



Nitrogen, carbon, and dry matter losses during composting of livestock manure with two bulking agents as affected by co-amendments of phosphogypsum and zeolite



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ABSTRACT

Loss of nitrogen (N) via ammonia (NH₃) volatilization during composting of livestock manure causes nutrient imbalance in the compost. The effects of phosphogypsum (PG) and zeolite amendments on reducing N loss (via suppressing NH₃ volatilization) and concurrent changes in carbon (C) and dry matter losses were investigated in a 100-day lab-scale mesophilic (27 °C) composting of cattle manure with rice hulls or sawdust as a bulking agent. The results showed that amendments PG and zeolite did not reduce NH₃ volatilization but decreased total N loss, and when combined with sawdust the N loss was further reduced. However, the effects of PG and zeolite on reducing N loss were neither additive nor synergistic, and thus co-amending PG and zeolite did not further reduce N loss. The C and dry matter losses were smaller when sawdust was used as a bulking agent compared to rice hulls, and PG and zeolite amendments also decreased the C and dry matter losses in the presence of bulking agents. Combining sawdust as a bulking agent with either PG or zeolite amendments was more efficient than other combinations in reducing N, C, and dry matter loss in mesophilic composting of cattle manure.

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1. Introduction

Composting of livestock manure produces biochemically stable organic materials that are easily handled and can be uniformly applied to soils (Larney et al., 2006). However, a greater loss of nitrogen (N) than other nutrients, such as phosphorus (P), during the composting process may cause nutrient imbalance such as a lower N to P ratio (N/P) as well as environmental problems such as atmospheric pollution (Hao et al., 2004). The loss of N during composting occurs mainly via ammonia (NH₃) volatilization in the early stage of composting when decomposable organic N is abundant and pH increases with protonation of amine (Eghball et al., 1997; Ogunwande et al., 2008). Therefore, suppression of NH₃ volatiliza-

tion may help produce more agronomically valuable compost with reduced environmental impact.

Cost-effective chemical amendments that either have low pH (e.g., phosphogypsum) or have negatively charged sites that electrostatically hold NH₄⁺ (e.g., zeolite) can reduce NH₃ volatilization (Koenig et al., 2005). Phosphogypsum (PG) is an acidic by-product of phosphate fertilizer, consisting mainly of gypsum (CaSO₄·2H₂O) which reacts with NH₄⁺ to produce acidic NH₄⁺ salt, (NH₄)₂SO₄, reducing NH₃ volatilization (Prochnow et al., 1995; Tubail et al., 2008) and thus increasing N concentration in the compost (Hao et al., 2005; Zvomuya et al., 2005). Zeolite minerals are microporous, crystalline, and hydrated aluminosilicates of alkali or alkaline-earth metals with high negatively-charged sites that are capable of sorbing cations including NH₄⁺ in environmental media such as water (e.g., Liberti et al., 1981; Gikas and Tsihrintzis 2012), soils (e.g., Lim et al., 2016), and composting piles (e.g., Koenig et al., 2005). As the mechanisms of suppression of NH₃ volatilization by PG and zeolite differ, the co-addition of both amendments may further decrease NH₃ volatilization compared to PG or zeolite alone. However, there is no relevant study that has investigated

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the co-amendment effects on NH_3 volatilization and N loss in the composting of livestock manure.

Bulking agents, such as wood-based materials and crop residues, are often added in order to adjust the water content of composting piles (Larney et al., 2006). The type of bulking agent also affects NH_3 volatilization and N loss due to their different decomposability and the ratio of carbon (C) to N (C/N) (Lim et al., 2009). It has been reported that N loss relative to initial N ranged from 8 to 26% for wood-based materials and from 15 to 43% for crop residues (Barrington et al., 2002; Larney et al., 2006), with the difference attributed to both biotic and abiotic retention of NH_4^+ ; i.e., fast microbial immobilization of NH_4^+ due to a higher C/N (e.g., >200) and binding of NH_4^+ on to phenolic compounds of wood materials, respectively (Lim et al., 2009). Therefore, the effects of PG and zeolite on NH_3 volatilization and thus N loss during the composting processes might differ with the bulking agent type; however, such interactive effects are also unknown.

The primary objective of this study was to investigate the effects of PG and zeolite co-amendments on reducing NH_3 volatilization and N loss during composting of livestock manure with sawdust or rice hulls as a bulking agent. The hypotheses of this study were 1) NH_3 volatilization and thus N loss may be further reduced by co-amendments of PG and zeolite compared to that with single amendment of either PG or zeolite alone as a result of additive or synergistic effects of lowered pH by PG and increased NH_4^+ sorption by zeolite and 2) co-amendments of PG and zeolite with sawdust rather than rice hulls as a bulking agent may result in lower NH_3 volatilization and thus N loss due to a higher NH_4^+ retention capacity of sawdust than rice hulls. As C content and total dry matter (and associated nutrients concentrations) of the final compost are important parameters that need to be considered when the composts are applied to the fields, C and dry matter losses of the composting mixture were also investigated.

2. Materials and methods

2.1. Manure, bulking agents, and amendments

Around 1 kg each of cattle manure and bulking agents (rice hulls and pine sawdust) were obtained from the livestock experiment station (126°53'E, 35°10'N) of Chonnam National University, South Korea. The samples were dried using a freeze dryer (FREEZE DRYER, Ilshin-lab, Korea) to remove water while minimizing loss of volatile compounds. The manure sample was hand-ground with a mortar and passed through a 2-mm sieve to obtain a homogeneous sample. Rice hulls and sawdust samples were passed through a 4-mm sieve to mimic coarser particle size of bulking agents than manure under field composting conditions. A portion (around 20 g) of the samples was further ground to a fine powder with a ball mill (MM200, Retsch BmgH, Haan, Germany) and used for chemical analyses; pH at 1-to-10 of sample to water ratio, total C and N using a combustion method (Nelson and Sommers, 1996) with an elemental analyzer (FLASH EA-1112, Thermo, USA), total P with the vanadomolybdo-phosphoric acid colorimetric method after digestion with perchloric acid (Kuo, 1996), and cation exchange capacity (CEC) using ammonium acetate method (Sumner and Miller, 1996) (Table 1). The sawdust had a lower pH (4.9), higher C/N (250.9), and higher CEC (16.0 cmol kg⁻¹) than rice hulls (pH 6.9, C/N 80.6, CEC 0.1 cmol kg⁻¹) (Table 1).

The PG sample was obtained from a P fertilizer manufacturing company (Namhae Chemical, Yeosu-city, Chonnam province) and clinoptilolite zeolite ((Na, K, Ca)₂₋₃Al₃(Al, Si)₂Si₁₃O₃₆·12H₂O) was purchased from Handoo Trade (Gyeongju, Gyeongbuk province). The amendment samples were homogenized after passing through a 0.3-mm sieve and freeze-dried to remove trace water. The sam-

ples were analyzed for pH, total C, N and P, and CEC (only applicable for zeolite) following the procedures described above. The PG had a low pH (2.5) and zeolite had a high CEC (107.0 cmol kg⁻¹) (Table 1).

2.2. Lab-scale mesophilic composting experiments

A total of 36 composting reactors (250 mL jars) were prepared for 12 treatments in triplicate: manure with three bulking agents (none, rice hulls, and sawdust) × four amendment treatments (none, PG, zeolite, and PG + zeolite) (Table 2). An additional three empty reactors were also prepared for background CO₂ and NH₃ measurements. In all the reactors except the blank, 30 g of manure was placed, and then a bulking agent (30 g) or amendment (15 g) were added following the treatment schedule (Table 2). The contents were homogeneously mixed using a spatula. The dry matter, total C and N concentrations and contents, and C/N of the mixture were calculated using the corresponding values of the individual components of the mixtures (Table 2). A portion (2–5 g, see the footnote of Table 2 for details) of the mixture was sampled from each reactor and measured for pH, and thus the dry matter used for the composting experiment was 28 g for manure, 28 g for bulking agent, and 14 g for amendment (Table 2). The water content of the mixture was adjusted to 50% (w/w based on the dry weight) by adding distilled water. The ratio of manure to bulking agent (1:1) was determined following the conventional composting procedure of local farms (Lim et al., 2009) and the amendment rate (25% of total dry matter of manure and bulking agent mixture) is similar to the upper limit of amendment rates (20–30%) tested in other studies (e.g., Hao et al., 2005; Koenig et al., 2005; Tubail et al., 2008).

Unlike a large scale composting experiment, the reactors in this study were placed into water baths set at 27 ± 0.2 °C to keep reactor temperature constant against the fluctuation of ambient temperature. Thus, our laboratory scale results may not reflect the field composting environments; however, by increasing the number of reactors, it was possible to address the complicated interactive effects of the amendments and bulking agents on NH_3 volatilization and N loss during mesophilic composting. Thermocouples (TR-52, T&D Corporation, Nagano, Japan) were installed in the center of four randomly selected reactors and outside of the reactor, and temperature was monitored every 30 min. During the experiment period, the ambient temperature fluctuated from 16.5 to 28.2 °C, but the temperature inside the reactor was maintained between 27 and 28 °C and no further increase in temperature was found due to the small size of composting mixture that limits heat accumulation. The reactors were sealed with an air-tight screw-top lid and aerated with a continuous air flow from an air cylinder (Fig. 1). The air was first passed through 10 N NaOH and 10 N H₂SO₄ solutions to remove ambient CO₂ and NH₃, respectively. The CO₂- and NH₃-free air was supplied to the reactors at 0.5 L min⁻¹, and exhaust gas was passed through each of two consecutive CO₂ (25 mL of 2 N NaOH) and NH₃ (25 mL of 2 N H₂SO₄) traps. The CO₂ traps were replaced with new ones at 1, 2, 4, 12, 16, 18, 22, 25, 26, 29, 32, 39, 46, 53, 63, 68, 82 and 100 days after composting and NH₃ traps were replaced at 1, 12, 18, 25, 39, 53, 68 and 100 days. The CO₂ traps were replaced more frequently than NH₃ traps due to the greater CO₂ emission. During traps replacement, the air tubing valves were closed to minimize gases loss. Because water loss was minimized, water was not added during the composting period. On day 25, the composting materials were mixed thoroughly using a spatula for 30 s to mimic turning practiced in field composting as turning is often carried out for aeration and temperature control of the composting windrow (Ogunwande et al., 2008).

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