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The potential value of biochar in the mitigation of gaseous emission of nitrogen



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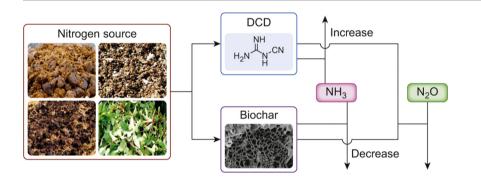
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HIGHLIGHTS

Biochar and dicyandiamide (DCD) effects on N transformation and losses were studied.

- DCD decreased N₂O emission from N sources applied soil but increased NH₃ emission.
- Although DCD significantly reduced N₂O emission, biochar decreased total N loss by 25%.
- Biochar can replace chemical nitrification inhibitors thereby mitigating gaseous N loss.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrogen (N) losses through gaseous emission of ammonia (NH₃) and nitrous oxide (N₂O) can contribute to both economic loss and environmental degradation. This study examined the effect of biochar and a chemical nitrification inhibitor, dicyandiamide (DCD), on N transformation and N losses via gaseous emission of NH₃ and N₂O from agricultural soils treated with a range of organic and inorganic N sources. The addition of DCD reduced N₂O emission from both organic and inorganic N sources treated soils by 75%, but increased ammonium (NH₄⁺) concentration and subsequently induced high NH₃ emission from the soils. In contrast, the addition of biochar reduced both N₂O and NH₃ emissions from organic and inorganic N sources treated soils by 23% and 43%, respectively. The effectiveness of biochar and DCD in reducing NH₃ volatilization and N₂O emission depends on the nature of the N sources and their initial mineral N concentration. The study demonstrated that biochar can be used to mitigate N losses resulting from NH₃ volatilization and N₂O emission.

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Abbreviations: BB, blood and bone mix; BS, biosolids; CM, chicken manure; CoM, cow manure; DCD, dicyandiamide; DOC, dissolved organic carbon; GWC, green waste compost; H⁺, hydrogen; HM, horse manure; Milli-Q, MQ; NII, nitrification inhibition index; Nis, nitrification inhibitors; OAs, organic amendments; OH⁻, hydroxyl; SM, sheep manure; SOM, soil organic matter; TIC, dissolved inorganic carbon.

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1. Introduction

An upsurge of interest in gaseous losses of nitrogen (N) as ammonia (NH₃) and nitrous oxide (N₂O) from soil has occurred during recent decades because of the environmental impacts of these losses. Strategies of regulating the fate and behavior of N in agricultural systems focus mainly on improving the nutrient use efficiency of fertilizer N and reducing environmental N pollution. In addition, farmers are facing significant economic loss due to poor growth yield caused by N loss as NH₃ and N₂O emissions. Increasingly, the use of inhibitors with N fertilizers is becoming an important strategy for the sustainable management of nutrients in agricultural production. Nitrification inhibitors (NIs) reduce N₂O flux from N fertilizers (Di and Cameron, 2008), urine deposits in pasture systems (De Klein et al., 2011; Luo et al., 2013), and organic manures (Asing et al., 2008; Li et al., 2014), but they are reported to increase NH₃ volatilization losses (Zaman et al., 2008). This increase in NH₃ volatilization may negate the beneficial effects of NIs on the reduction in N₂O emission (Singh et al., 2010). Dicyandiamide (DCD) is the most extensively studied and used NI because it is highly effective in inhibiting nitrification and reducing N2O emissions. Most studies involving DCD in reducing N losses as N2O have focused on its value in enhancing fertilizers in pasture systems, but little research has investigated its effect on N gaseous losses (NH₃ and N₂O) from various N sources in agricultural soil. It is essential to understand the influence of DCD on both NH₃ and N₂O emissions in relation to the quantity of added N in order to retain more N in the soil-plant system.

In recent years, biochar has received increasing attention because of its agronomic benefits (Sohi et al., 2010) and influence on carbon (C) and N transformations in soils (Clough and Condron, 2010; Spokas et al., 2012). For example, biochar addition has been shown to impact NH₃ volatilization (Steiner et al., 2010), N-leaching (Singh et al., 2010), and N2O emissions (Spokas et al., 2009; Van Zwieten et al., 2010). The ability of biochar in reducing NH₃ volatilization due to its sorption capacity has been known for some time (Holmes and Beebe, 1957). Seredych and Bandosz (2007) have recorded a range of NH₃ sorption capacities (<1 mg NH₃/g for non-oxidized biochars to >60 mg NH₃/g for oxidized biochars). Several laboratory and field studies have documented the suppression of N2O emissions by biochar addition to soils (Clough and Condron, 2010; Singh et al., 2010). For example, Rondon et al. (2005) noticed 80% and 50% reduction in N₂O emissions when biochar was added to grass and soybean systems, respectively. Most studies investigated the effect of biochar in reducing NH₃ and N₂O emissions separately. However, the influence of biochar on both NH₃ and N₂O emissions should be simultaneously evaluated to properly assess N retention in the soil-plant system.

The objective of this study was to compare the effects of biochar and DCD on the fate and behavior of various N sources (organic and inorganic) in an agricultural soil. The specific objectives were to: (i) examine the effect of biochar and DCD application on mineral N transformations in soil amended with various organic amendments (OAs) and urea, (ii) study the influence of biochar and DCD on N gaseous losses (NH $_3$ and N $_2$ O) from soil receiving urea and various OAs, and (iii) compare and assess the effectiveness of biochar and DCD in reducing total N loss from soil receiving various N sources.

2. Materials and methods

2.1. Soil, nitrogen sources, DCD, and biochar

Fresh soil used in this study was collected from an agricultural field in Port Wakefield, South Australia (34.157751°S; 137.787201°E). Soil was identified as Andisol in Australia soil classification. The N sources include horse manure (HM), sheep manure (SM), blood and bone mix (BB), cow manure (CoM), green waste compost (GWC), biosolids (BS), chicken manure (CM), and urea. Commercially available DCD (99%) obtained from Alfa Aesar (Massachusetts, USA) was used in this study.

Biochar produced from macadamia (*Macadamia tetraphylla*) nut shell at pyrolytic temperature of 465 °C was used in this study. Physicochemical properties of the biochar are detailed in Table 2. Biochar-Milli-Q (MQ) water mixture (1:10 ratio- dw/v) was shaken in an end-overend shaker for 1 h, and analyzed for pH and EC using smartCHEM-LAB Laboratory Analyser. To quantify dissolved organic carbon (DOC), biochar was shaken with MQ water (1:10 ratio- dw/v) for 3 h in a horizontal shaker, centrifuged at 3000g for 20 min, and filtered using 0.45 µm syringe filter. The filtrate was analyzed for total dissolved inorganic carbon (TIC) in an automated TOC analyzer (Shimadzu TOC-LCSH, Kyoto, Japan). Total C and N were determined by combustion of 0.25 g of oven dried and ground biochar sample at 1100 °C in a Leco C/N analyzer (Leco TruMac® CNS/NS, USA).

Inductively coupled plasma optical emission spectrometry (ICPOES) was used to measure total elemental composition of biochar (P, K, and S) after microwave digestion of 0.1 g of oven dried biochar with 4 ml 69% HNO $_3$ and 1 ml 33% H_2O_2 (Sparks et al., 1996). Specific surface area (Brunauer–Emmett–Teller, BET) and pore volume (Barrett–Joyner–Halenda, BJH) of biochar were determined using a Quantachrome NOVA (Quantachrome Instruments, USA) 1000e Analyzer by adsorbing/desorbing N_2 at 77 K on/from the samples previously dried and out–gassed at 160 °C for 16 h.

Soil and amendment characteristics are presented in Table 1. The pH values of the OAs ranged from 6.84 to 9.09, C:N ratios ranged from 5 to 14, and mineral N concentrations varied widely from 23 mg N/kg to 33,379 mg N/kg. The blood and bone mix had the lowest pH value, and CM had the highest pH value. The soil had a pH of 7.99, C:N ratio of 24, and mineral N concentration of 99 mg N/kg soil. The biochar had a pH of 10.08, C:N ratio of 113, and mineral N concentration of 28.93 mg N/kg soil. The NH₄⁺-N concentration was below the detectable limit. Biochar showed a specific surface area of 104.68 m²/g with a low pore volume of 0.085 cm³/g (Table 2).

2.2. Experiments

Two sets of experiments were conducted to separately examine the effect of biochar and DCD on N transformation (Experiment 1) and N gaseous losses (Experiment 2) in soils treated with a range of OAs and urea. The treated soils were incubated in dark at field capacity at a room temperature ranging from 18 to 21 °C for 51 days.

In both experiments, 18 treatments with three replicates as described below were studied. Nine treatments with N sources at 300 mg N/kg soil and biochar at 7.18 mg C/kg soil (Singh et al., 2010) included the following: Soil with biochar; Soil with HM and biochar; Soil with SM and biochar; Soil with BB and biochar; Soil with CoM and biochar; Soil with GWC and biochar; Soil with BS and biochar; Soil with CM and biochar; Soil with urea and biochar. Similarly, nine treatments with N sources at 300 mg N/kg soil and DCD at 25 mg/kg soil (Singh et al., 2008) were prepared and studied. For each treatment, 250 g soil was mixed thoroughly with the respective N sources, biochar, and OAs, and placed in plastic zip lock bags.

2.2.1. N transformation and pH

A sub-sample (5 g oven dry equivalent) from each treatment bag was extracted with 2 M KCl solution by shaking in an end-over-end shaker for 1 h (1:10 soil: extractant ratio). The extracts were analyzed for ammonium (NH $_4^+$) colorimetrically by the salicylate-nitroprusside method of Mulvaney (1996) on a Skalar autoanalyzer (Skalar UK Ltd., York, UK). Nitrate in the KCl extract was also determined colorimetrically using the same Skalar autoanalyzer in which a Cd–Cu column was used to reduce NO $_3^-$ to NO $_2^-$ (Jones et al., 2004). A sub-sample (1 g oven dry equivalent) from each bag was shaken with 10 ml of 0.01 M CaCl $_2$ in an end-over-end shaker for 1 h and measured for pH using a pH/conductivity meter (smartCHEM-LAB Laboratory Analyzer, VWR International Pty Ltd., Australia).

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