



## Influence of bulking agents on CH<sub>4</sub>, N<sub>2</sub>O, and NH<sub>3</sub> emissions during rapid composting of pig manure from the Chinese Ganqinfen system\*

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**Abstract:** Mismanagement of the composting process can result in emissions of CH<sub>4</sub>, N<sub>2</sub>O, and NH<sub>3</sub>, which have caused severe environmental problems. This study was aimed at determining whether CH<sub>4</sub>, N<sub>2</sub>O, and NH<sub>3</sub> emissions from composting are affected by bulking agents during rapid composting of pig manure from the Chinese Ganqinfen system. Three bulking agents, corn stalks, spent mushroom compost, and sawdust, were used in composting with pig manure in 60 L reactors with forced aeration for more than a month. Gas emissions were measured continuously, and detailed gas emission patterns were obtained. Concentrations of NH<sub>3</sub> and N<sub>2</sub>O from the composting pig manure mixed with corn stalks or sawdust were higher than those from the spent mushroom compost treatment, especially the sawdust treatment, which had the highest total nitrogen loss among the three runs. Most of the nitrogen was lost in the form of NH<sub>3</sub>, which accounts for 11.16% to 35.69% of the initial nitrogen. One-way analysis of variance for NH<sub>3</sub> emission showed no significant differences between the corn stalk and sawdust treatments, but a significant difference was noted between the spent mushroom compost and sawdust treatments. The introduction of sawdust reduced CH<sub>4</sub> emission more than the corn stalks and spent mushroom compost. However, there were no significant differences among the three runs for total carbon loss. All treatments were matured after 30 d.

**Key words:** Organic waste, Composting, Bulking agent, Gaseous emission, Pig manure

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### 1 Introduction

China's agricultural industry has been intensified significantly since the early 1980s. However, intensive agricultural activities generate large

amounts and different types of organic waste (Dias *et al.*, 2010). Therefore, the pressure to properly handle the organic waste has been mounting in China. Composting, one of the most effective technologies for treating organic waste, can reduce the mass and volume of the waste, destroy the pathogens and weed seeds, and provide organic fertilizers as valuable end-products for agriculture. However, harmful gases emitted from mismanagement of the composting process have caused severe environmental problems (He *et al.*, 2000; Fukumoto *et al.*, 2003; Szanto *et al.*, 2007). Ammonia (NH<sub>3</sub>), among others, can cause acidification and nutrient loss, which is also one of the

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principal malodorous compounds produced in composting. Nitrous oxide ( $\text{N}_2\text{O}$ ) and methane ( $\text{CH}_4$ ) are both greenhouse gases, which effect global warming potentials over a 100-year time horizon of 23 times for  $\text{CH}_4$  and 296 times for  $\text{N}_2\text{O}$  per mole of gas compared to  $\text{CO}_2$  (Jiang *et al.*, 2011; Shen *et al.*, 2011).

The emissions result from physical and biological reactions (El Kader *et al.*, 2007). Other than  $\text{CO}_2$ , ammonia gas is the main compound found in exhaust gases when organic wastes are composted (Beck-Friis *et al.*, 2001). Temperature, pH, and initial ammonium content are the most important parameters affecting the amount of nitrogen emitted as ammonia (Pagans *et al.*, 2006). The pattern of ammonia emissions is greatly dependent on the process temperature (Pagans *et al.*, 2006). Maintaining an alkaline pH during the thermophilic phase of composting may lead to substantial losses of gaseous ammonia (Jarvis *et al.*, 2009). Furthermore, the rate of intermittent aeration is an important factor influencing gas emissions during composting, and the emission of ammonia was reduced with a decrease in the aeration rate (Shen *et al.*, 2011). A lower C/N ratio is preferable to increasing the  $\text{NH}_3$  emissions, and the moisture content can affect the ammonia emission during composting, but not significantly (Jiang *et al.*, 2011).  $\text{N}_2\text{O}$  released from nitrification or denitrification can be the end-products of either ammonium oxidation or incomplete denitrification (Beck-Friis *et al.*, 2000).  $\text{N}_2\text{O}$  emission was a function of the compost age, pile depth, temperature, and water filled pore space (Czepiel *et al.*, 1996). The static system showed that higher  $\text{N}_2\text{O}$  emissions were due to the prevalence of anaerobic regions in combination with a high ammonia content and the absence of readily available carbon (Szanto *et al.*, 2007). In addition, the chemodenitrification of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$  plays an important role in the early  $\text{N}_2\text{O}$  emission (Hao *et al.*, 2001).  $\text{CH}_4$  is produced through biodegradation of the organic fraction of waste under anaerobic conditions (He *et al.*, 2000), which is found to have a high rate in the composting heap center during the thermophilic phase (Sommer and Moller, 2000). A high aeration rate can reduce the amount of  $\text{CH}_4$  emitted during composting (Jiang *et al.*, 2011; Shen *et al.*, 2011). Meanwhile, there is a possibility of changing the gas emission rates simply by changing the scale of the compost pile (Fukumoto *et al.*, 2003). Traditional

composting can take several months, but land shortage coupled with a large volume of animal manure in China requires more effective treatment (Liu *et al.*, 2011). Using composting technologies such as forced aeration and windrow turning can result in a shorter composting time (Szanto *et al.*, 2007). Therefore, we selected forced aeration that can accelerate the composting process and is widely used in China (Jiang *et al.*, 2011).

Organic manure cannot be composted alone due to the high moisture content and low C/N ratio, especially pig manure. This is the case even for its mechanically separated solid fraction (Imbeah, 1998). Therefore, the addition of a bulking agent is necessary to compost the separated solid fraction of pig manure (Nolan *et al.*, 2011). A bulking agent is the material that adjusts the C/N ratio, provides optimum free air space (FAS), and regulates the water content of the waste to be composted (Gea *et al.*, 2007; Kato and Miura, 2008; Iqbal *et al.*, 2010; Jolanun and Towprayoon, 2010; Doublet *et al.*, 2011), which are usually fibrous with carbonaceous material (Iqbal *et al.*, 2010). The bulking agent represents a large proportion of the composting mixture as a source of carbon and energy for micro-organisms (Adhikari *et al.*, 2009). The composting processes are affected by the type of bulking agent used, its particle size, and the proportion of bulking agent in the composting mixture (Atkinson *et al.*, 1996; Gea *et al.*, 2007; Chang and Chen, 2010). The addition of biodegradable C fractions will balance the initial C/N ratio of the mixture and reduce the N losses during the composting process (Dias *et al.*, 2010). The type of bulking agent has a significant effect on N and C losses caused by volatilization (Barrington *et al.*, 2002), and the bulking agents with a high content in lignocellulose have a lower microbial degradability and lead to higher nitrogen losses (Martin *et al.*, 1993). In other words, a higher bulking agent content in the composting mixture increases the water absorption capacity and the composting rate, reduces the composting and acidification time, and lowers the pH value when food waste is composted with sawdust as the bulking agent (Chang and Chen, 2010). Numerous bulking agents, including sawdust, rice husk, and rice bran, were used extensively in Asian waste composting studies (Chang and Chen, 2010) for the composting of animal manure and other wet

feedstocks. Although most of these studies used several parameters for evaluating the composting performance, only a few studies have been conducted on the effect of bulking agent characteristics on  $\text{NH}_3$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  emissions during rapid composting.

In light of the above considerations, the objective of this investigation was to evaluate the influence of bulking agents (corn stalks, spent mushroom compost, and sawdust) on  $\text{NH}_3$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  emissions for composting with pig manure using rapid composting technology.

## 2 Materials and methods

### 2.1 Composting materials and experimental design

Three composting experiments were performed in insulated fermenters (Fig. 1) using the same pig manure mixed with three different bulking agents: corn stalks, spent mushroom compost, and sawdust. The pig manure was collected from the ZHOU Chun-sheng Pig Farm (Shujiatuo Town, Haidian

District, Beijing, China), where the Ganqingfen system was used for manure collection (there was a separate collection of the manure from the concrete floor before flushing the urine with water). Corn stalks, taken from Shangzhuang Station, China Agricultural University, were cut into 1–5 cm fragments. Spent mushroom compost, the solid residue generated at the end of edible fungus cultivation, was collected from Fangshan County, Beijing, China. The sawdust was obtained from fresh wood cuts from local sawmills. The mixing ratio was adjusted according to the same C/N ratio (18) of the three mixtures, and the initial moisture content was adjusted to around 65%. All mixtures were elaborated to identify the influence of each bulking material. Table 1 presents the physicochemical properties of the raw materials.

The volume of composting reactors is about 60 L (inner diameter, 0.36 m; height, 0.6 m; composting materials were added to a height of 0.5 m from the bottom of the reactor), with a temperature sensor connected to a computer and controlled by a C-LGX

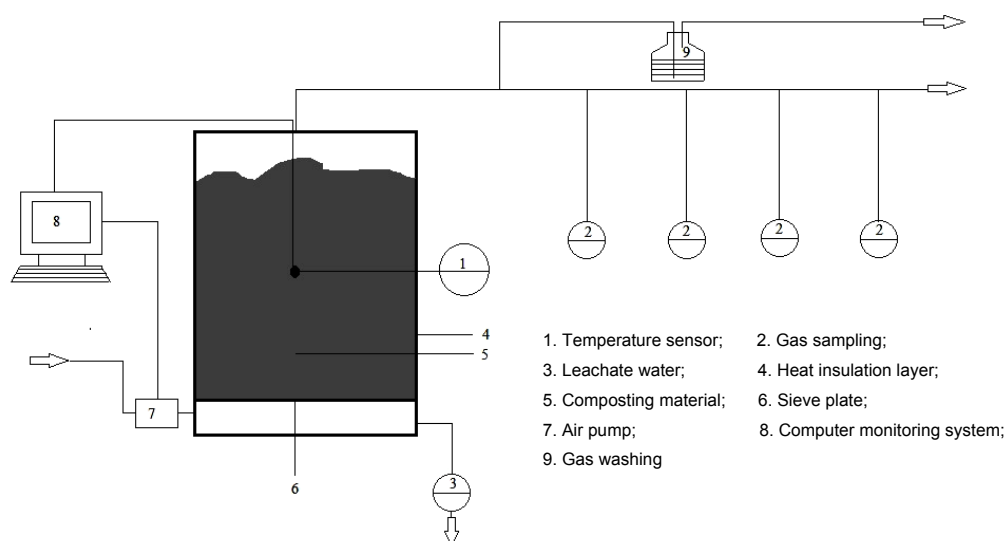


Fig. 1 Sketch map of the closed composting vessel

Table 1 Physicochemical properties of the organic materials used for the composting mixtures

Material	pH	Moisture (%)	TOC (g/kg)	Total N (g/kg)	C/N
Pig manure	8.70 (0.22)	75.0 (0.48)	350.0 (3.23)	27.0 (0.73)	12.9 (0.24)
Corn stalk	7.50 (0.08)	9.3 (0.06)	419.0 (2.98)	9.9 (0.25)	4.2 (0.18)
Sawdust	7.20 (0.09)	20.6 (0.12)	454.0 (1.35)	3.0 (0.09)	151.3 (0.89)
Spent mushroom compost	6.51 (0.42)	46.9 (0.32)	351.0 (3.97)	16.0 (0.30)	21.9 (0.49)

TOC: total organic carbon. Values are expressed as mean of triplicates (dry weight basis), values in parentheses are standard error

program designed by our laboratory, so that the aeration can be automatically controlled by time or temperature. The air flow under continuous aeration was 0.16 m<sup>3</sup>/h. Composting was performed throughout one month with turning on Days 5, 7, 14, and 22. Water was added to keep the moisture content at 55%–65% in the reactor during turning, and solid samples were taken. All samples were weighed before being introduced, as was each turning, and the mixtures and reactors were eventually sampled and re-introduced into the reactors, which were weighed again. The mass losses related to sampling and turning were taken into account in the overall mass balance of composting. The leachate was not measured or collected for analysis during the process. The design of the experiment is shown in Table 2.

**Table 2 Design of experiment**

Group	Pig manure (kg)	Corn stalk (kg)	Spent mushroom compost (kg)	Sawdust (kg)
CS	23.70	3.95		
SMC	13.57		15.08	
SWD	25.00			5.00

## 2.2 Compost sampling and analytical methods

Solid samples of the compost were collected four times during the experimental period (on Days 0, 5, 22, and 30) by mixing six subsamples taken from different locations in the reactor. The samples were divided into two parts, one part being analyzed immediately, and the other air-dried before being passed through a 1-mm sieve. Ammonia gas released during composting was captured in a boric acid wash bottle (sampling lasted 30 min) and was titrated using sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 0.1 mol/L), while O<sub>2</sub> was monitored using an oxygen sensor (DH6511A, China). Gas samples were taken from the gas sampling port and analyzed for CO<sub>2</sub> using a gas chromatograph (GC-9900, China). N<sub>2</sub>O and CH<sub>4</sub> were analyzed using a gas chromatograph (3420A, Beifen, China). N<sub>2</sub>O was examined using an electron capture detector at the following temperatures: detector 280 °C, injector 120 °C, and column 80 °C, while CH<sub>4</sub> was examined using a flame ionization detector at the following temperatures: detector 200 °C, injector 120 °C, and column 80 °C.

The total nitrogen (N) was analyzed using the

Kjeldahl method (Kimberly and Roberts, 1905). Samples were analyzed for organic carbon by oxidation with potassium dichromate (K<sub>2</sub>CrO<sub>7</sub>) (Yeomans and Bremner, 1988). Results are expressed in terms of dry matter. The moisture contents of different samples were determined based on weight loss at 105 °C and evaluating the constant weight at the end. Inorganic nitrogen (NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N) in the samples was extracted with 2 mol/L KCl at a 1:10 soil:water (w/v) ratio, and then analyzed using an auto analyzer (Auto Analyzer 3, Seal, Germany). To analyze the pH, electrical conductivity (EC), and germination index (GI), a 20-g fresh sample was extracted with 200 ml distilled water by stirring for 1 h and then centrifuged at 4000 r/min. The pH was then measured using a pH meter, while EC was measured using a DDS-12A conductivity meter.

Seed germination was used to assess the phytotoxicity (Sellami *et al.*, 2008): 20 *Lepidium sativum* seeds were evenly distributed on filter paper in Petri dishes (diameter 10 cm) and moistened with 5 ml compost extract. A total of 5 ml of distilled water replaced the extract as a control, and then, the dishes for each sample were incubated at 25 °C for 3 d. The number of germinating seeds and root length were measured at every treatment. GI was calculated as  $GI (\%) = \frac{\text{Seed germination of compost sample} \times \text{root length of compost sample}}{\text{seed germination of control} \times \text{root length of control}} \times 100\%$ .

## 2.3 Statistical analysis

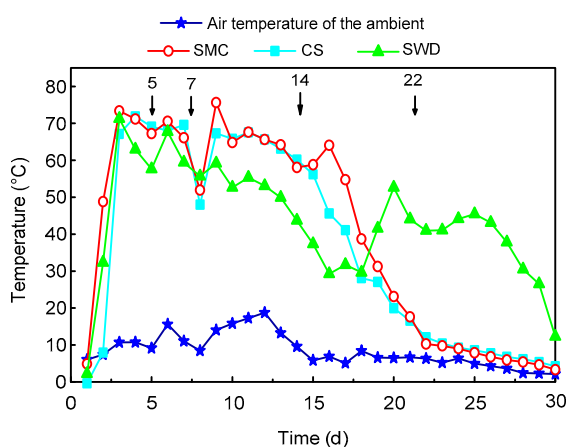
SAS 9.1 for Windows was used for all statistical analyses. One-way analysis of variance (ANOVA) was performed and shown for chemical parameters to compare the variations of different composting treatments. Data are reported as the mean and standard error of three replicates.

## 3 Results and discussion

### 3.1 General description of the composting progress

The changes in the compost temperature for all runs are shown in Fig. 2. The temperatures of all the runs increased rapidly after the first day; the peak temperatures (>55 °C) of the CS and SWD runs were obtained by Day 3, but that for the SMC run was obtained by Day 9, which shows that the temperature

increase during composting is due to the heat produced by aerobic degradation of the organic matter (Szanto *et al.*, 2007). The interruptions in the temperature curve by Day 7 due to a turning and a rapid recovery of thermophilic conditions were observed on the following day. Compost temperatures in the CS and SMC runs showed a downward trend after Day 17, and further turning did not result in a rapid temperature increase. However, the temperature in the SWD run increased rapidly after the fourth turning and then decreased gradually. The nature of bulking agents influences the time needed to reach similar organic matter (OM) stability and the biochemical evolution of OM (Doublet *et al.*, 2011). Sawdust had the higher content of lignocellulose materials and low available carbon sources for microorganism than corn stalk and spent mushroom compost, and therefore, temperatures in the SWD run were lower than others in the first 17 d. However, after that, turning activities made the composting materials more homogeneous especially the easily degradation lignocelluloses of sawdust, which made the activities of microbes increase after Day 17 in the SMC run. However, after the fourth turning, the easily degradation lignocellulose was exhausted. The temperature performance in all the runs fulfilled the Chinese National Standard (GB 7959-87: to maintain a temperature above 50–55 °C for 5–7 d) for sanitation in the composting application into the soil in China. The ambient temperature, which fluctuated during the experiment, was averaged at about 9 °C.



**Fig. 2** Temperature changes during composting by different treatments

Arrows show the turning days

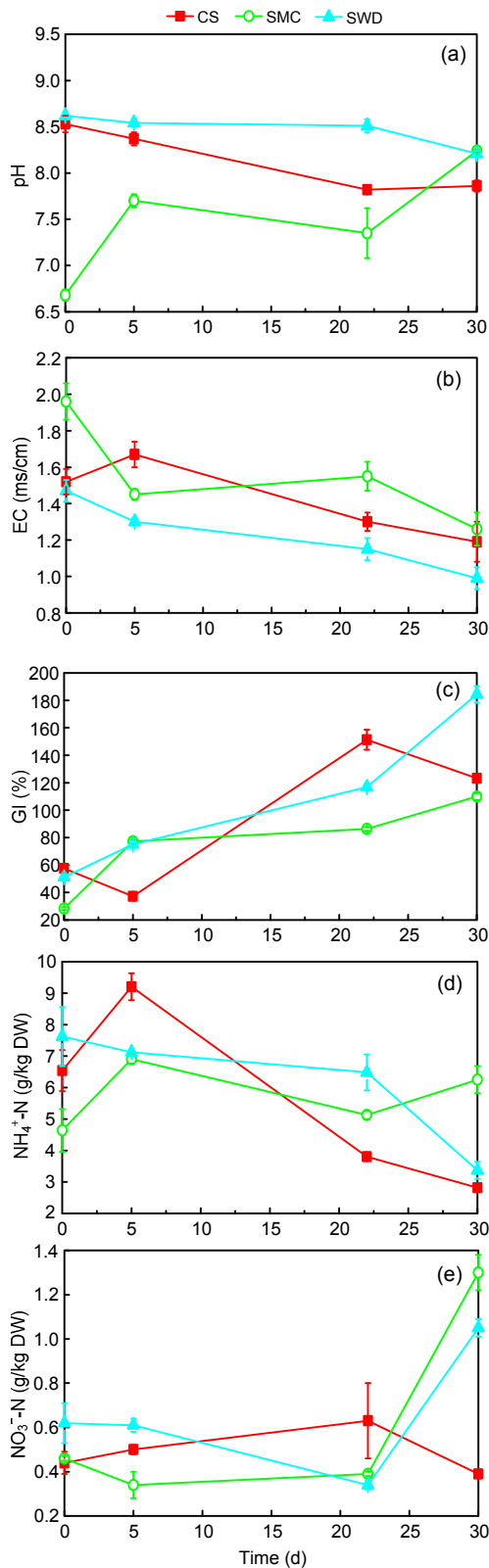
The changes in the absolute contents of total organic carbon (TOC) and total nitrogen in composting different runs are shown in Table 3. The initial TOC and TN absolute contents were influenced by the characteristics of the bulking agent used in the composting. TOC content varied from 1.41 to 3.51 kg, with the highest TOC value found in the SMC run (3.51 kg). Most of the degradation occurred after Day 5. The extractable nitrogen ( $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N) contents are shown in Fig. 3.  $\text{NH}_4^+$ -N increased in the first 5 d in the CS and SMC runs (Fig. 3d), possible because organic N changed to  $\text{NH}_4^+$ -N via ammonification (Ren *et al.*, 2010), and then decreased later on, which caused by  $\text{NH}_3$  emission and nitrification (Jiang *et al.*, 2011). Compared with  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N was always at a very low level (<1.3 g/kg DW) in the process (Fig. 3e).

The parameters pH and EC were also very important for the evolution of the composting process. The pH of the three runs was maintained at 6.68–8.62 during the composting process (Fig. 3a). A noticeable decrease in the pH of the CS and SWD runs was observed in the degradation progress, which could have

**Table 3** Chemical analysis of the organic wastes at different composting time

Composting time (d)	TOC (kg)	Total N (g)	C/N
CS pig manure: corn stalk			
0	2.89±0.03 <sup>a</sup>	160.62±0.12 <sup>c</sup>	18.0±0.32
5	2.65±0.02 <sup>a</sup>	157.27±0.10 <sup>b</sup>	16.8±0.14
22	1.71±0.01 <sup>b</sup>	132.24±0.13 <sup>a</sup>	12.9±0.18
30	1.53±0.06 <sup>c</sup>	129.10±0.08 <sup>a</sup>	11.9±0.17
SMC pig manure: spent mushroom compost			
0	3.51±0.07 <sup>a</sup>	194.74±0.07 <sup>d</sup>	18.0±0.26
5	3.01±0.09 <sup>b</sup>	188.79±0.15 <sup>c</sup>	15.9±0.32
22	1.95±0.01 <sup>c</sup>	178.47±0.11 <sup>b</sup>	10.9±0.10
30	1.69±0.04 <sup>d</sup>	173.18±1.02 <sup>a</sup>	9.8±0.16
SWD: pig manure: sawdust			
0	3.10±0.06 <sup>a</sup>	172.93±0.97 <sup>d</sup>	17.9±0.08
5	2.84±0.02 <sup>b</sup>	167.68±1.04 <sup>c</sup>	16.9±0.12
22	1.83±0.04 <sup>c</sup>	130.99±0.86 <sup>b</sup>	14.0±0.15
30	1.41±0.01 <sup>d</sup>	110.70±1.05 <sup>a</sup>	12.7±0.43

Values are expressed as mean±standard error of triplicates (dry weight basis). Means with different subscripts in the same column for the same trial were significantly different ( $P<0.05$ )



**Fig. 3** Changes of pH (a), EC (b), GI (c),  $\text{NH}_4^+\text{-N}$  (d), and  $\text{NO}_3^-\text{-N}$  (e) during different composting treatments

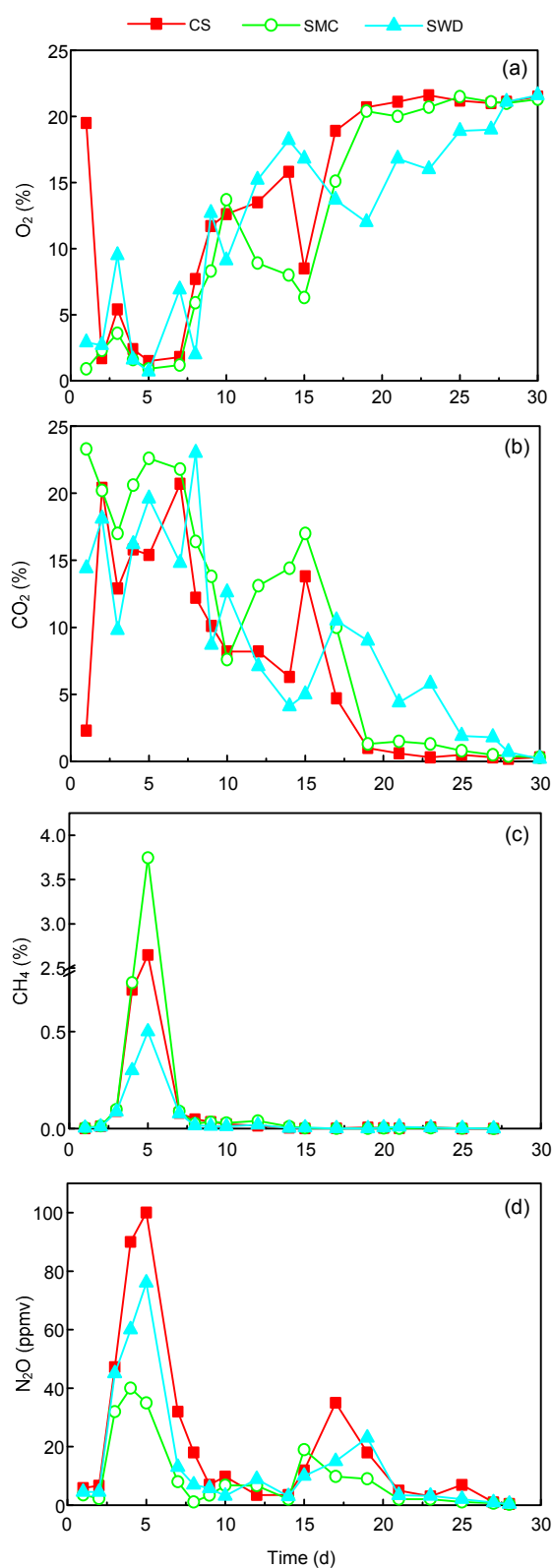
resulted from organic acids produced by incomplete oxidation of the organic matter (Liu *et al.*, 2011). Further, the large quantities of  $\text{CO}_2$  that are released during the composting process might be responsible for the decrease in pH (Huang *et al.*, 2004). After composting, the SMC and SWD runs had a higher pH value compared to the CS run, and the pH analysis of all runs indicated alkaline conditions.

EC and GI were used to test the salinity and phytotoxicity of the compost (Shen *et al.*, 2011). EC values of the CS, SMC, and SWD runs from 1.52, 1.96, and 1.47 ms/cm decreased to 1.19, 1.26, and 0.99 ms/cm, respectively, during the composting process (Fig. 3b), lower than 3.00 ms/cm, which was identified as the limit for safe growth of plants (García *et al.*, 1991). At the end of the experiment, the GI of all treatments was higher than 80%, and consequently the mixtures were mature (Fig. 3c).

### 3.2 Influence of bulking agents on kinetics of $\text{O}_2$ and $\text{CO}_2$ concentrations and emissions of $\text{N}_2\text{O}$ and $\text{CH}_4$

The  $\text{O}_2$  and  $\text{CO}_2$  concentrations in the outlet of the composting reactors are shown in Figs. 4a and 4b, respectively. The decrease in  $\text{O}_2$  was accompanied by an increase in  $\text{CO}_2$ . One-way ANOVA for  $\text{CO}_2$  concentrations showed no significant differences among the three runs ( $F=1.07$ ,  $P=0.3493$ ). For the three runs, oxygen concentration decreased rapidly to 1.7%, 2.3%, and 2.7% by Day 2 in the CS, SMC, and SWD runs, respectively. Oxygen concentration in the CS and SMC runs was maintained at a low level before the second turning, while it increased gradually after the third turning. The low  $\text{O}_2$  level inside the composting reactors indicated that these systems had more anaerobic regions, which were confirmed by its high  $\text{CH}_4$  content. The result was similar to the finding of Szanto *et al.* (2007). However, the pattern of  $\text{O}_2$  concentrations in the SWD run was higher than those in the CS and SMC runs during the first 17 d. It reached 18.2% by Day 14 and then decreased until the fourth turning. One-way ANOVA showed no significant differences among the three runs ( $F=0.48$ ,  $P=0.6234$ ).

$\text{CH}_4$  content from all runs was high in the first several days with low  $\text{O}_2$  concentration, but it was at a very low level, and there were no significant differences among the three runs during the rest of the



**Fig. 4** Changes of concentrations of O<sub>2</sub> (a), CO<sub>2</sub> (b), CH<sub>4</sub> (c), and N<sub>2</sub>O (d) in different composting treatments ppmv: parts per million by volume

composting time (Fig. 4c). The emission patterns of CH<sub>4</sub> in this study resembled those reported by other works (Osada *et al.*, 1997; Fukumoto *et al.*, 2003; Shen *et al.*, 2011). The maximum value of CH<sub>4</sub> concentration appeared on the fifth day, reaching 2.65%, 3.75%, and 0.5% for the CS, SMC, and SWD runs, respectively. The high CH<sub>4</sub> emission demonstrated the involvement of anoxic/anaerobic micro-organisms (He *et al.*, 2000). The higher CH<sub>4</sub> value of the SMC run should be explained in two aspects. First, CH<sub>4</sub> was produced through degradation of soluble lipids, carbohydrates, organic acids, and proteins (Fukumoto *et al.*, 2003), which are limited to strict anaerobic conditions (Jiang *et al.*, 2011). Thereby, the higher value of CH<sub>4</sub> concentrations in the SMC run by Day 5 was probably due to the large amount of organic acids inferring from the pH value of the SMC run. Second, the characteristics of the bulking agent in the starting mixture may be related to the amount of released CH<sub>4</sub>. The spent mushroom compost used in the experiment contains particles with diameters of some centimeters, in which oxygen cannot infiltrate into the center. One-way ANOVA showed no significant differences among the three runs ( $F=0.52$ ,  $P=0.5961$ ).

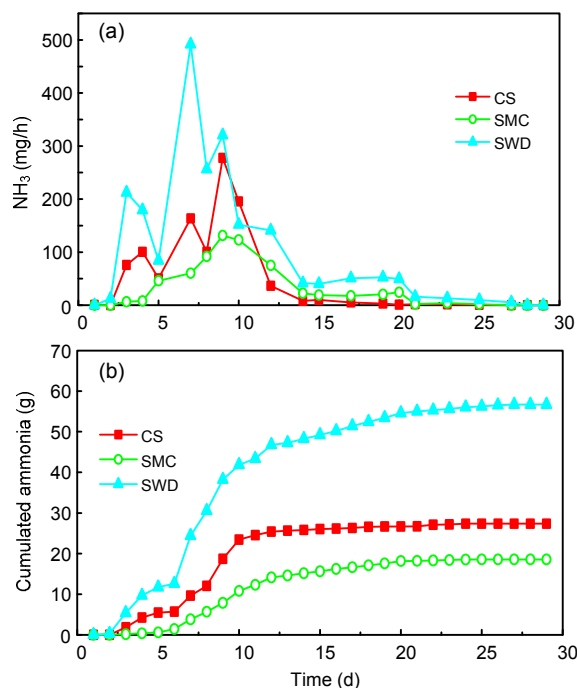
The N<sub>2</sub>O emissions composting in all the runs started and increased until the first turning (Fig. 4d). The nitrification process would not have occurred because autotrophic nitrifier activity ceases above 40 °C, and thus N<sub>2</sub>O would not have been generated from this step (Sanchez-Monedero *et al.*, 2001; Fukumoto *et al.*, 2003). Therefore, the emission of N<sub>2</sub>O in the early stages of composting was probably due to N<sub>2</sub>O produced in the manure before the pile was made (El Kader *et al.*, 2007). On the contrary, Angnes *et al.* (2013) showed that nitrification was not inhibited by high temperature. The highest N<sub>2</sub>O emissions of all runs were observed in the first week, similar to previous studies (He *et al.*, 2000; El Kader *et al.*, 2007; Shen *et al.*, 2011). There were two other high emission periods around the first and third turnings, which confirmed previous observations (Fukumoto *et al.*, 2003; El Kader *et al.*, 2007; Jiang *et al.*, 2011). They attributed this to the fact that the turning could enable the transportation of NO<sub>2</sub><sup>-</sup>/NO<sub>3</sub><sup>-</sup> from the aerobic portion (the surface layer of the pile) to the anoxic portion (the center of the pile), resulting in a homogeneous product. However, it may be

assumed that denitrification caused the highest  $N_2O$  emission as a result of the low available carbon levels, which was supported by the decrease of compost temperature and low  $CO_2$  emission, especially the third turning. The same result was observed by He *et al.* (2000), which reported that  $N_2O$  emission began to increase shortly after the depletion of available organic carbon. For the CS, SMC, and SWD runs, the maximum concentration of  $N_2O$  reached 100, 35, and 76 parts per million by volume (ppmv), respectively, on the fifth day. The higher  $N_2O$  concentration of the CS and SWD runs could be explained by the fact that the  $N_2O$  emission in the early stage of the composting resulted from the preparation of pig manure. Therefore, the amount of pig manure added in order to maintain the C/N ratio for the experiment could result in this phenomenon, in such an order as CS>SWD>SMC. The same trend has been found in the study of He *et al.* (2000), who observed that  $N_2O$  emission was linearly correlated with  $NO_2^-$  content in waste in the manure-applied treatments, while no significant correlation was observed in non-manure treatments. One-way ANOVA showed no significant differences among the three runs ( $F=1.31$ ,  $P=0.2772$ ).

### 3.3 Influence of bulking agents on emission of $NH_3$

$NH_3$  concentration in the outlets for all the runs was between 0 and 492 mg/h (Fig. 5a), and the emission patterns of ammonia showed a similar trend for the CS, SMC, and SWD runs (Fig. 5b). In general, ammonia emission surged with the rising temperature during the first 4 d. The first peak of the  $NH_3$  emission came on the fourth day and then decreased from Days 4 to 5 as the temperature dropped. The subsequent increase came after the first turning. The emission patterns were similar to that in the previous studies (Ren *et al.*, 2010; Jiang *et al.*, 2011; Shen *et al.*, 2011). A possible explanation for the ammonia emission pattern is that, at the initial stage of composting, degradation of large amounts of easily biodegradable organic compounds with high nitrogen content provokes a release of ammonia gas that is exponentially dependent on temperature, as is expected for free soluble ammonia (Pagans *et al.*, 2006).  $NH_3$  concentration had two other peaks on Days 7 and 10, which were sustained as the high temperature accelerated the emission of gaseous components inside the compost pile due to intensive

microbiological activity (Fukumoto *et al.*, 2003).  $NH_3$  emission at a relatively high level was observed during the composting process except on Day 10 in the SWD run. The maximum concentrations of  $NH_3$  reached 277.63, 131.39, and 491.57 mg/h for the CS, SMC, and SWD runs, respectively. Ammonia emissions are expected to depend strongly on the temperature and substrate pH (Komilis and Ham, 2006), due to the fact that ammonia emissions could begin to appear at thermophilic temperatures ( $>45^\circ C$ ) (Sommer and Moller, 2000), and based upon the data of the pH,  $NH_4^+-N$ , and the temperature in three runs, the  $NH_4^+-N$  potential is less negative when the  $NH_4^+-N$  content is higher. Therefore, the higher pH value could possibly result in higher ammonia emissions in this study, especially in the SWD run, which had the highest pH value that is influenced by the characteristic of the sawdust.  $NH_3$  emissions ceased in all the runs 28 d after composting began. One-way ANOVA showed no significant differences between the CS and SWD treatments, but a significant difference between the SMC and SWD treatments.



**Fig. 5 Emission of  $NH_3$  in different composting treatments**

Changes of the  $NH_3$  concentration (a) and cumulated ammonia (b)



### 3.4 Carbon and nitrogen balance during composting

The loss of carbon in the study was over 40% during the composting process (Table 4). For the SWD run, the TOC loss reached 54.40%, of which only 1.99% was emitted in the form of CH<sub>4</sub>, and it reached 8.55% and 8.40% in the CS and SMC runs, respectively (Fig. 6). The introduction of sawdust induced a higher biodegradability of the initial mixture than corn stalk and spent mushroom compost. Woody materials have a high content of lignin, which is extremely resistant to chemical and enzymatic degradation (Nolan *et al.*, 2011). Michel *et al.* (2004) and Hao *et al.* (2004) found a lower decomposition of the compost substrate when using bulking materials rich in lignin (woodchip and sawdust) compared to composting with straw, which had a lower lignin content. In this study, the higher degradability of the sawdust may have been associated with its larger surface area-to-mass ratio, and also with the fact that the small bulking agent particles create a real porous structure and a homogeneous porous size distribution inside the material that acts as an efficient oxygen diffuser (Gea *et al.*, 2007). However, an experiment with pig manure alone or pig manure with an inert bulking agent was not performed in this study, so it was not possible to evaluate the degradability of the bulking agents alone. Szanto *et al.* (2007) found that CH<sub>4</sub> emissions are due to complete anaerobic degradation of organic matter to CH<sub>4</sub> in the turned system lower than that in the static system when composting straw-rich pig manure. Fukumoto *et al.* (2003) showed that a large-scale compost pile increased the emission rate of gaseous components, especially N<sub>2</sub>O and CH<sub>4</sub>. The bulking agent influenced the C dynamics during composting, which was related to their own degradability, more

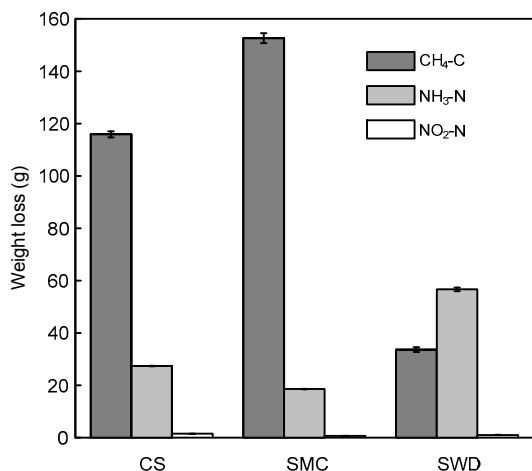
specifically, the nature and recalcitrance of their holocellulosic fractions (Doublet *et al.*, 2011), so that they could influence the biodegradability of organic matter during the composting process. However, CH<sub>4</sub> production was not only related to the content of carbohydrates (Fukumoto *et al.*, 2003), but more importantly to the physicochemical characteristics of the composting mixture (e.g., temperature, strict anaerobic condition, and compost structure) (Szanto *et al.*, 2007; Beck-Friis *et al.*, 2000; Jiang *et al.*, 2011). This was probably because sawdust used as the bulking agent in the study had a higher degradation rate of TOC whereas a lower emission rate of CH<sub>4</sub>-C for the composting of pig manure.

Considering carbon loss, the SWD run also showed a higher N loss (35.69%) than the CS (19.42%) and SMC (11.16%) runs (Table 4). During composting, the comparative carbon losses were larger than that of nitrogen. However, the small composting reactors and no replicated treatments of this experiment may limit the validity of the carbon and nitrogen balances. Nitrogen loss in the form of NH<sub>3</sub>-N reached 87.85%, 85.38%, and 92.1% for the CS, SMC, and SWD runs (Fig. 6), respectively, which was in accordance with other previous works (Ren *et al.*, 2010; Shen *et al.*, 2011). Some management strategies reducing NH<sub>3</sub> emission such as regulating the C:N ratio in the substrate, controlling temperature, controlling pH through chemical additives and controlling the microbial populations during the composting process, have been studied (Velasco-Velasco *et al.*, 2011). In this study, the use of corn stalks might have a positive effect on reducing N losses. Losses of nitrogen compounds in leachate were not accounted for, since they were negligible. The ammonia emission could be related to the effect of free air space, and it also depends on the carbon available for micro-organisms (El Kader *et al.*, 2007).

**Table 4 Carbon and nitrogen balance during composting**

Group	TOC					TN				
	$W_{\text{initial}}$ (kg)	$W_{\text{final}}$ (kg)	Loss <sup>a</sup> (%)	CO <sub>2</sub> -C (kg)	CH <sub>4</sub> -C (g)	$W_{\text{initial}}$ (kg)	$W_{\text{final}}$ (kg)	Loss <sup>a</sup> (%)	NH <sub>3</sub> -N (g)	N <sub>2</sub> O-N (g)
CS	2.89 (0.12)	1.53 (0.07)	46.97	1.13 (0.03)	115.91 (0.13)	160.37 (0.12)	129.22 (0.07)	19.42	27.36 (0.08)	1.48 (0.02)
SMC	3.51 (0.11)	1.69 (0.06)	51.77	1.54 (0.05)	152.61 (0.10)	194.84 (0.18)	173.11 (0.06)	11.16	18.56 (0.09)	0.68 (0.008)
SWD	3.10 (0.13)	1.41 (0.08)	54.40	1.51 (0.07)	33.61 (0.09)	172.39 (0.09)	110.86 (0.08)	35.69	56.67 (0.10)	1.06 (0.009)

<sup>a</sup> Nutrient loss is calculated as  $(W_{\text{initial}} - W_{\text{final}}) \times 100\% / W_{\text{initial}}$ . TOC and TN mentioned above are the absolute contents. Values are expressed as the mean (standard error) of triplicates on the dry weight basis



**Fig. 6** Loss of CH<sub>4</sub>-C, NH<sub>3</sub>-N, and NO<sub>2</sub>-N for different treatments during composting

Values are the mean±standard error of triplicates

Velasco-Velasco *et al.* (2011) reported that the addition of C readily available to microorganisms in the pre-composting process can significantly reduce NH<sub>3</sub> emission by up to 50%, but adding cellulose such as paper and straw did not show any significant differences on ammonia emission (Liang *et al.*, 2006). In this study, the N<sub>2</sub>O-N emissions were varied from 1.72% to 4.76% of the total nitrogen loss, and reached 4.76%, 3.12%, and 1.72% for the CS, SMC, and SWD runs, respectively (Fig. 6). These results were similar to those of Fukumoto *et al.* (2003) and Jiang *et al.* (2011). The bulking agent could increase the N availability by enhancing the N organization and limiting N losses by volatilization during composting (Doublet *et al.*, 2011), and the loss of N by volatilization was affected by the loss of C during the composting process rather than by the moisture content or aeration regime (Barrington *et al.*, 2002), and also by the initial C/N ratio of the composting mixtures and the presence of recalcitrant carbon fractions such as lignin (Goyal *et al.*, 2005). However, N<sub>2</sub>O produced by both nitrifiers and denitrifiers was optimized under microaerobic conditions (Czepiel *et al.*, 1996). Szanto *et al.* (2007) believed that N<sub>2</sub>O emissions became prevalent when readily available carbon was depleted, and it was also closely related to the forms and amount of the nitrogen (He *et al.*, 2000). Therefore, in the study, it could be seen that the emission pattern of NH<sub>3</sub> was the same as the pattern of nitrogen loss but the N<sub>2</sub>O-N emission had a different trend, in an order of corn stalks>sawdust>spent mushroom compost.

## 4 Conclusions

The effect of bulking agents (corn stalks, spent mushroom compost, and sawdust) on CH<sub>4</sub>, N<sub>2</sub>O, and NH<sub>3</sub> emissions was investigated in this study. The introduction of corn stalks is preferable to increasing the NO<sub>2</sub> emission. The introduction of spent mushroom compost induced a higher CH<sub>4</sub> emission by reducing the air spaces and increasing the large amount of organic acids inferring from the pH value, whereas the emissions of N<sub>2</sub>O and NH<sub>3</sub> reduced. The concentration of NH<sub>3</sub> from composting pig manure with sawdust was higher than that mixed with corn stalk or spent mushroom compost. The nature of bulking agents mixed with pig manure before composting had only a small influence on the loss of total organic carbon, whereas it significantly influenced the loss of total nitrogen.

## Compliance with ethics guidelines

Xiang-ping SUN, Peng LU, Tao JIANG, Frank SCHUCHARDT, and Guo-xue LI declare that they have no conflict of interest.

This article does not contain any studies with human or animal subjects performed by any of the authors.

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## 中文概要:

**本文题目:** “干清粪”系统猪粪快速堆肥过程中添加剂对甲烷、氧化亚氮和氨气排放的影响

**Influence of bulking agents on CH<sub>4</sub>, N<sub>2</sub>O, and NH<sub>3</sub> emissions during rapid composting of pig manure from the Chinese Ganqinfen system**

**研究目的:** 在“干清粪”系统猪粪堆肥过程中,不同添加剂(玉米秸秆、锯末和蘑菇渣)处理对甲烷、氧化亚氮和氨气排放的影响。

**创新要点:** 将不同的添加剂(玉米秸秆、锯末和蘑菇渣)应用到快速堆肥系统中进行堆肥,测定了猪粪堆肥过程中甲烷、氧化亚氮和氨气的排放规律,为国内猪粪堆肥的应用提供理论指导。

**重要结论:** 玉米秸秆作为添加剂能增加猪粪堆肥过程中氧化亚氮的排放;蘑菇渣添加剂增加了堆肥过程中甲烷的排放,然而减少了氧化亚氮及氨气的排放;锯末处理能增加堆肥过程中氨气的排放。添加剂能显著影响堆肥过程中氮素的损失。

**关键词组:** 有机废弃物;堆肥;添加剂;气体排放;猪粪