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Study on the Morphological Change and Reduction of Nitrogen and Phosphorous in Litter and Compost of Cowshed

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Litter and compost were obtained at a cowshed of a livestock farm in Andong city in Korea. The morphological change of nitrogen and phosphorous from these samples were examined and suggested a more useful and realistic way for reducing them. Constituents and their content of sample were identified by XRF. The nitrite ion (NO_2^-), nitrate ion (NO_2^-) and phosphate ion (PO_4^{3-}) and ammonium ion (NH_4^+), total phosphorous (T-P) and total nitrogen (T-N) released from sample were analyzed using ion chromatograph and UV/Vis spectrometry. As the results of this study, the ammonia in the early stage of cow excretion is a need to make an ammonia gas state that can be immediately volatile by increasing the pH. Nitrogen and phosphorous, the main source of nutrition in green algal bloom can be reduced by transforming insoluble salts such as calcium phosphate ($CaHPO_4{\cdot}3H_2O$) and struvite ($NH_4MgPO_4{\cdot}6H_2O$), respectively, with addition of Ca and Mg after stimulating fermentation of compost.

Keywords: Nitrogen, Phosphorous, Litter, Compost, Struvite.

INTRODUCTION

The livestock industry in Korea has developed rapidly since the 1980's as a life industry and as an industry at the forefront of food sovereignty. According to the press release from Ministry of Environment in 2016, it was estimated that about 3 million cows were raised at farms across the country and excretions produced from cows per day reached 1.3 million tones [1]. Korean livestock industry has much difficulties in running livestock farms due to the narrow farmland and the lack of grasslands. Despite government's effort, administrative complaints from local residents have increased because of water pollution and bad odours inflicted by the inappropriate handling and the discharge of livestock excretions [2]. Livestock excretion contains nitrogen, phosphorus, bacteria and organic matter. If they exceed the environmental load standard, they cause environmental problems such as odour, water pollution, soil pollution, air pollution, *etc*. and negatively affect the human body and the natural ecosystem. In particular, because the overuse of compost and liquid fertilization of livestock excretions sprayed on farmlands is recognized as a major source for the generation of green algae in soil and rivers, environmental regulations such as revision of the Livestock Excretions Act are continuously being strengthened [3,4].

Cow excrement is stagnant on the floor of the cowshed for 1 to 3 months after excretion, then fermented for at least 1 month before being used as compost [5]. In the fermentation process, morphological changes of nitrogen and phosphorus causing algal blooms occur. The cow excrement is mainly composed of fiber. During cow goes through the digestive process, nitrogen and phosphorus are discharged into the environment as ammonia and nitrate ions, and as organic phosphorus salt and phosphate ions, respectively. Such morphology changies of nitrogen and phosphorus are caused by natural oxidation or aerobic microorganisms in the process of contact with air after moisture from excrement evaporates into the air. In addition, even under the condition where moisture from excrement is not evaporated, the morphology of nitrogen and phosphorus

Fig. 1. Sampling of (a) litter and (b) compost

are also changed in the decomposition process of excrement by anaerobic microorganisms [6-11].

In this study, the process of changing morphology of nitrogen and phosphorous produced when cow excrement is fermented in compost was investigated and also examined a suitable structure of the morphology, which can immobilize nitrogen and phosphorus in insoluble forms. In addition, the conditions are established, which can reduce nitrogen naturally by volatilizing it into the atmosphere at the excretion stage of cow excrement.

EXPERIMENTAL

Sample preparation: The samples were collected from litter of the cowshed where excrement accumulates on the floor and compost as shown in Figs. 1 and 2, respectively. Cows were raised on a 10 cm thick layer of chaff used as litter at the bottom of the cowshed. After the cow breeding, the litter was first dried and then transferred to the composting ground. The compost obtained was re-dried again and fermented the litter for about 30 days.

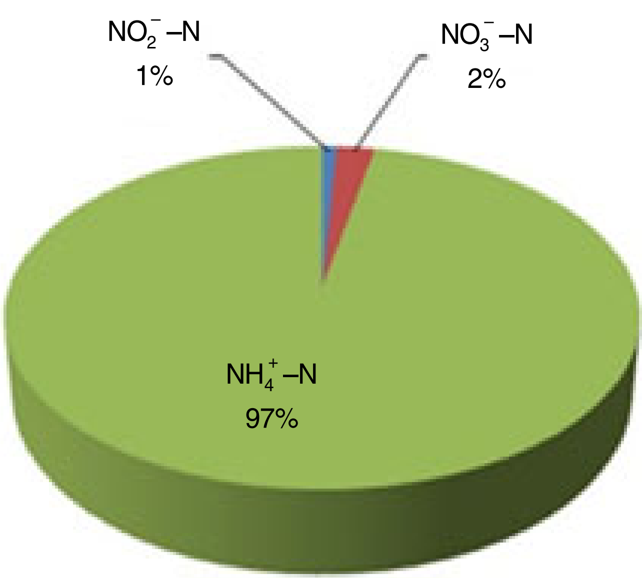

Fig. 2. Morphological content (wt. %) of nitrogen in litter

Sample charaterization: The oxides and their contents of the samples were investigated using an X-ray fluorescence analyzer (ZSX Primus II, Rigaku, Japan). The samples, prior to analysis, were first burned at 800 ºC and the resulting ash was produced into pellets. Inorganic components in the samples were determined with an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, 720 series, Agilent Technologies, USA). Before analysis, the samples were dried at 120 ºC and after powdering, put in a 6 mL of mixed acid mixed with 0.25 g of nitric acid, hydrofluoric acid and perchloric acid. The samples in mixed acid were completely dissolved using a high pressure microwave melting device at 220 ºC. The final sample volume for analysis was made to be 25 mL by adding distilled water after volatilizing the acid in a Teflon container. Nitrite ion (NO_2^-), nitrate ion (NO_2^-) and phosphate ion (PO_4^{3-}) and ammonium ion (NH_4^+), total phosphorous (T-P) and total nitrogen (T-N) released from the sample were analyzed using ion chromatograph (DX-600, Dionex, USA) and UV/Vis spectrometry (Cary-5000, Varian Technology, Australia), respectively. For sample analysis by ion chromatograph (IC), the dried powder samples were filled with distilled water and pulverized using a blender. The solution was further centrifuged at 4,000 rpm for 5 min to remove fine particles. The concentration of nitrite ion, nitrate ion and phosphate ion in the supernatant was determined using IC. Ammonium ion, total nitrogen and total phosphorus were measured according to the Water Quality Process Test Act. Ammonium ion was pretreated by the indophenol method, which is an absorbance method and analyzed at a wavelength of 630 nm. Total phosphorous and total nitrogen were pretreated with potassium persulfate and then measured at wavelengths of 220 nm and 880 nm, respectively.

RESULTS AND DISCUSSION

XRF analysis: The results of XRF analysis for litter and compost are shown in Table-1. Each constituent (wt.%) consisted of litter and compost represented almost similar levels. Their main components were Na_2O, MgO, SiO_2, P_2O_5, Cl, K_2O and CaO, while Al_2O_3, SO_3, MnO and Fe_2O_3 were in negligible amounts. Sodium, chlorine, potassium, phosphorus and sulfur may be partially included in the litter itself, but most of them are accumulated in large quantities from influx of cow excrement. Other ingredients exists in common in both litter (chaff) and excretions. In particular, the content of silicon was higher than other ingredients because the chaff contains usually a lot of silicon. Sodium and chlorine are related to the food source. Cow usually intakes a mixture of grains and straw. Therefore,

TABLE-1
CONSTITUENTS AND THEIR CONTENT (wt. %) OF LITTER AND COMPOST BY XRF

Sample	Litter	Compost
Na_2O	6.96	7.43
MgO	9.67	9.92
Al_2O_3	1.27	1.10
SiO_2	20.52	18.11
P_2O_5	11.24	12.62
SO_3	2.44	2.61
Cl	9.05	10.05
K_2O	20.98	20.87
CaO	16.18	15.58
MnO	0.34	0.26
Fe_2O_3	1.33	1.45

there was no significant difference in the content of sodium and chlorine affecting digestive function in litter and compost.

ICP-AES analysis: Table-2 shows inorganic elements and their contents (wt. %) in litter and compost using ICP-AES. As shown in Table-2, the content of inorganic elements did not show a noticeable difference before and after fermentation. In litter and compost, content of calcium and magnesium was higher than the inorganic elements such as manganese and zinc. Calcium and magnesium basically have a tendency to bind to phosphorus. For this reason, they can be an alternative to reduce the discharge of phosphorous from compost when they are contained in large amounts. However, if these elements exist in insoluble form, they cannot play any role in reducing phosphorous. Therefore, in order to remove phosphorous by precipitation, it is necessary to convert phosphate ion in water into a form of insoluble salt by adding calcium, magnesium, aluminum, iron, *etc*. after transforming phosphorous into phosphate ion that ionizes well in water [12-16].

TABLE-2
INORGANIC COMPONENTS OF LITTER AND COMPOST (wt. % BASED ON DRY SAMPLE) BY ICP-AES

Sample	Ca	Mg	Al	Fe	Mn	Zn
Litter	1.52	0.99	0.10	0.16	0.025	0.019
Compost	2.77	0.69	0.16	0.10	0.004	0.017

Eluate analysis: In general, nitrogen present in the protein in cow feed source is mostly converted to ammonia while excreting through the digestive process. Ammonia in excretion is transformed into nitrate ion *via* nitrite ion by bacteria under the aerobic condition and then finally turned to nitrogen through the denitrification reaction. The analysis result for various forms of nitrogen in samples is listed in Table-3. Amount of total nitrogen in litter and compost was 6740 and 6920 mg/kg, respectively. Ammonium ions showed the highest level of content in total nitrogen, whereas the content of nitrite ion and nitrate ion appeared low. Generally, ammonium ion-N (NH_4^+-N) turns gradually to the form of nitrate ion-N (NO_3^--N) as the fermentation time goes by.

As shown in Table-3, the amount of NO_3^--N in compost obtained through a month of fermentation process was 4.5 times higher than that of litter. However, the transformation efficiency from NH_4^+-N to NO_3^--N in compost was not a very high level

TABLE-3
NITROGEN COMPONENTS OF LITTER AND COMPOST (wt. % BASED ON DRY SAMPLE)

Sample	Value based on dry sample (mg/kg)			
	NO_2^--N	NO_3^--N	NH_4^+-N	T-N
Litter	31	99	5,280	6,740
Compost	8	453	4,960	6,920

within 10 %. It is presumed that such low level results from the moisture contained in compost. Based on the analysis data, more chemical rather than a biological method is required since the efficiency of the nitrification reaction by means of the low microbial action. Consequentially, it is more efficient to volatilize ammonia into the atmosphere by increasing the pH of the excretions until alkaline nature is formed rather than lowing nitrogen through nitrification and denitrification processes.

Table-4 represents the analysis result for phosphorus present in various forms in samples. The amount of total phosphorus andphosphate ion-phosphorus (PO_4^{3-}-P) in litter and compost are 542 and 460 mg/kg and 14.36 and 48.93 mg/kg, respectively. In the initial excretion stage of cow, phosphorous exists in the form of organic phosphorous salt and then changed to the form of phosphate ions which dissolves in water through microbial activity and an oxidation reaction by contacting with air. As a result, more phosphate ions were generated in compost that experinced the fermentation process compared with litter. Phosphorous is difficult to transform immediately into a soluble form at the state of organic phosphorous salt after excretion of cow. Therefore, it needs to be transformed phosphorous as organic phosphorous salt into phosphorous as phosphate ions by increasing the action of microorganisms and the contact time with air. Phosphate ions are well soluble and easily ionized in water, thus they can become an insoluble material by adding calcium and magnesium [10,11].

TABLE-4
VARIOUS FORMS OF PHOSPHOROUS IN LITTER AND COMPOST (wt. % BASED ON DRY SAMPLE)

Sample	Value based on dry sample (mg/kg)	
	PO_4^{3-}-P	T-P
Litter	14.36	542
Compost	48.93	460

Morphological changes of nitrogen and phosphorus in cow excrement: The moisture in cow excrement was gradually reduced through drying and fermentation processes. During this process, various salts dissolved in moisture are solidified by ionic bonding. The solidified materials have the characteristics of ionizing again by being dissolved salts when water was added. In general, while the moisture in the cow excrement dried, nitrite ion, nitrate ion and phosphate ion form mainly ionic bonds with sodium ion (Na^+) or potassium ion (K^+), and ammonium ions exists as ammonium chloride salt by combining with chloride ions (Cl^-). Besides, phosphate ions become monosodium phosphate (NaH_2PO_4) and monopotassium phosphate (KH_2PO_4) as the moisture in the cow excrement dries. However, when NaH_2PO_4 and KH_2PO_4 were in contact with water, they are easily eluted as phosphate ions. In particular, phosphorus exists as phosphoric acid (H_3PO_4) in strong acidity, as dihydrogen phosphate ion ($H_2PO_4^-$) in weak acidity, as hydrogen phosphate ion (HPO_4^{2-}) in neutral and slightly alkaline, and as phosphate ion (PO_{43}^-) in strong alkalinity. Therefore, in order to precipitate phosphorus as an insoluble salt by adding calcium or magnesium, it is important to adjust the pH to a neutral or weakly base.

Ammonia exists as ammonium ion in the cow excrement, and then is transformed to ammonium chloride salt by combing with chloride ion as fermentation and drying proceed. The NH_4Cl salt is ionized into ammonia ions and chloride ions again when water added. However, when ammonium ions and phosphate ions coexist in the presence of Mg^{2+} ions, these three ions are chemically combined to form struvite salt ($NH_4MgPO_4 \cdot 6H_2O$), which is an insoluble salt [17-19].

Figs. 2 and 3 show the morphological content (wt.%)of nitrogen in litter and compost at the cowshed. Out of the total nitrogen, the content of NH_4^+-N, NO_2^--N and NO_3^--N accounted for 97%, 1% and 2% in litter, and 93%, 1% and 6% in compost, respectively. The NH_4^+-N, which is present in large quantities in the early stages of execretion, is converted into NO_3^--N by microbial activity. The content of NO_3^--N found in compost was three times higher compared with that of litter, indicating that the conversion rate of NH_4^+-N to NO_3^--N is 3 times faster. It is clear that the conversion rate of NH_4^+-N to NO_3^--N depends on whether the fermentation is present or not. The longer fermentation time, the more NH_4^+-N undergoes oxidation process and eventually increses the conversion rate. If the fermentation is not carried out normally due the short time, residual NH_4^+-N dissolves in water and flows into rivers, acts directly as a nutrient source for green algae as well as causes the damage such as gas disturbance of crops. If the excrement is dried without fermentation, NH_4^+-N becomes more difficult to reduce because it exists as a non-volatile ammonia salt and is easily soluble in water.

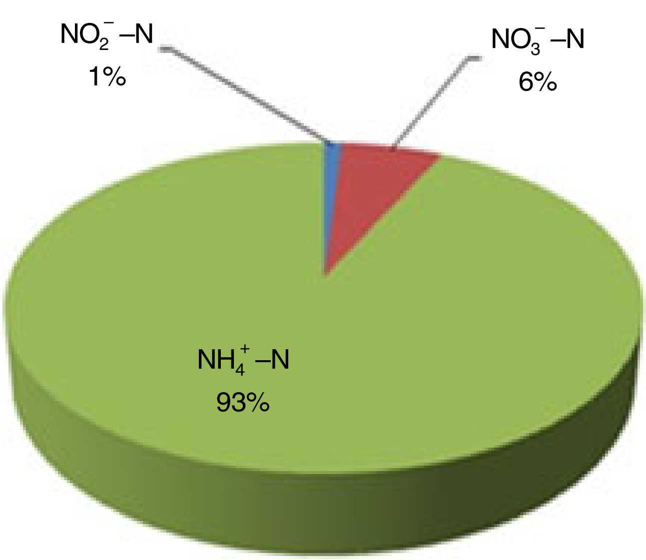

Fig. 3. Morphological content (wt. %) of nitrogen in compost

Typically, phosphorus almost exists as an insoluble organic phosphorous salt when just drying without the fermentation process by microorganisms. The organic phosphorous salt returns to phosphate ion and dissolves in rainwater as fermentation progresses after spraying into the soil. Excess phosphate ion that flows into rivers and streams cause green algae. Figs. 4 and 5 show the morphological content (wt.%) of phosphorous in litter and compost at the cowshed. The content of phosphate ion was found to be 8% in litter and 33% in compost, respectively. As seen in Fig. 3, the content of phosphate ion in compost was about 4 times higher than that of litter. It points out that the conversion of organic phosphorus salt to phosphate ion has been made easily while the fermentation is in progress. If substances such as calcium and magnesium is added to compost to make it insoluable material, green algae can be prevented to some extent.

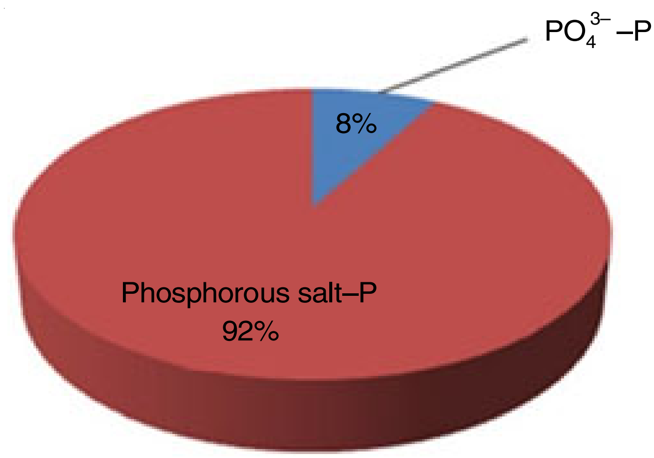

Fig. 4. Morphological content (wt. %) of phosphorous in litter

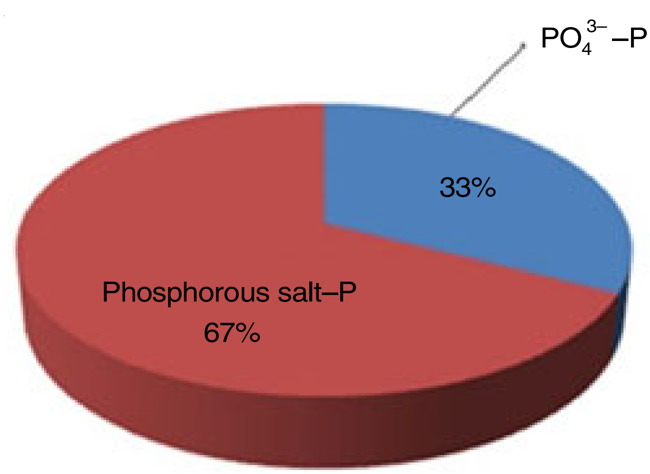

Fig. 5. Morphological content (wt. %) of phosphorous in compost

Conclusion

Nitrogen is present primarily as ammonia when execreted through the digestive process. Ammonia begins to change to nitrate ion *via* nitrite ion through a nitric oxidation as the fermentation proceeds. When only dried without fermentation, ammonia remains in the form of a salt and is easily dissolved when in contact with water. According to present analysis, the content of nitrate ion in compost was around 4.5 times higher than that of litter. It can be explained that the transition from ammonia to nitrate ion occurs more quickly when the fermentation process has gone through. However, the conversion rate from ammonia to nitrate ion was not very large within 10%. It means that even if nitrate ion content is increased through fermentation, the change in nitrogen morphology is not significant. In addition, the pHs of the sample measured were in the range of 7.1 to 7.3, and under this condition, the volatilization rate of ammonia was quite low. For this reason, no significant change of nitrogen morphology occurred in litter and compost. Therefore, it is necessary to find a way to reduce ammonia in the early stage of excretion. One of the most promising ways to easily volatilize ammonia is to increase alkalinity of execrement. Phosphorus is present as an insoluble organic phosphorous salt at the beginning of excretion. And, as fermentation by microbial activity progresses, most of the organic phosphorous salt was converted to phosphate ion. According to the analysis data, the content of phosphate ion in compost was about 4 times higher than that of litter. It suggests that the conversion from organic phosphorous salt to phosphate ion was done better by the fermented compost compared with the just dried litter. Therefore, conversion rate will be higher if fermentation time of compost is extended further. The best way to prevent phosphorous leakage from compost by converting organic phosphorous salt to phosphate ions, followed by the addition of calcium and magnesium to combine chemically them into insoluble forms such as calcium phosphate ($CaHPO_4 \cdot 3H_2O$) and struvite ($NH_4MgPO_4 \cdot 6H_2O$).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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