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# Emission potential of volatile sulfur compounds (VSCs) and ammonia from sludge compost with different bio-stability under various oxygen levels

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## ABSTRACT

Volatile sulfur compounds (VSCs) and ammonia from biowaste-derived residues is influenced by both the degree of bio-stability and atmosphere of oxygen level (i.e., either anaerobic, aerobic or anoxic conditions). By means of odor emission potential (OEP) test, present study directly examined how these two factors jointly affected the emissions of different odorous compounds from sludge compost. Results reveal that (1) the cumulative amount of ammonia and VSCs ranged from 0.08 to 0.38 mg/g-DM and 1.92 to 6.42 µg-S/g-DM, respectively. (2) High degree of bio-stability and oxygen level decreased the emission rates and cumulative amounts of ammonia, carbonyl sulfide, carbon disulfide, and especially methylmercaptan, who was even extinguished in the late stage. (3) Dimethyl sulfide and dimethyl disulfide showed no decline trend with increasing of bio-stability degree and oxygen level, suggesting their formation was mainly abiotic; cumulative amount of dimethyl disulfide was even higher under an atmosphere of high oxygen level. (4) Methylmercaptan was the dominant contributor to odor nuisance. The olfactory threshold of ammonia, dimethyl sulfide and dimethyl disulfide also exceeded their limited value. Hence, these odor compounds are priority when came to odor management of sludge compost. Overall, high stability degree and oxygen level alleviated the emission of ammonia, carbonyl sulfide, carbon disulfide and methylmercaptan, while the abatement of dimethyl sulfide and dimethyl disulfide should lie in controlling oxygen level in a certain range rather than extremely high oxygen level. Methylmercaptan can be regarded as an alternative indicator of the degree of bio-stability.

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## 1. Introduction

The treatment of sewage sludge is a significant challenge in contemporary society (Fytili and Zabaniotou, 2008; USEPA, 1999; Yang et al., 2015). Generally, composting is considered an efficient, economically viable, and environmentally sustainable method that is widely utilized for sewage sludge management (Cabañas-Vargas et al., 2013; Külcü and Yaldiz, 2014; USEPA, 2002). Unfortunately, a significant odor problem originating from the deconstruction of

organic matter can arise from sludge composting such as odor nuisance originating from the deconstruction of organic matter. Odor compounds can cause negative environmental problems and have a substantial impact on the well-being of humans (Caro and Gallego, 2009; Mustafa et al., 2017). Unpleasant odor emissions during sludge composting usually contain ammonia (NH<sub>3</sub>) (Chen et al., 2011; Meng et al., 2016; Pagans et al., 2006; Zigmontiene and Zuokaite, 2010) and volatile sulfur compounds (VSCs), which have gain special attention recently due to their low olfactory coefficient (He et al., 2009; Kim et al., 2014; Maulini-Duran et al., 2013; Zhu et al., 2016).

NH<sub>3</sub> is regarded as a dominant pollutant in exhaust gas from composting, which has a significant effect on health and the well-being of nearby residents. This compound derives from the ammonification which is responsible for the transformation of organic nitrogen into NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup> (Guardia et al., 2008). VSCs are an essential group of compounds responsible for the generation

**Abbreviations:** COS, Carbonyl sulfide; CS<sub>2</sub>, Carbon disulfide; DMS, Dimethyl sulfide; DMDS, Dimethyl disulfide; DN, Dissolved nitrogen; DOC, Dissolved organic carbon; H<sub>2</sub>S, Hydrogen sulfide; MC, Moisture content; MM, Methylmercaptan; NH<sub>3</sub>, Ammonia; TOC, Total organic carbon; VOSCs, Volatile organic sulfur compounds; VSCs, Volatile sulfur compounds.

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of offensive odors during organic waste composting (Zang et al., 2016, 2017; Zhang et al., 2016; Zhu et al., 2016). They are produced as a result of the bacterial reduction of sulfate and decomposition of sulfur-containing organic constituents under anaerobic conditions. Although the concentrations of VSCs are limited, their olfactory thresholds are so low (Yoshio, 2004) that they have a significant contribution to the malodor problem with compost.

The formation of malodor compounds is affected by many factors, including degree of bio-stability and oxygen content in composting pile. Bio-stability is associated with several aspects of material properties (e.g., moisture content, the mass ratio of carbon to nitrogen (C/N), pH, and temperature). In literature, the effects of bio-stability on odor emissions are usually reflected in the different fermentation stages of composting. Generally, the composting process is an aerobic, solid state biological process consisting of a high rate active phase, and a curing phase. Odor emissions appearing in the active phase are characterized by an intense microbial activity leading to the decomposition of the readily biodegradable materials until biological stability is reached (Adani et al., 1997; D'Imporzano et al., 2008; Hsu. and Lo., 1999; Orzi et al., 2010). Chen et al. (2011) identified that hydrogen sulfide ( $H_2S$ ) was mainly produced during the first 40 h of a large scale sewage sludge composting facility, and  $NH_3$  emissions were reported to be the highest during the first several days. Results obtained by (Maulini-Duran et al., 2013; Scaglia et al., 2011; Wu et al., 2010; Zang et al., 2017; Zhang et al., 2013) demonstrated that VSCs were mainly produced in the early stage of composting of municipal solid waste (MSW), food waste, and sludge.

Oxygen level, another ineligible factor in the microbial niche dictates the metabolic pathways for the formation of volatile metabolites, therefore, playing an important role in the type and concentration of odor molecules. Guardia et al. (2008) concluded that the aeration rate, a parameter directly influencing oxygen levels, was a main factor affecting nitrogen dynamics since it can control ammonification reactions. Chen et al. (2011) found that  $H_2S$  production can be controlled as long as the volumetric oxygen content in composting pile higher than 14%. Furthermore, insufficient aeration is always considered as the main factor for VSCs, which are generally considered to be mainly produced under anaerobic conditions or incomplete aerobic fermentation (He et al., 2010; Zhang et al., 2013). Work done by Zhang et al. (2016) indicated VSCs were more significant at low aeration rates (0.1 L/kg-DM/min) relative to two other higher aeration rates (i.e., 0.2 and 0.3 L/kg-DM/min).

Unfortunately, most researches study the indirect influence of aeration or ventilation on odor molecules, rather than directly studying the influence of oxygen levels on the metabolic pathways for odor generation. Owing to the heterogeneity of pilot or large-scale compost piles and particles, the previously referenced studies obtained mixed output results from a bulk pile including aerobic, anoxic, and anaerobic zones, despite the fact that all piles were adequately aerated (D'Imporzano et al., 2008; He et al., 2000; Wu et al., 2010; Zang et al., 2017). Therefore, it makes the dependence of odor emissions on aeration uncertain. Some researchers found that VSCs were mainly generated under anaerobic condition (Zang et al., 2017; Zhang et al., 2016), however, Higgins et al. (2006) obtained opposite results related to the formation of some VSCs expected to mainly formed under aerobic conditions. Hence, it is difficult to understand whether offensive odor molecules are produced under aerobic or anaerobic conditions, even when composting materials are completely ventilated. It is then necessary to explore odor release patterns under various oxygen levels in conjunction with evaluating the degree of bio-stability with a focus on understanding the potential implications on the storage and land application of compost.

Therefore, with the goal of better understanding the odor generation mechanisms to define favorable conditions for odor management, the present study aimed to investigate the formation profiles of odorous VSCs and  $NH_3$  from sewage sludge compost with different degrees of bio-stability and under conditions with three redox levels by changing the inlet oxygen content.

## 2. Materials and methods

### 2.1. Sludge composting

In order to obtain sludge composts with different degrees of bio-stability, sludge composting was conducted with dewatered sewage sludge using rice straw as a bulking agent. Dewatered sewage sludge was obtained from Quyang Municipal Wastewater Treatment Plant in Shanghai, China. This plant treats approximately 75,000 m<sup>3</sup>/d of wastewater (93% domestic and 7% industrial sewage), using an anaerobic–anoxic–oxic process. Rice straw was shredded to a particle size less than 5 mm and then mixed with dewatered sewage sludge at a mass ratio of 2:1 (sludge:straw) on a wet basis (Zhao et al., 2011).

The mixture was put in a 150 L stainless-steel vessel with a diameter of 0.45 m and height of 1.2 m (Fig. 1a). The vessel was thermally isolated with a vacuum to avoid heat loss. A perforated plate was fitted at the bottom of the vessel to support the added materials, allow for the removal of leachate, and to facilitate ventilation. Three orifices were set at the bottom of the vessel, separately for vacuum, ventilation, and leachate removal. Two orifices were situated at the top of vessel for air renewal and to mount temperature sensors for the materials located at the middle and top.

No water was added during the composting process. Ambient, top, and middle temperatures of the composting pile were recorded continuously. The composting material was turned and sampled on days 6, 12, and 22. The collected samples, named “A”, “B” and “C”, respectively, were used for subsequent odor emission potential tests and characterization.

### 2.2. Odor emission potential (OEP) test of composts

Sludge composts of different degrees of bio-stability were tested for their odor emission potential under atmospheres of different volumetric oxygen levels (3.4%, 7.8%, and 20.0%, named “L”, “M” and “H”, respectively). These tests were carried out in 1.5 L Erlenmeyer flasks for 15 days. Each scenario was tested in duplicate.

Sample of approximately 30 g of compost (wet basis) was spread evenly on the bottom of the flask, as showed in Fig. 1b. A gas cylinder containing the mixture of  $O_2$  and  $N_2$  with the proportion of  $O_2$  controlled at the intended value was used. The mixed gas was supplied at a frequency of 12 s run/3 min stop through a time relay (ZYS-S, Shanghai Toone Electronic Co., China) and a flow rate of 0.1 L/min. A micro-vacuum pump (FAA4002-24V, Chengdu Qihai Electromechanical Manufacturing Co., China) and a gas-flow meter (LZB-10, Shanghai Instrument Co., China) were used for ventilation. The off-gas was collected in a 10 L black Tedlar® bag and then analyzed for odor compounds, carbon dioxide ( $CO_2$ ), and gas volume. The composts after each test were analyzed for physio-chemical characteristics.

### 2.3. Analytical methods for solid composts

Moisture content (MC), volatile solid (VS) of composts, pH, electrical conductivity (EC), dissolved organic carbon (DOC), dissolved

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