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Combined use of nitrification inhibitor and struvite crystallization to reduce the NH_3 and N_2O emissions during composting

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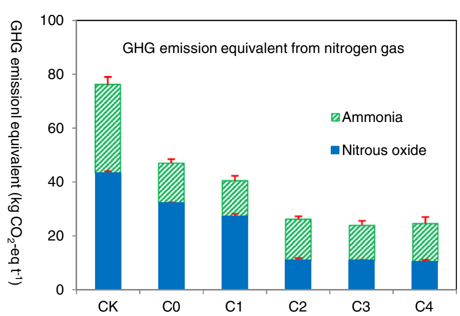
HIGHLIGHTS

- DCD reduces the N_2O emission by 76.1–77.6%.
- Struvite crystal process reduces the NH_3 loss by 45–53%.
- DCD is decomposed faster in thermophilic phase.
- DCD added by 2.5% of TN is enough to inhibit nitrification at maturing stage.

GRAPHICAL ABSTRACT

CK: control; C0: 15% Mg and P salts; C1: 15% Mg and P salts + 2.5% DCD; C2: 15% Mg and P salts + 5.0% DCD; C3: 15% Mg and P salts + 7.5% DCD; C4: 15% Mg and P salts + 10.0% DCD. GHG: greenhouse gas. Global warming potential calculation: 1 mol NH_3 = 3.86 mol CO_2-eq, 1 mol N_2O = 298 mol CO_2-eq.



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ABSTRACT

Struvite crystallization (SCP) is combined with a nitrification inhibitor (dicyandiamide, DCD) to mitigate the NH_3 and N_2O emission during composting. The MgO and H_3PO_4 were added at a rate of 15% (mole/mole) of initial nitrogen, and the DCD was added at rates of 0%, 2.5%, 5.0%, 7.5% and 10% (w/w) of initial nitrogen respectively. Results showed that the combination use of SCP and DCD was phytotoxin free. The SCP could significantly reduce NH_3 losses by 45–53%, but not the DCD. The DCD significantly inhibits nitrification when the content was higher than 50 mg kg^{-1}, and that could reduce the N_2O emission by 76.1–77.6%. The DCD degraded fast during the thermophilic phase, as the nitrification will be inhibited by the high temperature and high free ammonia content in this stage, the DCD was suggested to be applied in the maturing periods by 2.5% of initial nitrogen.

1. Introduction

Composting of animal manure is a widely used and effective technology, however harmful gasses, such as ammonia (NH_3), and nitrous oxide (N_2O), are emitted during the process as secondary pollution. N_2O for example is a significant greenhouse gas (GHG) with global warming potential 298 times higher than that of carbon dioxide (CO_2) (IPCC, 2007) and is considered to be an important factor in ozone depletion (Ravishankara et al., 2009). Ammonia has been shown to be a significant, and increasing, component of airborne fine particulate matter (PM2.5) in

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northern China (Li et al., 2013), from 2003 to 2012 its proportion has increased from 7.5% to 12%. Unlike nitrate and sulphate pollution, ammonium in the atmosphere is largely generated from agricultural activities (Shen et al., 2011).

During composting, N_2O can be produced through both nitrification and de-nitrification processes. One formation mechanism is through incomplete nitrification of NH_3 which is oxidized to hydroxylamine (NH_2OH) by ammonia mono-oxygenase (AMO), which can be further oxidized to nitroxyl (NOH) by hydroxylamine oxidoreductase which produces N_2O after polymerization and dehydration (Canfield et al., 2010). During denitrification, nitrite is reduced to NO by nitrite reductase, which is further reduced by nitric oxide reductase to N_2O (Moenne-Loccoz and Fee, 2010). As a result of these processes, 0.4–9.9% of total nitrogen (TN) is emitted as N_2O during the composting of animal manure (Tsutsui et al., 2015). The N_2O emission rate is affected by the feedstocks C/N ratio, aeration conditions, and turning frequency (Jiang et al., 2011). When compost is well operated, the global warming potential of N_2O can be reduced to about 11–18 CO_2-eq t^{-1}, but this still accounts for 35–74% of total GHG emission (Jiang et al., 2013). NH_3 emission accounts for 9–32% of initial total nitrogen (Fukumoto et al., 2011; Jiang et al., 2011). The emission rate can be affected by C/N ratio, aeration condition, moisture content, porosity, pile density, and so on (El Kader et al., 2007; Jiang et al., 2011).

Stuvite crystallization (SCP) is one of the most effective methods of mitigating NH_3 emission in waste water treatment and in recent years has been used in composting to reduce NH_3 loss and to increase the compost quality (Fukumoto et al., 2011; Wang et al., 2013; Chan et al., 2016). When the application ratio of phosphate and magnesium salts is 1:1, the first reaction is:

$$Mg(OH)_2 + H_3PO_4 \rightarrow MgHPO_4 + 2H_2O$$

Subsequently, the following reaction occurs under alkaline conditions and the struvite was formatted

$$MgHPO_4 + NH_4^+ + OH^- + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O$$

The best H_3PO_4 and MgO application rate is about 10–20% of total nitrogen (mole/mole) (Jeong and Hwang, 2005), and with appropriate application rate, SCP can decrease NH_3 emission by 40–84% (Zhang and Lau, 2007; Ren et al., 2010).

Dicyandiamide (DCD, $C_2H_4N_4$) is a well-known nitrification inhibitor that has been studied for over 90 years (Kelliher et al., 2008). DCD works by reducing the *amoA* gene in ammonia oxidizing bacteria (AOB) especially at high nitrogen application rates (Dai et al., 2013). Slowing nitrification results in decreased N_2O production and emission rates, and reduced nitrate concentrations in soil decreases the potential for N_2O production from denitrification (Kelliher et al., 2008). DCD operates in a bacteriostatic mode and does not kill soil bacteria but rather inhibits or reduces their activity. O'Callaghan et al. (2010) reported that AOB are significantly affected by DCD in which reduces population size and activity, while having little impact on the overall soil bacterial activity. DCD has been widely used in agriculture due to its low cost, minimal volatility, and solubility in water (Tian et al., 2015).

It has been documented that DCD is effective at decreasing N_2O emissions from fields treated with mineral fertilizer or urine. Depending on the crop system and climate, the N_2O emission rate was reduced by 17–90% (Kelliher et al., 2008; Dai et al., 2013; Cahalan et al., 2015; Wang et al., 2015).

While literature relating to DCD is extensive, only few published studies examine the use of DCD during composting, especially in combination with the SCP process. The purpose of the present study is to evaluate this combination of nitrification inhibitor and stuvite crystallization on NH_3 and N_2O emission during composting and to determine the most effective application rate and application time.

2. Methods

2.1. Raw materials and composting installation

Pig feces and corn stalk were used as raw materials in this research. Pig feces were taken from a pig fattening farm located in Beijing. Corn stalk was obtained from Shangzhuang research station of China Agricultural University. To achieve the appropriate moisture content and C/N ratio, pig feces and corn stalks were mixed at a ratio of 7:1 (wet weight). Compositions of the raw materials and the mixture are shown in Table 1.

In order to simulate the forced aeration system, trials were carried out in a series of 60 L composting vessels (Fig. 1). Aeration of the vessels was controlled by a program, which also recorded the temperature automatically.

2.2. Experiment design and sample collection

Six treatments were conducted in triplicate to evaluate the combination effects of the nitrification inhibitor and stuvite crystallization and to determine the best DCD application rate (Table 2). The CK without any chemical additives was used as a control treatment. For C0–C4, H_3PO_4 + MgO were added to induce struvite crystallization. The application rates were all supplemented on a molar basis equivalent to 15% of the initial nitrogen. For C1–C4 treatments, DCD was added as a nitrification inhibitor. Application rates were set as 2.5%, 5%, 7.5% and 10.0% of the initial nitrogen (w/w) (Table 2). The DCD application times are also shown in Table 2. Continuous aeration was employed in all experiments and the aeration rate of all treatments was 0.25 L kg DM^{-1} min^{-1}. Materials were composted for 4 weeks and turned at days 4, 10, and 17 in order to homogenize the materials and improve the porosity.

During each turning, about 100 g samples were removed for analysis. Samples were separated into 2 parts: one part was air-dried, ground, passed through a 0.1 mm sieve and stored as a dry sample while the other part was immediately frozen as a fresh sample.

2.3. Analytical methods and calculations

Gaseous (N_2O, NH_3, O_2) concentrations were measured daily during the first 2 weeks, and then 3–4 times per week thereafter. Cumulative emissions for the whole composting period were calculated from the daily flux. Data for non-measured days were obtained by averaging the closest measured days.

N_2O and O_2 were analyzed by gas chromatograph equipped with electron capture detectors (Agilent 7890A, USA) and thermal conductivity detector (Beifen 3420A, China) respectively. NH_3 was absorbed by a washing bottle with boric acid (2%) and then titrated using 0.05 M H_2SO_4. Total nitrogen content (TN) and total organic carbon content (TOC) were measured using an Element analyzer (Elementar vario MACRO cube, Germany). To determine moisture content, fresh samples were dried at 105 °C in an oven until they reached a constant weight. Inorganic nitrogen (NH_4^+–N, NO_3^-–N) was extracted with 2 M KCl (1:20) and analyzed using a segmented flow analyzer (Technicon Autoanalyser II System, Germany). Fresh samples were mixed with deionized water at a ratio of 10:1 (w/w) and shaken for 30 min, filtered and the supernatant was used for the measure of germination index (GI) and pH value (Guo et al., 2012). The GI was determined in triplicate using cucumber seeds. Supernatant (8 ml) was pipetted into petri dishes packed with a