science, engineering and health studies

Research Article

Science, Engineering and Health Studies
https://li01.tci-thaijo.org/index.php/sehs
ISSN (Online): 2630-0087

Nitrogen transformation during composting: A comparison of cow manure and mixed cow and pig manure

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***Received**: 30 November 2022*
***Revised**: 26 December 2022*
***Accepted**: 26 December 2022*
***Published**: 30 December 2022*

***Citation**: Obsuwan, K., Phuekvilai, P., Yookongkaew, N., Chaneam, S., Wanichacheva, N., Panishkan, K., Piachart, P., Artjinda, P., and Sanmanee, N. (2022). Nitrogen transformation during composting: A comparison of cow manure and mixed cow and pig manure. Science, Engineering and Health Studies, 16, 22030013.*

ABSTRACT

Compost derived from manures is widely used and considered as a source of environmentally friendly nutrients to improve soil qualities. Two composts—cow manure compost and mixed cow and pig manure—were investigated for comparison. Forms of nitrogen—organic nitrogen (Org-N), ammonia nitrogen (NH_4^+), and nitrate nitrogen (NO_3^-)—and other physicochemical parameters were also studied. Results showed that composting increased total nitrogen and Org-N, and reduced organic matter. Nevertheless, the dynamics of NH_4^+ and NO_3^- differed between the composts. Cow compost has a higher nitrate fraction than a mixed compost throughout the study. This finding indicated mineralization via nitrification with low pH range between 6.59-6.88. In particular, the ammonification of mixed compost was greater than that of cow compost, especially during the thermophilic phase with the high pH range of 6.95–8.84. However, in the mature phase, the nitrification of mixed compost was greater and the amount of NO_3^- increased with time. The opposite trend was observed in cow compost. Therefore, adding pig manure may improve organic matters, particularly nitrogen input.

Keywords: compost; nitrogen; cow manure; pig manure; fertilizer

1. INTRODUCTION

Manure composts are an environmentally friendly approach in amending soil nutrients. However, the varieties of manures induce significantly different changes in soil improvement according to the different amounts of nutrients and the potential of composts in releasing them (Anwar et al., 2018). Fresh and fermented manures are commonly used to improve soil quality. However, fresh manure and immature compost might carry some pathogens and weed seeds, leading to other issues in agricultural practice. High temperature during thermophilic phases helps eliminate these problems. Thus, studying compost maturity and the potential of releasing nutrients is still necessary.

A variety of manure composts are used for quality improvement, such as mixing with grape marc, green waste, woodchip, sawdust, biochar, corn stalk, wheat straw, bean dregs, and sugarcane leaves (Bustamante et al., 2008; Nolan et al., 2011; Zhang et al., 2016; Jiang et al., 2019; Li et al., 2019; Yu et al., 2019; Yang et al., 2020). Composting could reduce agricultural waste and increase its value as an organic fertilizer. However, information about mixed manures and the potential of releasing their nutrients is lacking.

Nitrogen (N) is one of the three major essential nutrients of plants, along with phosphorus and potassium. Transformation of organic matter (OM) increases organic nitrogen (Org-N) and reduces carbon to N ratio (C/N). Content of available nitrogen, which consists of ammonium (NH_4^+) and nitrate (NO_3^-), may vary. Factors affecting available N contents include types of compost, pH, moisture, OMs, C/N, ventilation, and temperature (Bustamante et al., 2008; Zhang et al., 2016; Shi et al., 2020).

The aims of this study were to simultaneously transform manures as agricultural waste and use them as a new source of nutrients. The transformation of N and the potential for releasing available N and in cow manure compost and mixed cow and pig manure compost were also investigated and compared. The changes in C and N contents, including the mobility of N species, would provide insights into improving the quality of the composts.

2. MATERIALS AND METHODS

2.1 Compost preparations and samplings

Two sets of composts were prepared using two types of manures: one contained main fraction with cow manure, and the other one was 1:1 of cow and pig manures. Each compost was 1,000 kg in wet weight and was made by mixing 91.4% manure, 0.94% bat manure, 3.15% rice bran, and 4.57% fish fermented juice. After mixing, the composts were stored in ten 15-kg air-flow bags under shedding with good ventilation. Compost temperature was measured in the center of three bags. Each bag was manually turned over before collecting 250 g of the sample at the center. All samples from the ten bags were combined into a single composite sample. The sampling was done on days 0, 3, 7, 14, 21, 28, 35, 42, 49, and 63.

2.2 Analytical methods

The samples were homogenized, passed through 2-mm sieve, and oven-dried at 105°C to reach a constant weight for determining moisture content and dry weight (Tong et al., 2019). OM was measured by ignition at 550°C for 4 h in a furnace (Tong et al., 2019). Organic carbon (OC) was calculated using Van Bemmelen Factor by multiplying OM with then 0.58 (Sparks et al., 1996). The pH and electrical conductivity (EC) were determined in the diluted sample with distilled water (1:5 w/v), after stirring for 15 min using Fisher Scientific accumet AB150 pH meter (USA) and Hanna microprocessor conductivity meter HI 9835 (USA), respectively. Total nitrogen (TN), NO_3^-, and NH_4^+ were analyzed using AOAC official method 955.04, 920.03, and 892.0, respectively (Latimer, 2012).

TN was examined using the improved Kjeldahl method for nitrate-containing material. In brief, 40 mL of sulfuric acid (H_2SO_4) containing 2 g of salicylic acid was prepared, occasional shaken for 30 min, added with 5 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) shaken, and allowed to stand for 5 min. The sample was heated over low flame until frothing ceased. After the heat was turned off, 0.7 g of mercury oxide (HgO) and 15 g of powdered potassium sulfate (K_2SO_4) were added and broiled until the solution cleared. Broiling was continued for another 30 min. The sample was cooled, added with 200 mL of distilled water, 25 mL of 80 g/L $Na_2S_2O_3 \cdot 5H_2O$, and few zinc granules, followed by 70 mL of concentrated sodium hydroxide (NaOH). The flask was immediately connected to the distilling condenser, with the end of condenser tip immersed in 50 mL of 0.025 M hydrochloric acid (HCl). Heating was then performed until ammonia was completely distilled. Excess standard acid was titrated in distillate with standard NaOH using 4-5 drops of methyl red indicator.

NH_4^+ was determined by magnesium oxide method using Kjeldahl instrument. In brief, 3 g of samples was placed in a distillation flask with 200 mL of distilled water and 2 g of carbonate-free magnesium oxide (MgO). The flask was connected to condenser, and the tip was immersed in 25 mL of 0.025 N H_2SO_4. Heating was continued until NH_4^+ was completely trapped. The excess standard acid was quantified as described above.

The remaining solution in Kjeldahl flask was analyzed for NO_3^- using Devarda method. In brief, 3 g of Dervarda alloy and 50 mL of distilled water were added into the solution. The flask was assembled back to the heating unit, with the end of the tip immersed in 25 mL of 0.025 N H_2SO_4. Heating was continued until the volume of the solution was less than 150 mL or the converted NH_4^+ was completely trapped. The excess standard acid was quantified as described above. Org-N was calculated by subtracting NO_3^- and NH_4^+ from TN. All analyses were conducted in triplicate.

2.3 Statistical analysis

Relationships among parameters were analyzed using Pearson correlation. Relationships between physicochemical parameters and all forms of N were examined by stepwise multiple regression analysis. Statistical analysis was performed with SPSS Version 23.

3. RESULTS AND DISCUSSION

3.1 Characteristics of two composts

The composts were divided into three stages according to temperature: initial stage (day 0), thermophilic stage (day 0-13), and mature stage (from day 14) as shown in Figure 1. The mixed manure showed longer period of higher temperature in the thermophilic stage, compared with the cow manure. This phenomenon might have occurred because adding pig manure helped improve the amounts of OM, mainly nitrogen input, which promoted the activities of microbial organisms. Composts mixed with pig manures to enhance N levels include of rice straw, maize straw, corn straw, and saw dust (Huang et al., 2004; Wu et al., 2017a; Li et al., 2019). It is shown in Table 1 that at the date of mixing, the OM content of mixed compost was 1.36 times greater than that of cow compost with C/N of 15.2 (mixed compost) and 21.5 (cow compost). Hence, adding pig manure enhanced the nutrient contents as shown by the high EC for entire study. Both composts reached mature stage within 14 days with the C/N ratio of cow and mixed composts at 14.2 and 13.2, respectively.

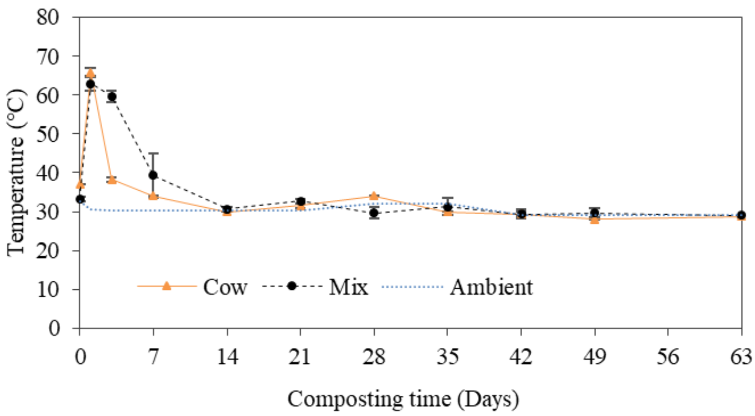

Figure 1. Temperatures of two composts

Table 1. Compost characteristics

	Cow compost		Mixed compost	
	0 day	**63 days**	**0 day**	**63 days**
pH	6.7 (0.1)	6.7 (0.1)	7.5 (0.1)	7.4 (0.1)
% moisture	70.4 (2.5)	19.1 (0.2)	54.2 (0.1)	15.3 (0.1)
EC (dS/m)	2.30 (0.02)	2.63 (0.01)	3.38 (0.09)	5.45 (0.01)
% OM	48.2 (0.9)	37.2 (3.9)	65.5 (0.8)	60.8 (0.9)
C/N	21.5 (0.5)	14.2 (1.1)	15.2 (0.3)	13.2 (0.2)

Note: The numbers in parentheses are standard deviation.

3.2 Nitrogen fractions

Compost is considered as a good source of N. The TN of cow and mixed compost was 1.2-1.6% w/w, and 2.3-2.8% w/w, respectively. Any amount greater than 1-2% is considered to be appropriate to apply to the soil with minimal effect on crop production; if the amount is greater than 2%, the compost can replace the typical N fertilizer (Sullivan et al., 2018). However, most N forms in the compost are in organic form, which is not immediately plant-available. The varieties of the raw materials and the compost conditions influence the releasing N in all forms. The factor was applied in this research, in which two different composts were studied in tropical region, where ambient temperature were rather high around 29-35°C. Org-N was still the most abundant in both composts accounting for 71.51-95.45% in cow compost and 88.26-96.54% in mixed compost (Figure 2). However, the orders of other fractions were quite different. Ammonia nitrogen fraction was abundant in the mixed compost, and nitrate was rich in the cow compost. The average fractions were in the following order:

Cow compost:

Org-N >> NO_3^- > NH_4^+
84.73% 10.27% 5.00%

Mixed compost:

Org-N >> NH_4^+ > NO_3^-
90.56% 7.19% 2.25%

Given that the pH range of the mixed compost was rather high between 6.95 and 8.84, the increase in NH_4^+ was significantly correlated to the elevated pH (r = 0.684, $p<0.01$), as shown in Table 2. However, this relationship was not observed in the cow compost because its pH range was between 6.59 and 6.88. An increase in pH indicated intensified volatilization of ammonia and increased nitrogen loss (Meng et al., 2020). Some organic materials that are rather difficult to decompose, such as lignin, cellulose, and hemicellulose, showed positive relationship in immobilizing NH_4^+ (Mao et al., 2019; Yu et al., 2019). Thus, roughage containing lignin and cellulose in the diet of cow resulted in less readily available nutrients in the compost (Hue and Silva, 2000). The released NH_4^+ from cow compost was rather low than that from mixed compost. Nevertheless, adding pig manure improved overall OM contents, corresponding to the increasing amounts of Org-N. The stable nitrogen form in this fraction restored TN in the mixed compost and released less amounts of NO_3^-. Therefore, the range of NO_3^- in mixed compost was between 0.05% and 4.04% and that in cow compost was between 3.18% and 18.04%.

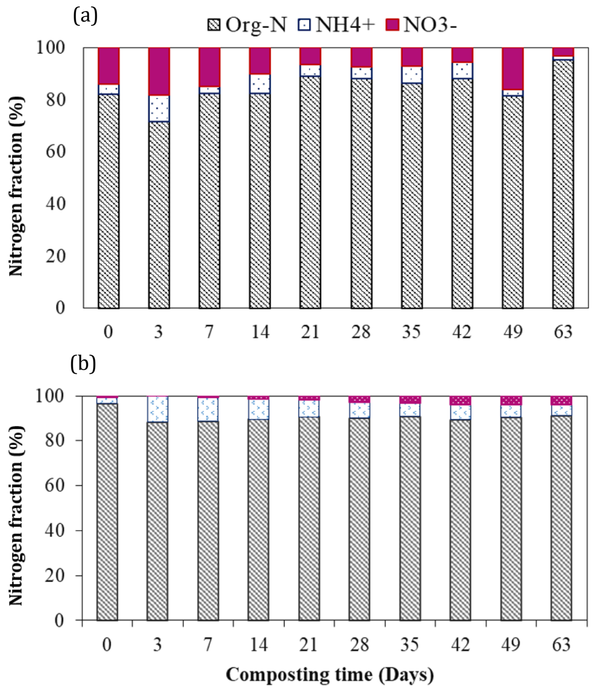

Figure 2. Nitrogen fractions: organic nitrogen (Org-N), ammonia nitrogen (NH_4^+), and nitrate nitrogen (NO_3^-) of (a) cow compost and (b) mixed compost

Table 2. Pearson correlation between physicochemical parameters with total nitrogen and nitrogen forms

Cow manure	TN	Org-N	NH_4^+	NO_3^-
Time	0.885**	0.815**	-0.375*	-0.485**
Temp (°C)	-0.711**	-0.681**	0.310	0.443*
% moisture	-0.829**	-0.748**	0.230	0.482**
pH	0.064	0.117	-0.184	-0.084
% OM	-0.466**	-0.585**	0.358	0.528**
C/N	-0.691**	-0.686**	0.127	0.581**
Mixed manure	**TN**	**Org-N**	**NH_4^+**	**NO_3^-**
Time	0.773**	0.656**	-0.348	0.947**
Temperature (°C)	-0.862**	-0.909**	0.540**	-0.671**
% moisture	-0.736**	-0.496**	-0.073	-0.748**
pH	-0.734**	-0.808**	0.684**	-0.788**
% OM	-0.416*	-0.275	0.020	-0.529**
C/N	-0.897**	-0.778**	0.266	-0.838**

Note: ** Correlation is significant at the 0.01 level, *Correlation is significant at the 0.05 level
TN = total nitrogen, Org-N = organic nitrogen, NH_4^+ = ammonia nitrogen, NO_3^- = nitrate nitrogen, OM = organic matter

3.3 Dynamics of N species during composting

The changes of TN corresponding with time are shown in Figure 3a. The TN of both composts significantly increased with time ($r = 0.885$ and 0.773, respectively, $p<0.01$; Table 2). The fraction accounting for more than 80% in both composts was Org-N (Figure 3b), which also corresponded with time ($r = 0.815$, 0.656, respectively, $p<0.01$). This finding confirmed that the decomposition of OM released a large amount of Org-N into the environment. When the amounts of OM decreased, the amounts of TN increased ($r = -0.466$, -0.416, $p<0.05$). Similar change was found in other composts (Li et al., 2012; Zhang et al., 2016; Tong et al., 2019). However, a reduction in TN was observed during thermophilic phase prior to the increase in TN in the mature stage (Zhou, 2017; Yu et al., 2019; Yang et al., 2020). The situation depended on the varieties of compost materials that might require high amounts of N for ammonification, including the potential to fix or release ammonia gas (Yu et al., 2019; Yang et al., 2020).

The change trends of NH_4^+ and NO_3^- were different between the composts (Figures 3c and 3d). The change of NH_4^+ and NO_3^- of the cow compost corresponded with time ($r = -0.375$, $p<0.05$ and -0.485, $p<0.01$, respectively).

Meanwhile, only NO_3^- was correlated with a positive trend in the mixed compost ($r = 0.947$, $p<0.01$). The amount of NH_4^+ was the highest on day 3 in both composts and increased slightly on day 7 in the mixed compost but dropped dramatically in the cow compost. Afterward, the amount of NH_4^+ in the mixed compost tended to decline and that in the cow compost fluctuated (Figure 3d). When the pH in the cow compost was below 7, nitrification played a significant role for the entire period of composting, even in the thermophilic phase. For the mixed compost, whose pH was elevated during the thermophilic phase (day 0-14), ammonification prevailed and increased the amount of NH_4^+, compared with that in the mature stage; only small amount of NO_3^- was found in this period (Figure 3c). In the mature stage, a slow increase in NO_3^- was observed, indicating the nitrification in the mesophilic stage. This result was in agreement with the phenomenon observed in manure compost mixed with other biogenic wastes (Ren et al., 2016; Zhou, 2017). Therefore, adding pig manure increased Org-N, NH_4^+ and eventually TN, and played a significant role in increasing NO_3^- toward the end of composting.

The Pearson relationships among Org-N, NH_4^+, and NO_3^- are shown in Figure 4. The amount of Org-N in cow and mixed composts decreased, and the amount of NH_4^+ increased ($r = -0.436$, $p<0.05$ and -0.677, $p<0.01$, respectively), confirming mineralization via ammonification. Only the mixed compost showed a correlation between the amounts of NH_4^+ and NO_3^- ($r = -0.413$, $p<0.05$), indicating prominent nitrification between the two forms. As a result, the increase in Org-N was also related to NO_3^- ($r = 0.756$, $p<0.05$). In cow compost, other processes might influence immobilization because the reduction in NO_3^- happened with the increase in Org-N ($r = -0.806$, $p<0.01$). The NH_4^+/NO_3^- ratio is a nitrifying index supported the maturity of the compost. The range of the NH_4^+/NO_3^- of the cow compost was 0.14-1.15 and that of the mixed compost was higher at 1.22-214.50. A nitrification index greater than 3 indicates that organic materials are immature and continue to decompose (Zhang et al., 2016). This finding implied that type of manure related to the amount of nitrogen corresponded to microbial activities. Wu et al. (2017b) showed that NH_4^+ and NO_3^- were indirect parameters regulating the formation of humic substances by the microbial activities. Other factors also had an influence on the mobility of some nitrogen forms. For example, a high pH that might favor ammonia volatilization and eventually the transformation of OM. Nevertheless, in adding pig manure to enhance N qualities, the TN, Org-N, and NH_4^+ in mixed compost were greater than those in cow compost by 1.73-2.01, 1.66-2.36, and 1.43-7.70 times, respectively.

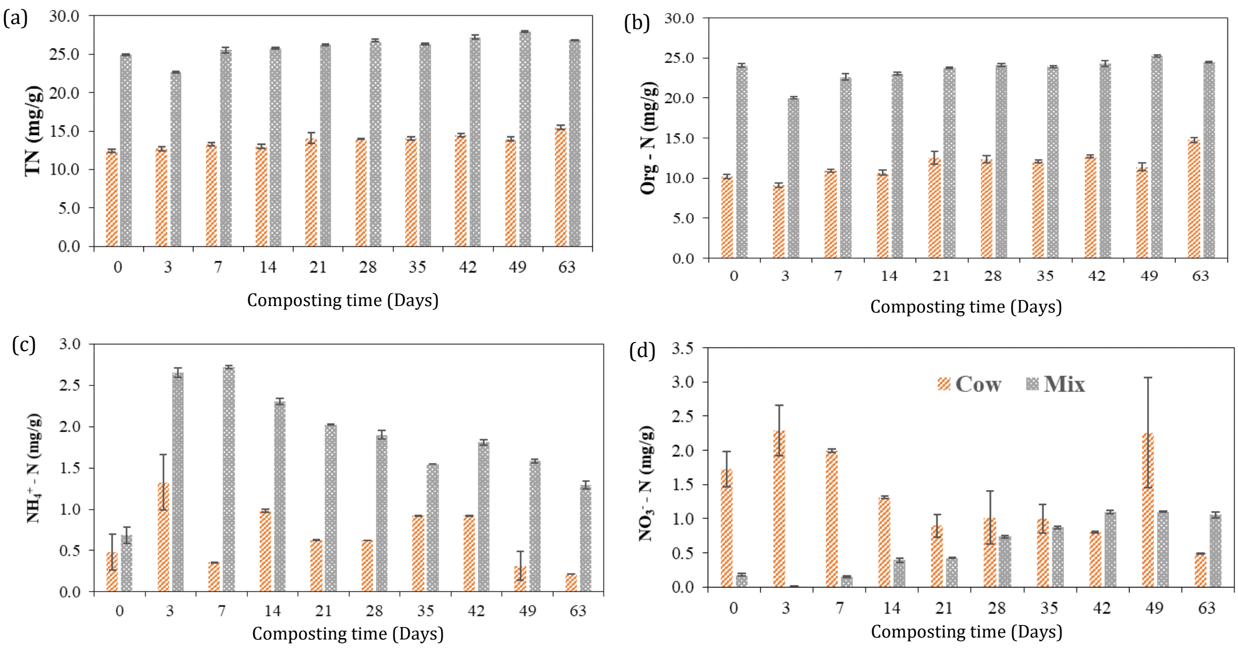

Figure 3. Content of nitrogen in different forms: (a) total nitrogen (TN), (b) organic nitrogen (Org-N), (c) ammonia nitrogen (NH_4^+), and (d) nitrate nitrogen (NO_3^-)

Multiple regression analysis between different forms of nitrogen and physicochemical properties from Table 1 was presented as follows:

Cow compost

$$TN = 0.575\ EC - 0.031\ Moisture - 0.110\ C/N + 15.357 \quad R^2 = 0.782$$

$$NO_3^- = 0.143\ C/N - 1.011 \quad R^2 = 0.337$$

$$Org\text{-}N = -0.048\ Moisture - 0.210\ C/N + 17.007 \quad R^2 = 0.647$$

Mixed compost

$$TN = 0.388\ OM + 0.014\ Temp - 1.765\ C/N - 0.126\ pH + 26.926 \quad R^2 = 0.993$$

$$NH_4^+ = 0.398\ pH + 0.028\ Temp - 0.057\ Moisture - 0.577\ EC + 2.059 \quad R^2 = 0.738$$

$$NO_3^- = -0.395\ pH - 0.044\ OM - 0.013\ Moisture + 6.787 \quad R^2 = 0.927$$

$$Org\text{-}N = -0.101\ Temp - 0.816\ pH + 33.457 \quad R^2 = 0.912$$

TN varied with the properties of the initial compost materials: the C/N ratio was one of the same main factors in both composts. The pH affected all transformations of N, including TN only in the mixed compost. Other physicochemical factors showed different effects on the transformation of N in both composts. Hence, the dynamics of N were different in response to different mobility and eventually compost qualities.

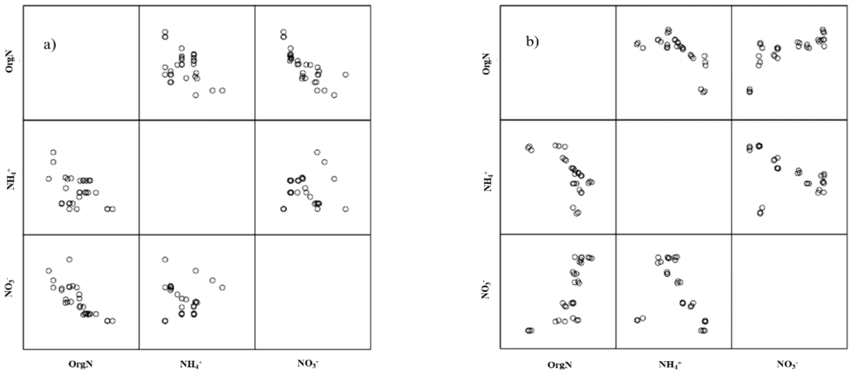

Figure 4. Pearson correlation among all forms of nitrogen in (a) cow compost and (b) mixed compost

4. CONCLUSION

Compost qualities varied according to the raw materials that affected the composting process. Adding pig manure increased OM and N content, leading to increased activities of microbial organisms, especially during thermophilic phase, and intensified volatilization of ammonia as shown by the elevated pH. For cow compost, when the pH was low (below 7), nitrification prevailed and led to the high fraction of NO_3^-. Therefore, controlling composting factors and understanding the sources and types of compost materials is necessary to deter the compost quality and completely utilize the compost.

ACKNOWLEDGMENT

This research was funded by Faculty of Science, Silpakorn University (grant number SRIF-JRG-2565-01) and Silpakorn University Research, Innovation and Creativity Administration Office.

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