

## STRUVITE CRYSTALLIZATION MITIGATES REACTIVE N LOSSES FROM SWINE MANURE IN-VESSEL COMPOSTING

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**ABSTRACT:** We assessed the addition Mg and P salts to promote struvite crystallization and mitigate reactive N losses from a rotating drum (12 m<sup>3</sup>) used for in-vessel composting of swine manure. The tested treatments were: mixture of sawdust and swine manure (baseline) and the same mixture with the addition of magnesium sulfate and phosphoric acid (MgSO<sub>4</sub>+H<sub>3</sub>PO<sub>4</sub>). Struvite crystallization decreased NH<sub>3</sub>-N and TN losses by 96.5 and 46%, respectively. Higher N<sub>2</sub>O-N emissions were related with resolubilization of the struvite under lower pH conditions. Further research is needed to assess strategies for the stabilization of struvite crystals, minor N losses and increasing nutrient concentration value of the organic compost.

**Keywords:** ammonia, nitrous oxide, methane, carbon dioxide.

### INTRODUCTION

Composting is an emerging technology for swine manure management in large confined animal feeding operations in Southern Brazil (Kunz et al., 2009). Unfortunately, during composting processes relevant nitrogen (N) losses may occur (up to 60% of N input) contributing to potential greenhouse gases (GHG) emissions (El Kader et al., 2007; Angnes et al., 2013). For instance, NH<sub>3</sub>-N and N<sub>2</sub>O-N emissions may represent 15 and 5%, respectively, of the total N losses during the composting process (Angnes et al., 2013). Thus, several strategies to mitigate reactive N losses from swine slurry composting have been evaluated in lab-scale with promising results, including nitrification inhibition (Luo et al., 2013), and struvite crystallization (Jiang et al., 2016). We investigated the effect of the addition of magnesium sulfate (MgSO<sub>4</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) in order to promote struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O) crystallization and mitigate reactive N losses in field-scale rotating drums used for in-vessel composting of swine manure.

### MATERIAL AND METHODS

This study was conducted with a rotating drum (RAC-120, Agrobona, Matelândia, PR) used for in-vessel composting of swine manure with sawdust as bulking agent. The equipment consisted of a 12 m<sup>3</sup> cylindrical vessel (1.75 m x 5 m; diam. x L) insulated with 50 mm polystyrene sheets. The swine manure was obtained from a fattening farm at Embrapa Swine and Poultry (Concordia, Brazil: 27°18'46"S, 54°59'16"W) and processed through a screw-press (Fornari Indústria, Concórdia, SC) for the separation of the solid phase that was used in this study. We mixed 660 kg of swine manure (1 m<sup>3</sup>) with 200 kg of sawdust (1 m<sup>3</sup>) in order to achieve an estimated C/N ratio within the 25-30 ranging for the composting material (Table 1). The weight and volume of the mixture was measured (860 kg, 2 m<sup>3</sup>) and the material was loaded to the rotating drum (day 0). The procedure was repeated at days 3 and 7 when the maximum loading capacity of the equipment was achieved (6 m<sup>3</sup>), totaling 2,560 kg of composting material. The experiment was carried out for 21 days and two treatments were tested: mixture of swine manure and sawdust without additives (baseline) and addition of fertilizer grade magnesium sulfate (14.5 kg MgSO<sub>4</sub>·7H<sub>2</sub>O, 9%S) and phosphoric acid (1.7 kg H<sub>3</sub>PO<sub>4</sub>, 85%) for every 860 kg of the mixture of swine manure and sawdust (MgSO<sub>4</sub>+H<sub>3</sub>PO<sub>4</sub>). The application of Mg and P salts were calculated in order to provide 0.09 and 0.06 mol kg<sup>-1</sup> swine manure DM (dry matter) of MgSO<sub>4</sub>·7H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub>, respectively, which were determined as the better application rates in a previous lab-scale assessment (Sardá et al., 2016). The rotating drum was equipped with an axial blower providing a

continuous air flow of  $212 \text{ m}^3 \text{ h}^{-1}$  or 1.7 air changes per minute and was controlled by an analogical timer set for 150 minutes stationary and 30 minutes revolving cycles ( $\sim 0.15 \text{ rpm}$ ).

Samples of swine manure, sawdust and compost material were collected on triplicates every 2-3 days for physical-chemical characterization. DM content was determined by weight ( $105^\circ \text{ C}$  overnight). Total organic Carbon (C), Kjeldahl nitrogen (TKN), ammonium-nitrogen ( $\text{NH}_4\text{-N}$ ), nitrate- ( $\text{NO}_3\text{-N}$ ) and nitrite-nitrogen ( $\text{NO}_2\text{-N}$ ), pH as well as total phosphorus (P) and potassium (K) were analyzed by standard protocols (APHA, 2005). Total and organic N (TN and Org-N) were then calculated (Angnes et al., 2013). Non-volatile P and K inputs and recovery on compost samples were used to check the mass balance within the piles. The average errors determined for P and K mass balance ( $<5\%$  for P and  $<10\%$  for K, Table 2) was low in comparison to similar studies (El Kader et al., 2007; Angnes et al., 2013). Gaseous C and N losses either as carbon dioxide ( $\text{CO}_2\text{-C}$ ), methane ( $\text{CH}_4\text{-C}$ ), nitrous oxide ( $\text{N}_2\text{O-N}$ ) and ammonia ( $\text{NH}_3\text{-N}$ ) were monitored every 2 min using a multipoint gas sampler INNOVA 1309 connected to an infrared photoacoustic gas analyzer INNOVA 1412 (Lumasense Technologies, Denmark). Emissions rates were calculated as follow (Angnes et al., 2013):

$$E = Q \times (C_o - C_i) \quad (\text{Equation 1})$$

where, E is emission rate ( $\text{mg h}^{-1}$ ) of a particular gas ( $\text{CO}_2\text{-C}$ ,  $\text{CH}_4\text{-C}$ ,  $\text{NH}_3\text{-N}$  or  $\text{N}_2\text{O-N}$ ); Q is the air flow ( $\text{m}^3 \text{ h}^{-1}$ ); and  $C_o$  and  $C_i$  were the concentrations of the measured gases in the outlet and inlet air sample ( $\text{mg m}^{-3}$ ), respectively.

## RESULTS AND DISCUSSION

The cumulative  $\text{CO}_2\text{-C}$ ,  $\text{CH}_4\text{-C}$ ,  $\text{NH}_3\text{-N}$ , and  $\text{N}_2\text{O-N}$  losses from different treatments are shown in Fig 1. No differences were observed for  $\text{CO}_2\text{-C}$  losses from composting material receiving Mg and P salts ( $\text{MgSO}_4\text{+H}_3\text{PO}_4$ ) in relation to the baseline treatment (Fig. 1a). Total C losses during the composting process were 26 and 24.8% for baseline and  $\text{MgSO}_4\text{+H}_3\text{PO}_4$  treatments, respectively (Table 2). Thus, these additives had no effect over the aerobic microbial communities responsible for decomposition and stabilization of the composting material. The  $\text{CH}_4\text{-C}$  losses were negligible accounting for  $<0.3\%$  of the measured  $\text{CO}_2\text{-C} + \text{CH}_4\text{-C}$  losses (Fig. 1b). This result indicates that rotating drum turning regime (150/30 min. stationary/revolving cycles) provided continuous oxygen supply for the composting material. For comparison,  $\text{CH}_4\text{-C}$  losses in swine slurry composting piles mixed twice a week achieved 4.2% of total  $\text{CO}_2\text{-C} + \text{CH}_4\text{-C}$  losses (Angnes et al., 2013). Nonetheless,  $\text{CH}_4\text{-C}$  increased significantly after day 7 in  $\text{MgSO}_4\text{+H}_3\text{PO}_4$  treatment and was probably related with the lower dry matter content of the swine manure in comparison with the baseline treatment ( $271$  and  $243 \text{ g kg}^{-1}$ , respectively) and hygroscopicity of both Mg salt and struvite.

$\text{NH}_4\text{-N}$  content increased in the composting material treated with  $\text{MgSO}_4\text{+H}_3\text{PO}_4$  in comparison with the baseline treatment (Fig. 2a), thus indicating effective crystallization of struvite (Jiang et al., 2016). Struvite crystals ( $\sim 2 \text{ mm}$ ) were indeed visually identifiable within the composting material in the  $\text{MgSO}_4\text{+H}_3\text{PO}_4$  treatment. A previous study confirmed struvite crystallization in a lab-scale assessment by using scanning electron microscopy and X-ray powder diffraction techniques (Sardá et al., 2010). The  $\text{NH}_4\text{-N}$  immobilization as struvite decreased measured  $\text{NH}_3\text{-N}$  emission by 96.5% in the  $\text{MgSO}_4\text{+H}_3\text{PO}_4$  treatment in comparison with the baseline (Fig. 1d). The application of  $\text{MgO+H}_3\text{PO}_4$  (molar basis equivalent of 15% of initial N) to promote struvite crystallization during swine manure composting was already reported to decrease  $\text{NH}_3\text{-N}$  losses by 46% (Jiang et al., 2016).

However,  $\text{NH}_4\text{-N}$  content in  $\text{MgSO}_4\text{+H}_3\text{PO}_4$  treatment decreased significantly after day 15. This was concomitant with the decreasing pH (from 7.5 to 6.8) of the composting material in the  $\text{MgSO}_4\text{+H}_3\text{PO}_4$  treatment (Fig. 2b). Struvite is insoluble in neutral/alkaline conditions but the solubility of struvite crystals increases with decreasing pH (Jiang et al., 2016). The  $\text{NH}_4\text{-N}$  consumption would be mostly attributed to nitrification as inferred by a spike of  $\text{NO}_2\text{-N}$  content in the composting material at day 20 (data not shown) and increased  $\text{N}_2\text{O-N}$  emission (Fig. 1c). Nitrification and denitrification were already reported to be the main catabolic pathways favoring N losses, either as  $\text{N}_2\text{O}$  or  $\text{N}_2$ , during swine manure composting (Angnes et al., 2013).  $\text{N}_2\text{O-N}$  emissions are augmented under low C/ $\text{NO}_2\text{-N}$  ratios due to the lack of bioavailable C to support complete denitrification (Mezzari et al., 2013).  $\text{N}_2\text{O-N}$  losses

would be controlled either by supplying additional bioavailable C (Mezzari et al., 2013), application of nitrification inhibitors (i.e., dicyandiamide; Jiang et al., 2016) and preferably by regulating the pH of the composting material to avoid the solubilization of struvite crystals.

Nonetheless, TN losses decreased by 46% on the comparison of  $MgSO_4+H_3PO_4$  with the baseline treatment (21.3 and 9.7% of initial N, respectively) either by increasing N immobilization as org-N (156%) or decreasing  $NH_4-N$  losses (30%). As a result, the application of  $MgSO_4+H_3PO_4$  resulted in a composted material with lower C/N ratio (21.3) in comparison with the baseline compost (25.7). A previous study already reported that the application of  $MgO+H_3PO_4$  decreased TN losses by 51% on the comparison of treated and untreated (22.3 and 43.9% of initial N, respectively) swine manure composting lab-scale bioreactors (Jiang et al., 2016). However, TN losses observed in our study were much lower (~55%), probably due to differences on composting systems (in-vessel composting with high turning frequencies x static piles composting with forced aeration and intermittent turnings).

### CONCLUSION

The application of  $MgSO_4+H_3PO_4$  promoted the crystallization of struvite and the immobilization of  $NH_4-N$  in the composting material, decreasing  $NH_3-N$  (96.5%) and TN (46%) losses from rotating drums used for in-vessel composting of swine manure. However,  $N_2O-N$  emissions were increased due to the solubilization of struvite crystals promoted by decreasing pH of composting material. Further research is needed to assess strategies for the stabilization of struvite crystals, minor N losses and increasing nutrient concentration value of the organic compost.

### ACKNOWLEDGEMENTS

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**Table 1.** Characterization of sawdust and swine manure used in this study.

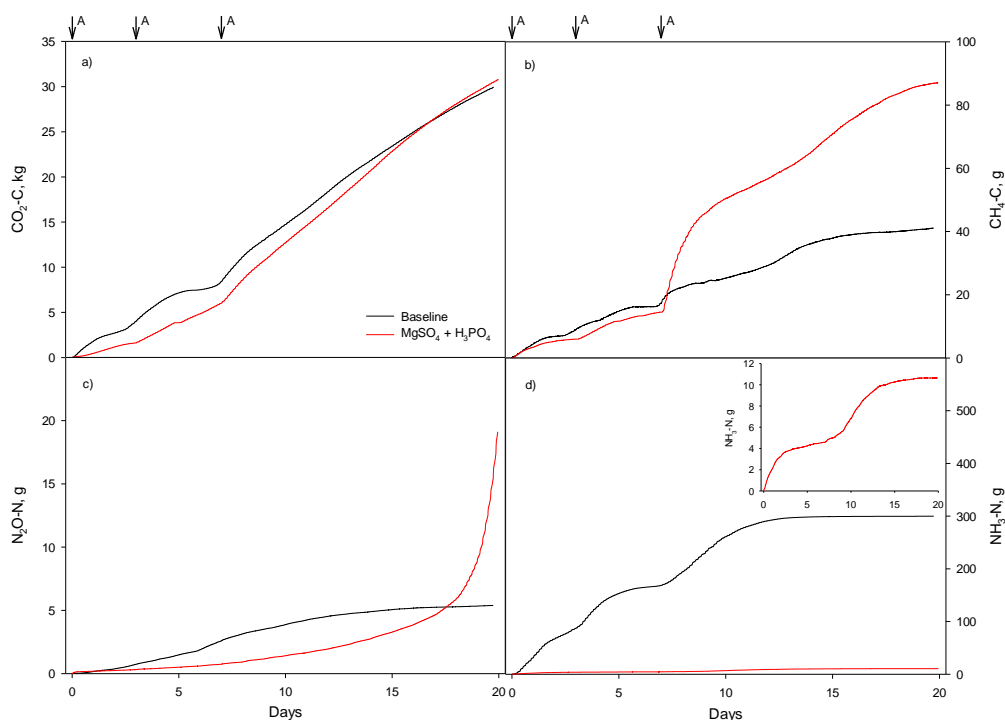
Parameter	Baseline			MgSO <sub>4</sub> + H <sub>3</sub> PO <sub>4</sub>		
	Sawdust	Swine manure	Mixture <sup>1</sup>	Sawdust	Swine manure	Mixture
Dry matter (DM)	g kg <sup>-1</sup> DM			g kg <sup>-1</sup> DM		
C	593±36 <sup>a</sup>	271±31	346±23	645±19	243±33	330±29
	465±75	411±16	433±11	468±48	413±13	437±95
TN	mg kg <sup>-1</sup> DM			mg kg <sup>-1</sup> DM		
Org-N	1,052±118	25,711±885	15,839±337	1,140±201	30,061±2,039	17,107±635
NH <sub>4</sub> -N	1,052±118	18,301±82	11,408±569	1,140±201	21,502±3,070	12,352±1,305
P	0±0	7,410±913	4,431±322	11±20	8,560±1,035	4,755±764
	563±240	12,084±2,678		491±155	13,397±2,200	9,239±1,403 <sup>b</sup>
K	1154±80	6,437±531	7,431±1,274	1,216±174	6,940±365	4,378±257
	kg kg <sup>-1</sup>			kg kg <sup>-1</sup>		
C/N ratio	445±53	16±1	27±1	421±86	14±1	26±1

<sup>1</sup>Calculated for a mixture of 200 kg of sawdust and 660 kg of swine manure (wet weight); <sup>a</sup>Mean±sd; <sup>b</sup>Input of 457 mg of P-H<sub>3</sub>PO<sub>4</sub> for every 860 kg of composting material.

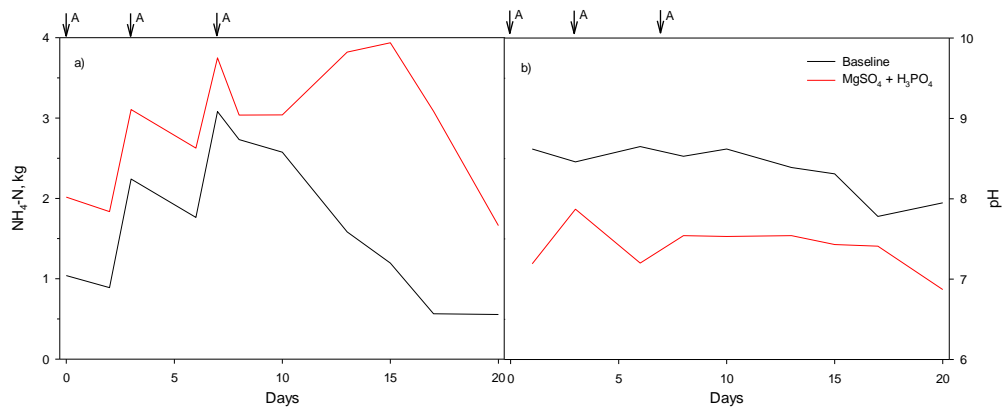
**Table 2.** Mass balance for swine manure in-vessel composting with or without the addition of magnesium sulfate (MgSO<sub>4</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>).

Parameter	Baseline				MgSO <sub>4</sub> + H <sub>3</sub> PO <sub>4</sub>			
	Inlet <sup>1</sup>	Outlet <sup>2</sup>	Mass balance	%	Inlet	Outlet	Mass balance	%
Wet weight	kg				kg			
	2,580	1,302	-1,278	-49.5	2,628 <sup>a</sup>	1,732	-897	-34.1
H <sub>2</sub> O	1,687	592	-1,095	-64.9	1,759	925	-835	-47.4
Dry matter	893	711	-182	-20.4	869	807	-62	-7.1
C	387	287	-101	-26.0	380	286	-94	-24.8
TN	14.1	11.1	-3.0	-21.3	14.9	13.4	-1.5	-9.7
Org-N	10.2	10.6	0.4	3.7	10.7	11.7	1.0	9.5
NH <sub>4</sub> -N	3.9	0.5	-3.4	-85.9	4.2	1.7	-2.5	-60.1
P	6.6	6.9	0.3	4.8	8.1	8.0	-0.1	-0.8
K	3.8	3.6	-0.2	-6.4	3.8	3.4	-0.4	-10.0
	kg kg <sup>-1</sup>				kg kg <sup>-1</sup>			
C/N ratio	27.4	25.7	-1.6	-6.0	25.6	21.3	-4.3	-16.9

<sup>1</sup>Inlet material: sum of sawdust and swine manure added to bioreactors at days 0, 3 and 7; <sup>2</sup>Outlet material: composted material at day 20; <sup>a</sup>48.6 kg from MgSO<sub>4</sub> (43.5 kg) and H<sub>3</sub>PO<sub>4</sub> (5.1 kg).



**Figure 1.** Cumulative carbon dioxide (a), methane (b), nitrous oxide (c), and ammonia (d) losses from swine manure in-vessel composting with or without the addition of magnesium sulfate (MgSO<sub>4</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). Arrows indicate the addition of composting material to bioreactors.



**Figure 2.** Ammonium-N (a) and pH (b) during swine manure in-vessel composting with or without the addition of magnesium sulfate (MgSO<sub>4</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). Arrows indicate the addition of composting material to bioreactors.