

Stoichiometric ratio of dissolved organic carbon to nitrate regulates nitrous oxide emission from the biochar-amended soils

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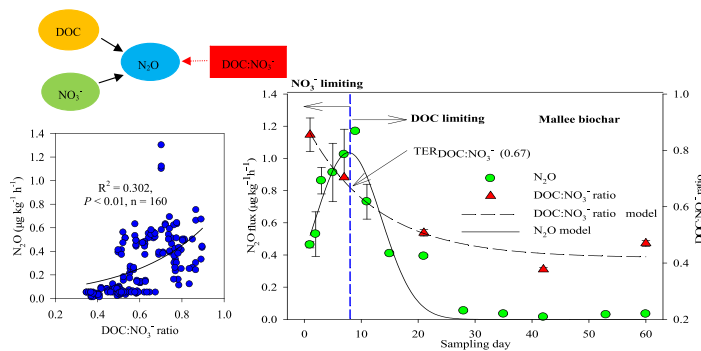
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HIGHLIGHTS

- Biochars can alter the biogeochemical properties and affect soil N₂O emission.
- Effects of biochars of different feed-stocks on soil N₂O emission were studied.
- All biochars reduce N₂O emission in Tenosol, but effect is inconsistent in Ferrosol.
- Biochar modifies stoichiometric ratio of DOC and NO₃⁻ and then affect N₂O emission.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 August 2016

Received in revised form 16 October 2016

Accepted 17 October 2016

Available online xxxx

Editor: Ajit Sarmah

Keywords:

Biochar

Stoichiometry

Dissolved organic C

Nitrate

Nitrous oxide

Denitrification

ABSTRACT

Biochar has the potential to mitigate nitrous oxide (N₂O) emissions from soils. However, the mechanisms responsible for N₂O emission in biochar-amended soils are yet to be elucidated. In this study, an incubation experiment was carried out to investigate the effects of seven biochars (eucalyptus, softwood mixture, mallee, jarrah, peanut shell, green waste and radiata pine) on the stoichiometric shifts of dissolved organic carbon (DOC), nitrate (NO₃⁻-N) and N₂O emission in two contrasting soils (Ferrosol with 5.3% total C, 0.46% total N; Tenosol with 0.4% total C, 0.01% total N). All biochar treatments were found to significantly reduce N₂O emission in Tenosol by 61–72%. However, in Ferrosol, biochars' impacts on N₂O emission were variable, with only peanut shell, green waste and radiata pine biochars significantly reducing N₂O emission by 17–23%. A decrease in NO₃⁻ availability in most biochar-amended treatments also was observed in both soils compared with the control. The N₂O fluxes in Ferrosol were mainly regulated by the shifts in the availability and stoichiometry of DOC and NO₃⁻ induced by the biochar amendments. The DOC derived from biochars increased DOC:NO₃⁻ ratio in Ferrosol at the beginning of the experiment, but these effects disappeared 7 days after incubation. Overall, the N₂O fluxes were C-limited due to the presence of high concentrations of NO₃⁻ in Ferrosol. However, in Tenosol, the relationship between stoichiometry of DOC:NO₃⁻ and N₂O fluxes was much weaker than Ferrosol and N₂O fluxes mainly limited by the concentration of NO₃⁻. This study demonstrated that the mechanisms responsible for biochar effects on soil N₂O fluxes are considered to be soil and biochar specific.

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1. Introduction

Biochar, a carbon (C)-rich solid product from biomass pyrolysis under oxygen-depleted conditions, has a wide range of inherent physical and chemical properties which are highly dependent on its feedstock and pyrolysis temperature, heating rate and residence time (Kloss et al., 2012). Applications of biochar to croplands have been suggested as a means of abating climate change (e.g. reduction of greenhouse gas emission), while at the same time improving soil fertility and increasing crop productivity (Woolf et al., 2010). The interaction between biochar and soil nitrogen (N) cycle is widely recognized (Biederman and Harpole, 2013; Clough and Condron, 2010; Clough et al., 2013). It has been suggested that combined applications of biochar and N fertilizers may increase crop yield, enhance N use efficiency and reduce nitrous oxide (N₂O) emission (Zhang et al., 2012).

Nitrous oxide is one of the major greenhouse gases, and has a global warming potential about 310 times that of carbon dioxide (CO₂) over a 100 years horizon, and is recognized as an important ozone depleting compound (Hartmann et al., 2013; Hu et al., 2016; Montzka et al., 2011). However, mitigating N₂O formation and release from soils is a great challenge due to various mechanisms involved. Suppression of N₂O emission from soils by biochar application has been observed in several studies (Case et al., 2015; Cayuela et al., 2013; Harter et al., 2014; Mukherjee et al., 2014), while some other studies showed no significant effect or even increased emissions (Ameloot et al., 2013; Castaldi et al., 2011; Singh et al., 2010; Suddick and Six, 2013). The reasons for such discrepancy in soil N₂O emissions in response to biochar application are still unclear, mainly due to the lack of mechanistic studies. Nitrous oxide is mostly formed in soil through three primary biological mechanisms of nitrification, nitrifier denitrification, and denitrification (Wrage et al., 2005). Bateman and Baggs (2005) reported that nitrification was the primary process of producing N₂O at 35–60% water-filled pore space (WFPS). However, denitrification has been proposed as the major contributor to soil N₂O emissions, particularly when WFPS exceeds 60% and oxygen (O₂) is deficient in soil (Dalal et al., 2003). Denitrification is the reduction of nitrate (NO₃⁻) to dinitrogen (N₂) via the intermediates of nitric oxide (NO) and N₂O (Harter et al., 2014). A suite of soil denitrifying communities is involved in the reduction of NO₃⁻. These microbial functional groups require organic C as an energy source for these reductive reactions and their growth (Harter et al., 2014; Zechmeister-Boltenstern et al., 2015), while NO₃⁻ is the essential N substrates for denitrification processes (Parton et al., 1996; Strong and Fillery, 2002). It has been suggested that N₂O fluxes are highly related to the concentration of NO₃⁻ (Bouwman et al., 2002; Pelster et al., 2011). Increasing soil NO₃⁻ concentration may stimulate soil denitrifying communities to use the mineral N and consequently produce more N₂O (Bouwman et al., 2002). Under less anaerobic conditions, the availability of organic C becomes critical for the NO₃⁻ denitrification function (Strong and Fillery, 2002).

Any biological system has to be operated within the fundamental stoichiometric constraints of energy (C) and nutrients (Davidson et al., 2007; Elser et al., 2000). The stoichiometric control of denitrification and movement of NO₃⁻ have been well studied in aquatic systems (Barnes et al., 2012; Konohira and Yoshioka, 2005; Taylor and Townsend, 2010). It has been proposed that about 1.25 mol of C is required by denitrifiers for the complete denitrification of 1 mol of NO₃⁻ (Saggar et al., 2013). However, little work has been done on the stoichiometric control of denitrification in soil. Biochar contains substantial amounts of C and N, with large surface areas and negative charges, but the chemical composition and nature of surface properties vary with biochar feedstock and pyrolysis condition. Furthermore, how these biochar properties modify the availability of organic C and NO₃⁻ in soil is largely unknown (Van Zwieten et al., 2015).

The specific objectives of this incubation study were to: (i) evaluate the interactive effect of different biochars and soil types on soil biochemical properties (ii) the effect of different biochars on N₂O emissions

under N fertilizer application, and (iii) quantify how the stoichiometric shifts in DOC and NO₃⁻ regulate the N₂O fluxes and affect the total N₂O emission. Seven different biochars produced from woody and crop residue biomass and two contrasting types of soil were used. It was hypothesized that biochar amendment would alter the availability of DOC and NO₃⁻, and then further modify the stoichiometric ratio of DOC to NO₃⁻, which regulates denitrification and the N₂O fluxes. It was further hypothesized that the mechanisms responsible for N₂O emission are soil and biochar specific and this study would shed light on such mechanisms.

2. Materials and methods

2.1. Soil and biochar

Two surface soils (0–10 cm) were collected from Yarraman (forestland, Ferrosol, 26° 50' 16" S, 151° 56' 51" E) in Queensland and Newman (agricultural land, Tenosol, 22° 44' 28" S, 120° 21' 28" E) in Western Australia, which are equivalent to Oxisol and Inceptisol in USDA soil classification, respectively. Soils were air-dried and passed through 2 mm sieve prior to the incubation experiment. Overall, Ferrosol was more fertile than Tenosol due to the higher contents of clay, total C and N, and higher concentrations of inorganic N (NH₄⁺ and NO₃⁻), microbial biomass C, and dissolved organic C (DOC) in the former than in the latter (Table 1).

The biochars used for the incubation experiments were produced from different feedstocks namely eucalyptus (*Eucalyptus globu*, E), softwood mixture (*Pseudotsuga menziesii* and *Araucaria cunninghamia*, SM), mallee (*Eucalyptus Genus*, M), jarrah (*Eucalyptus marginata*, J), peanut shell (*Arachis hypogaea*, PS), green waste (mixed species; GW), and radiata pine (*Pinus radiata*, RP), at different pyrolysis temperatures (e.g. 450–700 °C). Relevant properties of the biochars are shown in Table 2. Eucalyptus biochar used in this study was produced by a wild-fire in the eucalyptus forest (Peachester, Queensland) in 1969. It has been subject to the aging process and was highly acidic (pH = 3.4), while other biochars were alkaline (pH 7.6–10.2). The total C in biochar materials ranged from 53.1% (green waste) to 81.6% (softwood mixture), while total N from 0.12% (radiata pine) to 1.49% (peanut shell), with a range of C:N ratios from 45 (peanut shell) to 641 (radiata pine) (Table 2). Soluble organic C of biochar materials ranged from 514 μg g⁻¹ (radiata pine) to 1685 μg g⁻¹ (eucalyptus). The concentration of NO₃⁻ in all biochar materials was low (≤5 μg g⁻¹) except for peanut shell (273 μg g⁻¹), and concentrations of NH₄⁺ in all biochar materials were also low (≤0.3 μg g⁻¹) except for eucalyptus (38.7 μg g⁻¹) and peanut shell (24.8 μg g⁻¹). Biochars were firstly air-dried, then ground

Table 1
Selected properties of two soils used in the experiment.

Parameters ^a	Ferrosol ^b	Tenosol ^b
pH (1:5H ₂ O)	5.6	6.0
EC (dS m ⁻¹)	1.3	0.3
Total C (%)	5.3	0.4
Total N (%)	0.46	0.01
C/N ratio	11.5	40
Bulk density (g cm ⁻³)	1.0	1.4
NH ₄ ⁺ -N (μg g ⁻¹)	71	10
NO ₃ ⁻ -N (μg g ⁻¹)	417	3
MBC (μg g ⁻¹)	289	59
DOC (μg g ⁻¹)	488	29
Texture	Loam	Sandy loam
Sand, %	42.8	77.5
Silt, %	39.6	6.1
Clay, %	17.6	16.4

^a EC, electrical conductivity; MBC, microbial biomass carbon; DOC, dissolved organic carbon.

^b Ferrosol was collected from Yarraman, Queensland while Tenosol from Newman, Western Australia.

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