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Control of dimethyl sulfide and dimethyl disulfide odors during pig manure composting using nitrogen amendment

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HIGHLIGHTS

- Nitrogen electron acceptors were added to composts to reduce sulfur reduction.
- All the additives significantly reduced dimethyl sulfide and dimethyl disulfide.
- The reduction was quantified for different additives and doses.
- The additives had no adverse effects on compost quality.
- An in situ method was proposed to reduce sulfur odors during composting.

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ABSTRACT

Effects of nitrogen electron acceptors on dimethyl sulfide (Me_2S) and dimethyl disulfide (Me_2SS) odor emission during composting was investigated. The chemicals and doses used included sodium nitrate (NO_3^- at 10 mM, 20 mM and 40 mM), sodium nitrite (NO_2^- at 10 mM, 20 mM and 40 mM) and sodium nitrite (10 mM, 20 mM and 40 mM) with hexaammonium heptamolybdate tetrahydrate (HHT). The results showed that the addition of these chemicals restricted the emission of Me_2S and Me_2SS . The emission reduction effect of NO_2^- was greater than NO_3^- at the same dosage. A greater reduction was observed when HHT was also added. With 2 mM HHT + 40 mM NO_2^- addition, the emission of Me_2S and Me_2SS was reduced by 92.3% and 82.3%, respectively. Comparison of compost maturity indices for treated and untreated composts indicated that none of the additives adversely affected compost quality. These results indicate that nitrogen chemical addition may provide an efficient method to control sulfur odors during composting.

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1. Introduction

Odor emissions are one of the greatest impediments to the development of composting for organic waste management (McGinley and McGinley, 2005). As cities expand into rural areas, odor emissions must be minimized. Recently, many composting facilities have closed because of odorous gas emissions (Tsai et al., 2008).

Due to their extremely low odor threshold, volatile sulfur compounds, especially dimethyl sulfide (Me_2S) and dimethyl disulfide (Me_2SS), have proven to be the compounds most responsible for malodors from pig manure composts (Blazy et al., 2014; Giri et al., 2010; Maulini-Duran et al., 2013; Miller, 1993). During the early stages of composting, both aerobic and anaerobic regions exist within a pile. It is within these anaerobic regions that sulfate

reducing bacteria exist and generate reduced sulfur compounds that are highly odorous. Concentrations of both compounds are limited by regulations in the USA, Japan, China and Germany (Shareefdeen and Singh, 2005).

This problem however is not new. Me_2S and Me_2SS have long caused odor problems at industrial facilities including petroleum refineries, pulp and paper facilities, distilleries and waste water treatment plants. The methods used to control these odors include biofiltration, biotrickling, bioscrubbing and membrane bioreactor treatment (Giri et al., 2014; Prenafeta-Boldu et al., 2012; Shao et al., 2014; Soupramanien et al., 2012). While these ex-situ treatment methods have proven to be effective in many cases (Giri and Pandey, 2013), their use in composting is limited due to the fact that composting facilities use outdoor static piles and/or windrow systems that make off-gas collection difficult. Furthermore, when biofilters are used, the bacteria in the odor control systems usually convert sulfur compound to sulfate which can acidify and cause corrosion and nutrients have to be added to these systems

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and/or the media need to be replaced frequently to maintain microbial metabolism and activity. In addition, while biofilters work well when treating gases with low to moderate amounts of ammonia, they are less tolerant of the high concentrations found in compost off-gas (Pagans et al., 2007).

While composting overall is an aerobic process, the feedstocks may arrive in an anaerobic, odorous state and anaerobic regions exist within active piles where sulfur odors can form. The hypothesis of this study was that immediate addition of chemical amendments that inhibit sulfur metabolism could decrease this and that as the composting process progresses and becomes largely aerobic, the odor problem would eventually be eliminated.

To test this, an in-situ odor control method for Me₂S and Me₂SS was developed and investigated.

Sulfate reducing bacteria (SRB) have been shown to be important contributors to sulfur odor production (Xia et al., 2014). Organic compounds in compost are used by SRB as electron donors to reduce sulfate to sulfide and thereby produce H₂S. H₂S is a precursor of Me₂S and Me₂SS that is converted to these odorous compounds through methylation. Nitrogen compounds can also be used as electron acceptors during anaerobic respiration and are preferable to sulfur compounds due to their higher reduction potential. Nitrate, nitrite and molybdate are known to be efficient inhibitors of SRB metabolic activities and are used to reduce H₂S emissions in liquid systems at refineries and wastewater treatment plants (Hubert et al., 2005; Nemati et al., 2001). By providing a preferable electron acceptor, microbial metabolism is shifted from sulfate to nitrogen respiration. Although this effect has been known for years, the use of these compounds to control composting odors has not been previously investigated. In this study, nitrate, nitrite and molybdate were added to compost at small doses at the beginning of the composting process to determine their ability to reduce Me₂S and Me₂SS production during composting.

2. Materials and methods

2.1. Feedstock

Pig manure was collected from a pig farm using the Gan Qing Fen system located in Haidian, Beijing, China. This system is widely used in China, especially in the Beijing area where it is obligatory for pig fattening farms. In this system, faeces are collected manually while flush water is only used to remove urine thereby reducing water used for waste removal.

Corn stalks were taken from the Shangzhuang Research Station of China Agricultural University. After collection, corn stalks were milled using a crusher to pass through a 20 mm sieve screen. The properties of the feedstocks are shown in Table 1. Pig manure and corn stalks were mixed at a ratio of 6.9:1 (based on wet weight).

2.2. Reactor system

A pilot-scale compost system was used that was modified from a reactor and control system described previously by Guo et al. (2012). The compost reactors consisted of stainless steel cylinders

with 60 L effective volumes (600 mm high and 360 mm inner diameter) (Fig. 1). A rock-mineral cotton insulating material was used between the two stainless steel layers (50 mm) to limit heat transfer. The caps were made from the same material as the reactors. Rubber O-rings were placed between the cap and the main body to prevent gas leakage. There were three outlets on each cap, a tube (30 mm inner diameter) for routine exhaust of off gas, a smaller tube for collecting gas samples, and a third used for temperature measurement. At the bottom of each reactor, a sieve plate with 5 mm openings was installed to separate the leachate and distribute the air flow. There were two ports on the lateral lower part of each reactor; one for leachate collection and another for air input. Air was provided by an air pump and flow rates to each reactor were controlled at 3 L·min⁻¹.

2.3. Compost setup and design

Pig manure and corn stalks were mixed (6.9:1 mix ratio) and then divided into ten equal identical fractions and one fraction was used for each of the ten treatments. The properties of the feedstock mix are shown in Table 1. A control treatment (ck) received no odor control additives. Treatments 1, 2 and 3 were amended with 10 mM, 20 mM and 40 mM sodium nitrate (Na₂NO₃), respectively. Treatments 4, 5 and 6 were amended with 10 mM, 20 mM and 40 mM of sodium nitrite (Na₂NO₂), respectively. Treatments 7, 8 and 9 were all amended with 2 mM hexaammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, HHT) and with 10 mM, 20 mM or 40 mM Na₂NO₂, respectively. Air was pumped into reactors continuously at a rate of 3 m³·m⁻³·h⁻¹. The materials were composted for 15 days and manually mixed on the 3rd and 7th days.

2.4. Sample collection and analytical methods

Representative samples (300 g) of compost were taken on days 0, 3, 5, 7, 10 and at the end of the composting period from each treatment. A 30 g subsamples was used immediately for moisture content measurement. The remaining sample was separated into two equal parts: one half was air dried, milled with mixer mill (Retsch MM400, Germany) and passed a 0.15 mm mesh screen for total carbon (TC), total nitrogen (TN), total sulfur (TS) and ash analysis while the other was stored at 4 °C for measurement of pH, electric conductivity (EC), germination index (GI) and inorganic nitrogen (NH₄⁺-N, NO_x⁻-N).

Moisture content was determined in triplicate by drying samples at 70 ± 5 °C to a constant weight. Ash was measured after combustion at 550 °C in a muffle furnace for 2 h. pH and EC were measured by adding water to the samples at a solid to water ratio of 1:10(w/v) and using an EC meter (DDS-11A, China) and a pH meter (PHS-3C, China). 20 radish seeds were placed homogeneously in a sterile petri dish with 10 ml compost extract and a filter paper and incubated at 20 °C. Deionized water was used as a control. Germination rates and root length were measured after 48 h. GI was calculated using the formula of Yang et al. (2013). Inorganic nitrogen was extracted with 2 mol·L⁻¹ KCl (solid to KCl

Table 1
Properties of compost feedstocks and mixture.

Feedstock	Moisture (%) ^a	Ash (%) ^b	Total carbon (g·kg ⁻¹) ^b	Total nitrogen (g·kg ⁻¹) ^b	Total sulfur (g·kg ⁻¹) ^b
Pig manure	69.5 ± 0.17	29.94 ± 1.06	353.3 ± 10.0	25.6 ± 0.8	5.7 ± 0.1
Corn stalks	9.4 ± 0.99	13.36 ± 1.39	431.5 ± 7.8	10.2 ± 0.7	3.8 ± 0.1
Mixture	62.14 ± 0.79	24.41 ± 1.14	375.7 ± 16.0	21.8 ± 1.2	5.0 ± 0.1

Values are means ± standard deviation from three replications.

^a Wet weight basis.

^b Dry weight basis.

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