Effect of Different Amendments on Nitrogen Conservation During Simulated Composting

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Abstract: The objectives of this study were to evaluate the effects of different dosages of three amendments—peat, superphosphate, mixture of $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ ((Magnesium Hydroxide and Phosphorus Acid) on N (Nitrogen) conservation. The simulated composting experiment was carried out in a constant temperature water bath with pig manure and corn straw. The results showed that the ammonia volatilization could be inhibited to some extent under the treatments with fixing agents. Under the same simulated composting conditions, the nitrogen fixation effect of the three kinds of fixatives with the same proportion was as follows: $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4 > \text{superphosphate} > \text{peat}$. The fixation effect of N increased with the increase of the additives. The N fixation rate of $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ treatment was up to 66%. Compared with the CK (Control Group), the amount of cumulative ammonia emission decreased by 90.3% and the TN (Total Nitrogen) content increased by 39.31% in this treatment. Compared with other two kinds of fixing agents, $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ treatment could not only control N loss in composting process, improve the N nutrient content of compost products, but also could increase P (Phosphorus) and Mg (Magnesium) nutrients. Therefore, it had more popularization value and application prospect.

Key words: Simulated composting, amendment, effect of N conservation.

1. Introduction

Composting is one of the most important methods to realize the recycling and utilization of waste resources such as straw and livestock manure [1]. However, the N (Nitrogen) loss in the composting process could not only reduce the nutrient content and fertilizer efficiency of fertilizer, but also aggravate the environmental pollution [2] and become an important source of fine particulate matter (for example, $\text{PM}_{2.5}$) in the air [3]. At present, there are two main methods to control N loss: the one is to change the process conditions, such as appropriate C/N (Carbon/Nitrogen), pH, temperature, MC (Moisture Content), ventilation, turnover frequency, etc. [4]. The other is to use additives in the composting process. The common are physical, chemical and biological amendments, such as zeolite, biochar, metal salts, phosphates, N-fixing bacteria, EM (Effective

Microorganisms) bacteria, etc.. In previous work, different Mg (Magnesium) and P (Phosphorus) salts were used as N-fixing additives for struvite crystallization process. This process could decrease ammonia emission by generating struvite crystal ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), which was a poor water soluble, high-quality, slow-release fertilizer [5-7]. Several scholars have studied the effect of a certain type of additive on N morphological transformation in the composting process [8, 9], yet with lack of comprehensive comparative evaluation and analysis of several additives.

Based on the rule of N loss in composting process, the objectives of this study were to evaluate the effect of three amendments [peat, superphosphate and $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ (Magnesium Hydroxide and Phosphorus Acid)] at different dosages on N conservation during simulated composting. The best kind and amount of N fixation material were selected to provide a reliable N loss control scheme for the development of composting.

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2. Material and Methods

2.1 Raw Materials

In this experiment, fresh pig manure and corn straw were used as compost materials. The pig manure was taken from the Sujiatuo pig farm in Haidian district, Beijing. The corn straw was taken from the experimental field in the Science Park of China Agricultural University, which was cut into about 1 cm fragments. The basic properties of raw materials were shown in Table 1. Peat, superphosphate, $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ were chemically pure, which were added to the materials for composting.

2.2 Experimental Design and Sample Collection

Urea (pure C and N source) was used to adjust C/N of the raw materials to 20. The N fixatives—peat, superphosphate and $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ were named A,

B, and C and were also compared to a CK (Control Group) without additive. Three replicates were set for each treatment and the experimental design was shown in Table 2. Urea was dissolved in the aqueous solution completely, and then spread and mixed in raw materials evenly. The MC of the materials was controlled to 70%. Composting sealed fermentation bottles with capacity of 1 L were placed in a thermostatic water bath with adjustable temperature, and the temperature control simulated the outdoor composting temperature. Forced mechanical intermittent ventilation was adopted, and the ventilation rate was controlled at about $0.1 \text{ m}^3/(\text{min} \cdot \text{m}^3)$ for half an hour with a one-hour interval. The test lasted for 10 days and the test apparatus was shown in Fig. 1.

During the experiment, Samples of approximately 100 g were taken at 0, 3, 6, 8 and 10 days, respectively. Accurate weighing was performed before and after

Table 1 The properties of raw materials.

Property	Pig manure	Cornstalk
TOC (g/kg DM)	370 ± 3.18	430 ± 3.32
TN (g/kg DM)	19.3 ± 0.62	11.1 ± 0.04
$\text{NH}_4^+\text{-N}$ (g/kg DM)	0.97 ± 0.01	--
EC (ms/cm)	3.78 ± 0.14	2.15 ± 0.09
C/N	19 ± 0.49	39 ± 0.36
pH	8.5 ± 0.22	7.7 ± 0.34
MC (%)	72 ± 0.63	23 ± 0.21

DM: dry matter; TOC: total organic carbon; TN: total nitrogen; $\text{NH}_4^+\text{-N}$: ammonium nitrogen; EC: electrical conductivity; --, undetected.

Table 2 The dry weight proportion of composting materials and the dosage of adsorbents.

Treatments	Pig manure (%)	Cornstalk (%)	Urea (%)	Additive (%)	MC (%)	C/N	Type of additive
CK	16.67	12.90	0.43	0 ^a	70	20	--
A1	53.43	41.35	1.38	3.85	70	20	Peat
A2	52.42	40.57	1.35	5.66	70	20	
A3	51.45	39.81	1.33	7.41	70	20	
A4	50.51	39.09	1.30	9.09	70	20	
B1	53.43	41.35	1.38	3.85	70	20	Superphosphate
B2	52.42	40.57	1.35	5.66	70	20	
B3	51.45	39.81	1.33	7.41	70	20	
B4	50.51	39.09	1.30	9.09	70	20	
C1	53.43	41.35	1.38	3.85 (1:1) ^b	70	20	$\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$
C2	51.45	39.81	1.33	7.41 (1:2)	70	20	
C3	50.51	39.09	1.30	9.09 (1:3)	70	20	

^a Dry weight ratio; ^b Molar ratio of $\text{Mg}(\text{OH})_2$ to H_3PO_4 .

Fig. 1 Structure of simulated composting equipment.

1: pump; 2: filter humidifier; 3: constant temperature water bath; 4: compost materials; 5: 2% boric acid; 6: catheter.

each sampling to calculate the material balance. The sample was divided into two parts: one part was fresh sample, which was used to measure water content and other water-soluble indexes; the other part was air-dried and ground to pass through a 0.1 mm sieve as a dry sample. The MC of the compost was calculated according to the MC of the sample, which was used as the basis for supplementing the MC and keeping it 70%. The N fixation rate was calculated and the N control effect of the fixatives in composting process was studied.

2.3 Analytical Methods and Calculations

The MC of the samples was determined by drying at 105 °C for 8 h. TN content was measured by an elemental analyzer (Elementar vario MACRO cube, Germany). $\text{NH}_4^+\text{-N}$ was extracted with 2 M KCl (1:20) and was analyzed by a segmented flow analyzer (Technicon Autoanalyzer II system, Germany). The NH_3 was absorbed by a washing bottle with boric acid (2%) and then titrated using 0.1 M H_2SO_4 . Calculation method of N loss rate and fixation rate is:

N loss rate $X =$

$$(M_0 \times N_0 - M_1 \times N_1) / (M_0 \times N_0) \times 100\% \quad (1)$$

$$\text{N fixation rate } Y = (X_{\text{CK}} - X_{\text{Treatment}}) / X_{\text{CK}} \times 100\% \quad (2)$$

where M_0 is the initial weight of materials, dry weight, g; M_1 is the weight of the sample material on day 10, dry weight, g; N_0 is the TN content in the initial material, %; N_1 is the TN content of the sample material on day 10, %.

All data were analyzed using One-Way Analysis of

Variance (ANOVA). SPSS 17 for Windows was used for all statistical analysis.

3. Results and Discussion

3.1 Temperature

The test temperature was simulated to the composting temperature outdoor. Constant temperature water bath control was adopted in three stages of heating, high temperature and cooling. The high temperature phase lasted for five days (50 °C or higher) and the temperature change was shown in Fig. 2.

3.2 N Changes during Simulated Composting

3.2.1 Ammonia Emission

As could be seen from Fig. 3, only a small amount of ammonia gas was released during the 0-3 days of the heating period, and the ammonia emission amount accounted for 3.11%-14.91% of the total emission amount (Table 3). The high temperature period was

Fig. 2 The temperature changes during composting.

Fig. 3 Cumulative ammonia emissions of different treatments. (a) peat, (b) superphosphate, (c) $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$.

A1: 3.85% peat; A2: 5.66% peat; A3: 7.41% peat; A4: 9.09% peat; B1: 3.85% superphosphate; B2: 5.66% superphosphate; B3: 7.41% superphosphate; B4: 9.09% superphosphate; C1: 3.85% $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$; C2: 7.41% $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$; C3: 9.09% $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$.

Table 3 The proportion of ammonia emission amount in each phase to the total emission amount.

Treatments	Proportion (%)			
	0-3 d	3-6 d	6-8 d	8-10 d
CK	8.10	52.29	32.72	6.89
A1	7.32	57.30	28.64	6.74
A2	3.98	55.05	35.87	5.09
A3	5.81	58.85	30.98	4.36
A4	3.88	64.21	28.40	5.19
B1	3.11	48.19	45.32	3.38
B2	5.27	39.42	51.58	3.73
B3	10.17	53.07	35.53	1.22
B4	12.09	69.24	13.19	5.48
C1	4.38	60.40	31.54	3.67
C2	6.60	60.12	27.53	5.74
C3	14.91	58.79	24.67	1.62

the peak period of ammonia release, and the ammonia release amount was significantly increased in 3-6 days. The cumulative ammonia emission amount accounted for 39.42%-69.24% of the total amount. During 6-8 days, with the gradual decrease of composting temperature, the ammonia amount decreased, and the cumulative ammonia amount accounted for 13.19%-51.58% of the total release amount. After 8 days, ammonia release decreased and stabilized, accounting for only 1.22%-6.89% of the total amount. Ammonia emissions decreased gradually with the increase of the amount of fixative (Fig. 3), indicating that the greater the proportion of fixative within the range of the experimental design, the better the

fixation effect on ammonia N.

Compared with the CK, the three fixatives all controlled the ammonia volatilization to different extent. Under the same addition ratio, the $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ treatment had the highest reduction rate, which was 90.28% compared with the control. The treatment of superphosphate was the next (76.13%), the last one was the peat treatment (53.44%).

The effect of ammonia emission reduction was different due to the different fixation principles of N fixing agents. Peat was the remains of marsh plants, with organic matter content of more than 30%. The pH ranged from 5.0 to 6.9, showing slightly acidic,

which could absorb and fix ammonia emission to some extent. At the same time, its own nutrients could improve the fertility of compost products [10, 11]. The main components of superphosphate were $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Monocalcium Phosphate Monohydrate), containing 14%-20% of available P (P_2O_5), 40%-50% of calcium sulfate, and 3.5%-5% of free sulfuric acid and phosphoric acid. Studies have shown that the pH value of its saturated solution was 1.48, which was acidic [12]. By adding superphosphate, ammonia volatilization could be reduced by reducing the pH value of compost materials, and the following reactions may occur to generate relatively stable acidic ammonium phosphate or ammonium sulfate, so as to fix NH_4^+ -N and reduce the loss of N [13].

Different proportions of $\text{Mg}(\text{OH})_2$ and H_3PO_4 were mixed to produce an emulsion that was not completely soluble in water. It was a mixture containing MgHPO_4 , $\text{Mg}(\text{H}_2\text{PO}_4)_2$, $\text{Mg}_3(\text{PO}_4)_2$ and their crystalline water, which could react with ammonia:

Struvite crystal ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) was also a kind of high-quality inorganic fertilizer, which not only had a good fixation effect on ammonia, but also increased the content of P in the compost. Therefore, it was an ideal compost additive [14].

3.2.2 TN

The change of TN content in simulated composting with different treatments was shown in Fig. 4, and the TN content of the treatments with additives was significantly higher than that in the CK. More the fixative added, higher the TN content was. In the first 3 days of composting, all treatments with a ratio of 3.85% showed a downward trend, which may be due to the conversion of part of NH_4^+ -N into ammonia volatilization, and only a small amount of degradation

of the material itself. In the treatments of 5.66% and 7.41% ratio, only the TN content of the peat decreased slightly in the first 3 days. The TN content of the compost material increased gradually with the addition ratio of 9.09%, indicating that the additive had a fixation effect on the N of the compost material. With the progress of composting, organic matter began to degrade violently. Because of the double effects of concentration and fixation, the content of TN in each treatment with fixative presented an increasing trend. The peak period of ammonia generation was 4-6 days, and the rising period of TN content was less than 6-8 days generally.

At the end of the experiment, compared with the CK, from peat to superphosphate to $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ treatment, the TN content of the fixative with the addition of 3.85% increased by 2.53%, 9.08% and 13.08%, respectively. The addition amount of 5.66% increased by 9.40% and 18.77%. The addition amount of 7.41% increased by 10.85%, 18.19% and 32.76%, respectively. The TN content of 9.09% addition amount increased by 20.28%, 31.11% and 39.31%, respectively.

Compared with different fixatives, it could be seen that no matter which amount of addition, the treatment of $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ had the highest TN content, followed by the treatment of superphosphate and peat. The results showed that $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ treatment had the best N fixation effect among the three fixatives. There was no significant difference between the treatment with a proportion of 3.85% additives and the control (p values were 0.475, 0.212 and 0.132, respectively), while the difference between the other treatments and the control was significant, indicating that the N fixation effect on compost was limited when the dosage was low. The difference of the same additive in different proportion was extremely significant. The variance analysis between treatments with different proportions of peat was $F = 5.9$, $p = 0.003^{**}$ (P value less than 0.01 indicates that the difference between the two groups is extremely

Fig. 4 TN content of different treatments. (a) peat, (b) superphosphate, (c) $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$.

A1: 3.85% peat; A2: 5.66% peat; A3: 7.41% peat; A4: 9.09% peat; B1: 3.85% superphosphate; B2: 5.66% superphosphate; B3: 7.41% superphosphate; B4: 9.09% superphosphate; C1: 3.85% $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$; C2: 7.41% $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$; C3: 9.09% $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$.

Fig. 5 $\text{NH}_4^+\text{-N}$ changes of different treatments during simulated composting. (a) peat, (b) superphosphate, (c) $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$.

A1: 3.85% peat; A2: 5.66% peat; A3: 7.41% peat; A4: 9.09% peat; B1: 3.85% superphosphate; B2: 5.66% superphosphate; B3: 7.41% superphosphate; B4: 9.09% superphosphate; C1: 3.85% $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$; C2: 7.41% $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$; C3: 9.09% $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$.

significant, similarly hereinafter), variance analysis between superphosphate treatments was $F = 4.8$, $p = 0.007^{**}$, and $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$ treatment was $F = 6.0$, $p = 0.006^{**}$.

3.2.3 $\text{NH}_4^+\text{-N}$

The variation trend of $\text{NH}_4^+\text{-N}$ with three fixatives was shown in Fig. 5. In the CK group, $\text{NH}_4^+\text{-N}$ showed a declining trend, from 2.78 g/kg DM at the beginning to 1.75 g/kg DM, which was due to the large amount of $\text{NH}_4^+\text{-N}$ converted into NH_3 in the high temperature period. However, the $\text{NH}_4^+\text{-N}$ was fixed in the treatments with fixatives by different principles, which showed an upward trend.

Except for the low proportion treatment of A1, due to the large ammonia volatilization in the early stage of the peat treatment, the ammonia first dropped and then rose. In addition, the other treatments showed a gradually increasing trend, and with the increase of the addition proportion, the content of $\text{NH}_4^+\text{-N}$ also gradually increased. At the end of the experiment, four adding proportions $\text{NH}_4^+\text{-N}$ content were 3.26, 4.37, 5.57 and 6.89 g/kg DM, 1.8-3.9 times of the control. ANOVA results showed that the difference among treatments was extremely significant ($F = 6.7$, $p = 0.001$). $\text{NH}_4^+\text{-N}$ was fixed by reducing the pH value of materials and chemical reaction in the superphosphate

Fig. 6 Ratio of N fixation of different treatments.

A1: 3.85% peat; A2: 5.66% peat; A3: 7.41% peat; A4: 9.09% peat; B1: 3.85% superphosphate; B2: 5.66% superphosphate; B3: 7.41% superphosphate; B4: 9.09% superphosphate; C1: 3.85% $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$; C2: 7.41% $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$; C3: 9.09% $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$.

treatments, and the fixation effect was better than peat. At the end of the experiment, with the increase of additive proportion, the contents of $\text{NH}_4^+\text{-N}$ of superphosphate treatments were 5.09, 5.55, 6.81 and 8.13 g/kg DM, respectively, which were 2.9-4.6 times higher than that of the control treatment, and the difference between treatments was significant ($F = 3.54$, $p = 0.024$).

Compared with the other two fixatives of the same proportion, $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ treatment had the higher $\text{NH}_4^+\text{-N}$ content. Moreover, more the phosphoric acid added, higher the $\text{NH}_4^+\text{-N}$ content was. The analysis of variance showed that the difference between treatments was extremely significant ($F = 35.38$, $p = 0.009$). At the end of the test, compared with the same proportion of superphosphate treatment, the ammonia nitrogen content of the $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ treatment increased by 0.75, 2.98 and 3.92 g/kg DM with the increase of the addition proportion respectively. This was because the fixing agent combined with $\text{NH}_4^+\text{-N}$ to produce magnesium ammonium phosphate. Theoretically, this not only could control N loss, but also could produce a high-quality slow-release fertilizer, which was more potential than the former two.

3.2.4 N Fixation Rate

At the end of composting, the N loss rate of the control treatment was 55.72%. The change of N fixation rate of different treatments was shown in Fig. 6. As could be seen from the figure, the N fixation rate of each additive treatment increased with the increase of the additive. In addition to C1 treatment, among the treatments with the same addition ratio, the treatment of $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ showed the best N fixation effect, and the treatment with the 9.09% amount of the addition had the highest N fixation rate (being up to 66%), followed by superphosphate and peat treatment.

4. Conclusions

Under the same simulated composting conditions, the N fixation effect of the three kinds of fixatives with the same proportion was as follows: $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4 > \text{superphosphate} > \text{peat}$. Furthermore, within a certain range, the fixation effect of N increased with the increase of the additive. The N fixation rate of $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ treatment was up to 66%. Compared with the CK, the amount of cumulative ammonia volatilization decreased by 90.3% and the TN content increased by 39.31% of this treatment. Compared with other two kinds of fixing agents, $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$ could not only control N loss in composting process, improve the N nutrient content of compost, but also could increase P and Mg nutrients. Therefore, it had more popularization value and application prospect.

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