Agriculture, Ecosystems and Environment 202 (2015) 135–138

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Short communication

The molar H:Corg ratio of biochar is a key factor in mitigating N_2O emissions from soil

M.L. Cayuela [a,*], S. Jeffery [b], L. van Zwieten [c]

[a] Department of Soil and Water Conservation and Waste Management, CEBAS-CSIC, Campus Universitario de Espinardo, 30100 Murcia, Spain
[b] Department of Soil Quality, Wageningen University, 6708PB Wageningen, The Netherlands
[c] New South Wales Department of Primary Industries, Wollongbar, NSW 2477, Australia

ARTICLE INFO

Article history:
Received 20 October 2014
Received in revised form 12 December 2014
Accepted 14 December 2014
Available online 13 January 2015

Keywords:
Nitrous oxide
Electron transfer
Greenhouse gas
Agriculture
Meta-analysis
Field studies

ABSTRACT

A previously published meta-analysis of biochar impacts on soil N_2O emissions by Cayuela et al. (2014) found a “grand mean” reduction in N_2O emissions of $54 \pm 6\%$ following biochar application to soil. Here we update this analysis to include 26 additional manuscripts bringing the total to 56 articles. The updated meta-analysis confirms that biochar reduces soil N_2O emissions by $49 \pm 5\%$ (mean ± 95% confidence interval). Importantly, this meta-analysis has sufficient data to investigate the impact of biochar under field conditions, showing a statistically significant lower average reduction in the field ($28 \pm 16\%$) compared to controlled laboratory studies ($54 \pm 3\%$). A key finding is the importance of the molar H:Corg ratio of biochar in determining mitigation of N_2O. Biochars with a molar H:Corg ratio <0.3, indicative of a high degree of aromatic condensation, lowered N_2O emissions by $73 \pm 7\%$ while biochars with a molar H:Corg ratio >0.5 were less effective at $40 \pm 16\%$. Together with previously published information, our new results suggest that a key mitigation mechanism is linked to the degree of polymerization and aromaticity of biochar.

1. Introduction

A meta-analysis on the impact of biochar soil amendment on N_2O emissions was recently published by Cayuela et al. (2014). Since this study was completed (May 2013) until October 2014, the number of articles published on this topic has almost doubled; with a total of 31 new peer-review articles. In view of this increased number of publications and the interest and relevance of the topic in light of greenhouse gas driven climate change, we have updated the original database, using 26 of the 31 new articles.

The number of field studies included in the database has increased considerably (from 7 to 19). The most studied crops were rice (Bian et al., 2013; Xie et al., 2013; Zhang et al., 2013; Pandey et al., 2014; Shen et al., 2014; Zhao et al., 2014), pasture (Anderson et al., 2014; Felber et al., 2014; Schimmelpfennig et al., 2014) and wheat (Bian et al., 2013; Zhang et al., 2013; Zhao et al., 2014). Despite this increase, the number of field studies is still limited and are not representative of a wide range of agro-ecosystems, soil types, management and fertilization practices.

The length of the experimental periods of studies published in the primary literature has also increased, with some studies showing monitoring periods of one year (Angst et al., 2014; Sackett et al., 2014; Sun et al., 2014) or longer (Case et al., 2014; Hu et al., 2014; Schimmelpfennig et al., 2014).

A further development is that more studies include now the original biomass as a treatment, comparing N_2O emissions between control, biomass and biochar treated soi3ls (Van Zwieten et al., 2013; Hu et al., 2014; Schimmelpfennig et al., 2014; Shen et al., 2014; Zhu et al., 2014). This is an important development for life cycle assessment allowing identification of biochar effects per se, beyond those that would have occurred from application of the feedstock alone, as discussed in detail in Jeffery et al. (2013). Some studies also compare results from parallel lab and field experiments (Felber et al., 2014; Schimmelpfennig et al., 2014).

Finally there are some new studies focused on understanding N_2O origin and formation pathways and the mechanisms of interaction with biochar (Harter et al., 2014; Sánchez-García et al., 2014; Van Zwieten et al., 2014; Wells and Baggs, 2014). However, there remains an under representation of mechanistic publications.

This study aimed to build on the previous meta-analysis through inclusion of 26 new studies. Furthermore, two new parameters were included in the database, the biochar molar

* Corresponding author. Tel.: +34 968 396109.
E-mail address: mlcayuela@cebas.csic.es (M.L. Cayuela).

http://dx.doi.org/10.1016/j.agee.2014.12.015
0167-8809/

H:Corg ratio, and total soil organic carbon (SOC). These are reported more commonly in the recent studies and are factors which have the potential to interact with the biochar and the soil biota with influences on N_2O emission.

2. Methods

The methodology followed for data compilation, treatment and meta-analysis was the same as in Cayuela et al. (2014). The newly updated database includes a total of 56 articles published between 2007 and 2014 totaling 390 direct comparisons (see Supplementary information for database). Further to the studies included in (Cayuela et al., 2014), the new incorporated studies are showed in Table 1. In addition, data on the biochar molar H:Corg ratio and soil total organic carbon (SOC) (which were not included in the previous study) are introduced.

As well as the previous categories used for groupings as described in Cayuela et al. (2014), studies were grouped into the following categories for analysis: (i) scale: laboratory studies, field studies and greenhouse studies (including experiments performed in pots or columns in the greenhouse, 50% with plants); (ii) SOC: low (SOC < 2%), medium (2% < SOC < 6%) and high (SOC > 6%); and (iii) the molar H:Corg ratio: low (H:Corg < 0.3); medium (0.3 < H:Corg < 0.5) and high (H:Corg > 0.5).

3. Results and discussion

Fig. 1 shows the mean effect size in terms of N_2O emissions grouped by the scale of study (lab, field or greenhouse). This meta-analysis showed a "grand mean" reduction in N_2O emissions of 49 ± 5%, not significantly different than the 54 ± 6% found in the previous meta-analysis. The reason for this slight decrease may be, in part, due to the higher proportion of field studies included in the database. On average, field studies showed lower reductions in N_2O emissions (28 ± 16%) compared to 54 ± 5% in laboratory studies.

We hypothesize that this could be caused by the lower rate of biochar application in the field (average 1.4% w/w) compared to laboratory studies (average 3.8% w/w). However, several researchers have found lower mitigation in the field (compared to the lab) even with identical application rates (Felber et al., 2014; Schimmelpfennig et al., 2014). A possible explanation could be the higher moisture regimes usually kept in laboratory experiments. Soil moisture is a well-defined determinant of N_2O emissions (Ruser et al., 2006). This is more easily controlled under laboratory conditions and experiments are often maintained at high levels of water filled pore space (WFPS) to maximize N_2O production. For example, in the experiment of Felber et al. (2014), soils in the laboratory incubation were maintained at about 80% WFPS whereas their field experiment fluctuated between ca. 20% and 85% WFPS, remaining below 60% WFPS for the majority of the time. Also Van Zwieten et al. (2010) and Case et al. (2012) found higher mitigation with biochar during a flooding phase or after rewetting the soils compared to low moisture regimes.

Another reason for the lower mitigation in the field could be the less homogeneous mixing of the biochar with the soil as suggested by Felber et al. (2014).

Grouping by SOC did not distinguish significant differences in N_2O reduction following biochar application. In soils with SOC < 2.0% biochar reduced emissions by 45 ± 8%; in soils with SOC between 2% and 6%, biochar reduced N_2O emissions by 55 ± 7% and finally in soils with SOC > 6% biochar decreased N_2O emissions by 32 ± 16%.

The key finding of this updated meta-analysis is the strong and direct relationship between the molar H:Corg ratio of biochar and the reduction in N_2O emissions. The meta-analysis shows that, independently of other parameters (like biochar C:N ratio, application rate, type of soil), low molar H:Corg ratios are associated with a greater mitigation capacity (Fig. 2). Conversely, the higher the H:Corg, the weaker the effect. In the previous meta-analysis, this parameter was not evaluated as it was rarely reported in the earlier manuscripts. However, recent studies have shown the importance of this ratio to determine the degree of polymerization of biochar (Enders et al., 2012; Wang et al., 2013), with lower H:Corg implying a higher proportion of fused aromatic carbon rings, which has been found to increase redox activity (Klüpfel et al., 2014) and sorption properties (Qiu et al., 2014). For instance, an analysis of two thermosequences of grass and wood biochars revealed that when produced at intermediate to high temperatures (400–700 °C) they show the highest capacity to accept and donate electrons (Klüpfel et al., 2014). This study also showed that increasing temperatures from 200 °C to 700 °C resulted in the consistent decrease in the molar H:Corg ratio of the resulting biochar, and an increase in electron shuttling based principally on organic moieties.

Biochars have been recently found to increase direct interspecies electron transfer (Chen et al., 2014). Also Kappler et al. (2014) showed that a biochar with low molar H:Corg ratio (0.29) was able to stimulate the rate and extent of microbial reduction of the Fe (III) in oxyhydroxide by *Shewanella oneidensis* MR-1, demonstrating that biochar directly mediates environmental electron transfer processes.

The generally acknowledged main N_2O formation pathway in soils (denitrification) involves the sequential reduction of the electron acceptor NO_3^- to NO_2^-, N_2O and finally to N_2 (Zumft, 1997). Cayuela et al. (2013) observed a lower N_2O/N_2 ratio in soils amended with biochar and hypothesized that biochar enhances the last step of denitrification (i.e., the reduction of N_2O to N_2), acting as an "electron shuttle" that facilitates the transfer of electrons to soil denitrifying microorganisms. Higher aromaticity in biochar would increase the possibility of interactions between soil microorganisms with the delocalized pi-electron system in the biochar surface, facilitating electron exchange. Thus, results from this current meta-analysis support the hypothesis linking biochar N_2O mitigation with its redox properties. However, it remains unclear as to why biochar also decreased total denitrified N, and whether this could also be linked to its aromatic structure.

Table 1
New studies included in the updated meta-analysis in addition to those incorporated in Cayuela et al. (2014).

Type of study	References
Laboratory experiments	(Kettunen and Saarnio, 2013; Li et al., 2013; Wu et al., 2013; Xie et al., 2013; Borchard et al., 2014; Case et al., 2014; Felber et al., 2014; Harter et al., 2014; Nelissen et al., 2014; Sánchez-García et al., 2014; Schimmelpfennig et al., 2014; Van Zwieten et al., 2014; Wells and Baggs, 2014; Zhu et al., 2014)
Greenhouse experiments	(Fungo et al., 2014; Sun et al., 2014; Zhao et al., 2014)
Field experiments	(Bian et al., 2013; Van Zwieten et al., 2013; Zhang et al., 2013; Anderson et al., 2014; Angst et al., 2014; Case et al., 2014; Felber et al., 2014; Hu et al., 2014; Pandey et al., 2014; Schimmelpfennig et al., 2014; Shen et al., 2014; Watanabe et al., 2014)