of reduction in N₂O emitted from soil after application of biochars which pH had been adjusted to the same of the soil (pH 5.6).

We observed lower mitigation with adjusted-pH biochars compared to the original biochars where pH had not been adjusted, which demonstrates the importance of biochar liming capacity for its effectiveness reducing N₂O. When pH was not a factor, N₂O mitigation correlated with ash content ($r = 0.899$; $P < 0.01$), which might indicate that biochars with high salt content might induce a salting-out

effect through an increase of the ionic strength in the soil solution, which might reduce the solubility of N₂O [10].

Conclusion and perspectives

The characteristics of biochar imprint its ability to reduce N₂O emissions from soil. In this experiment no direct correlation was found between biochar C/N ratio and its ability to reduce N₂O emissions. After two weeks of incubation the amount of NO₃⁻ content in soil amended with high C/N biochar was higher than in the unamended soil, which suggests that N immobilization/adsorption is not the prevalent mechanism for the observed N₂O reductions during denitrification in the case of slow-pyrolysis, high-temperature biochars.

Acknowledgements

This work was possible thanks to the OECD Cooperative Research Program that funded MLC stay at Cornell University and to a European Community Marie Curie Fellowship (FP7-PEOPLE-2010-MC-European Re-integration Grants (ERG) #277069). We acknowledge additional funding by USDA Hatch, by the National Science Foundation's Basic Research for Enabling Agricultural Development (NSF-BREAD grant number IOS-0965336) and the Fondation des Fondateurs. Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the donors.

References

- [1] Rondon, M.A., J.A. Ramirez, and J. Lehmann. 2005. Greenhouse gas emissions decrease with charcoal additions to tropical soils. In: Proceedings of the 3rd USDA Symposium on Greenhouse Gases & Carbon Sequestration in Agriculture and Forestry.
- [2] Van Zwieten, L., Kimber, S., Morris, S., Downie, A., Berger, E., Rust, J., and Scheer, C. 2010. Influence of biochars on flux of N₂O and CO₂ from Ferrosol. *Aust. J. Soil Res.* 48(6-7): p. 555-568.
- [3] Clough, T.J. and L.M. Condron. 2010. Biochar and the nitrogen cycle: Introduction. *J. Environ. Qual.*, 2010. 39(4): p. 1218-1223.
- [4] Castaldi, S., Riondino, M., Baronti, S., Esposito, F. R., Marzaioli, R., Rutigliano, F. A., Vaccari, F. P., and Miglietta, F. 2011. Impact of biochar application to a Mediterranean wheat crop on soil microbial activity and greenhouse gas fluxes. *Chemosphere*, 85(9): p. 1464-1471.
- [5] Clough, T.J., Bertram, J. E., Ray, J. L., Condron, L. M., O'Callaghan, M., Sherlock, R. R., and Wells, N. S. 2010. Unweathered wood biochar impact on nitrous oxide emissions from a bovine-urine-amended pasture soil. *Soil Sci. Soc. Amer. J.* 74(3): p. 852-860.
- [6] Singh, B.P., Hatton, B. J., Singh, B., Cowie, A. L., and Kathuria, A. 2010. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *J. Environ. Qual.*, 39(4): p. 1224-1235.
- [7] Kammann, C., Ratering, S., Eckhard, C., and Müller, C. 2012. Biochar and hydrochar effects on greenhouse gas (carbon dioxide, nitrous oxide, and methane) fluxes from soils. *J. Environ. Qual.* 41(4): p. 1052-1066.
- [8] Case, S.D.C., McNamara, N. P., Reay, D. S., and Whitaker, J. 2012. The effect of biochar addition on N₂O and CO₂ emissions from a sandy loam soil – The role of soil aeration. *Soil Biol. Biochem.* 51(0): p. 125-134.
- [9] USDA (1999) Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys. In: USDA (Ed.). US Government Printing Office, Washington DC.
- [10] Heincke, M. and M. Kaupenjohann, 1999. Effects of soil solution on the dynamics of N₂O emissions: a review. *Nutr. Cycl. Agroecosys.* 55(2): p. 133-157