Journal of the Korean Society of Grassland and Forage Science 40(4): 274~278, 2020
https://doi.org/10.5333/KGFS.2020.40.4.274

ISSN 2287-5824 (Print)
ISSN 2287-5832 (Online)

Research Article

The Effects of Zeolite on Ammonia, Nitrous Oxide Emission, and Forage Yield from Pig Slurry Applied to the Forage Corn Cropping

Ah-Reum Choi[1], Sang-Hyun Park[2] and Tae-Hwan Kim[2*]

[1]Department of Animal Science, College of Agriculture & Life Science, Chonnam National University, Gwangju, 61186 Korea

[2]Institute of Environmentally-friendly Agriculture, Chonnam National University, Gwangju 61186 Korea

ABSTRACT

Pig slurry (PS) is the most applicable recycling option as an alternative organic fertilizer. The application of pig slurry has the risk of air pollution via atmospheric ammonia (NH_3) and nitrous oxide (N_2O) emission. The zeolite has a porous structure that can accommodate a wide variety of cations, thus utilizing for the potential additive of deodorization and gas adsorption. This study aimed to investigate the possible roles of zeolite in mitigating NH_3 and N_2O emission from the pig slurry applied to the maize cropping. The experiment was composed of three treatments: 1) non-N fertilized control, 2) pig slurry (PS) and 3) pig slurry mixed with natural zeolite (PZ). Both of NH_3 and N_2O emission from applied pig slurry highly increased by more than 3-fold compared to non-N fertilized control. The NH_3 emission from the pig slurry was dominant during early 14 days after application and 20.1% of reduction by zeolite application was estimated in this period. Total NH_3 emission through whole period of measurement was 0.31, 1.33, and 1.14 kg ha^{-1}. Nitrous oxide emission in the plot applied with pig slurry was also reduced by zeolite treatment by 16.3%. Significant increases in forage and ear yield, as well as nutrient values were obtained by pig slurry application, while no significant effects of zeolite were observed. These results indicate that the application of zeolite and pig slurry efficiently reduces the emission of ammonia and nitrous oxide without negative effects on maize crop production.

(**Key words**: Ammonia, Maize, Nitrous oxide, Pig slurry, Zeolite)

Ⅰ. INTRODUCTION

Animal manures, which is emitted over 48 million tons per year in Korea, is an over-burden to environment. Besides, they are an important organic resource as eco-friendly organic fertilizer containing nitrogen (N), phosphorus (P), potassium (K) and other nutrients. Among these, pig slurry utilization as an alternative organic fertilizer has become the most viable recycling option to improve crop yield and soil quality (Ndayegamiye and Côté, 1989; Bernal et al., 1992)

However, the application of pig slurry has the risk of the ecological pollution by emitting the greenhouse gas such as nitrous oxide (N_2O) and methane (CH_4), and nitrogen loss as ammonia (NH_3) and nitrate (NO_3^-) leaching. Of these, NH_3 volatilization contributing to an offensive odor, eutrophication and acidification of ecosystems. It results in nitrogen loss during manure composting and when applied onto field. When NH_3 is released into the air, it can rapidly react with acidic compounds, such as nitric acid and sulfuric acid, to form very fine particulate matter has a diameter of <2.5 microns, which is health concern affecting respiratory function (Bittman and Mikkelsen, 2009). Furthermore, NH_3 deposition may induce the formation of N_2O in the atmosphere (Moiser, 2001). The N_2O is a trace gas that cause global warming and reduces O_3 in stratosphere (Rodhe, 1990), accounting for 5% of the total greenhouse effect (Houghton et al., 1990). It has 290 - 310 times higher global warming potential than carbon dioxide (Keith et al., 2005).

Many strategies have been studied to reduce the NH_3 and N_2O. The acidification of manure has been widely studied and recently reviewed (Birkmose et al., 2013; Fanguerio et al., 2015; Park et al., 2018). Nitric acid or sulfuric acid can be used to drop the manure pH to 6.5 and then reduced NH_3 emission by up to 75% (Rotz, 2004). Also, the urease and/or nitrification inhibitors delay the rapid hydrolysis of urea and NO_3^- production by depressing the activity of bacteria. The use of urease and/or nitrification inhibitors increased N use efficiency by reducing N loss via gas emission and leaching (Di and Cameron, 2002; Park et al., 2016). The zeolite has a porous structure that can accommodate a variety of cations, such as sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and others, and widely

---

*Corresponding author: Tae-Hwan Kim, Department of Animal Science, College of Agriculture & Life Science, Chonnam National University, Gwangju 61186, Korea, Tel: +82-62-530-2126, Fax: +82-62-530-2129, E-mail: grassl@chonnam.ac.kr

utilized as water moderator, deodorization, additives to animal feed, and gas adsorption. During manure composting process, addition of artificial zeolite caused to decrease the NH_3 emission. Kithome et al. (1999) reported that the zeolite having a high affinity for NH_4^+ ions reduce NH_3 volatilization via decreasing concentration of free NH_4^+ ions.

Thus, the present study aimed to investigate the effect of natural zeolite and pig slurry application in mitigating of ammonia (NH_3) and nitrous oxide (N_2O) emission from pig slurry applied to maize.

II. MATERIALS AND METHODS

1. Experiment design

The present study was conducted in Chonnam National University, located in Gwangju, South Korea. The experiment was allocated with three treatments; control (non-N fertilizer, only water), pig slurry (PS) and pig slurry mixed with zeolite (PZ). Natural zeolite was mixed with pig slurry and applied at a rate 5% of the pig slurry (w/w). The pig slurry was obtained from the ECOBIO farming/agricultural association corporation (Namwon, Korea). The nitrogen property of pig slurry was shown in Table 1. The natural zeolite is commercially supplied by Han-Doo Corporation (Gampo, Korea). The chemical components of the natural zeolite were shown in Table 2.

2. Plant growth and harvest

Forage corn (*Zea mays*, C.V. Pioneer-35P95) was planted at 25th May in randomized complete block design with three replications; each treatment block measured 2 m × 10 m. The maize seeding was performed in lines keeping maize to maize distance 20 cm of seed spacing and 65 cm of row spacing. The plot of pig slurry (without or with zeolite) treatments was evenly applied with a rate of 200 kg N ha^{-1} (340 L), before 2 weeks of seedling. Harvesting of maize was conducted 103 days after seeding (3rd September).

3. Gas emission sampling

To collect NH_3 emission, modified acid trap system method described by Ndegwa et al. (2009). Each chamber (20 cm diameter × 30 cm depth) was connected to NH_3-N trapping bottles containing 20 ml of 50 mM sulfuric acid and a vacuum system to pull air through the chambers. The ammonia traps flow a rate of approximately 1 L per minute. The N_2O was collected from closed chamber using a syringe, then stored in 10 ml vacutainer tube prior to analysis. The gas sampling was done in the morning 09:00 in order to minimize diurnal variation in flux patterns. The gas emission was determined daily for the first 14 days, then at 7 d intervals afterward.

4. Chemical analysis

The concentration of NH_3 in the acid trap solution (e.g. ammonium sulfate) was colorimetrically determined with Nessler's ammonium color reagent after microdiffusion in a conway dish (Kim and Kim, 1996) and expressed as the content of NH_3-N emitted per hectare. N_2O concentration were analyzed by a gas chromatograph (7890A, Agilent technologies, USA) equipped with a thermal conductivity detector (TCD). Separation was achieved with a HP-Plot 5A column (30 m × 0.53 mm × 25 μm) using helium as the carrier gas, at a flow rate of 2 mL min^{-1}. The N_2O fluxes were calculated as described by Guo et al. (2012). Cumulative NH_3 and N_2O emissions over the entire experimental

Table 1. Nitrogen compounds of the pig slurry

	Total N ($g\ N\ kg^{-1}$)	NH_4^+ ($mg\ N\ kg^{-1}$)	NO_3^- ($mg\ N\ kg^{-1}$)	Organic N ($g\ N\ kg^{-1}$)
Pig slurry	1.16 ± 0.02	200.2 ± 10.3	147.2 ± 2.0	0.81 ± 0.01

Values are mean ± SE of three replicates.

Table 2. Chemical analysis of the natural zeolite

Component	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O
Content (%)	66.5	14.7	1.68	1.25	1.82	1.90	3.25	0.04	8.04

period were calculated by summing all daily measurements and period estimations (number of day × mean flux between sampling dates).

N property of pig slurry was determined according to the method of Bremner (1996). Total nitrogen was determined by digestion using the Kjeldahl procedure. Inorganic N was extracted with 2 M KCl and the NH_4^+-N was determined by distillation in an alkaline medium (MgO). The same procedure was used for NO_3^--N after reduction with Devarda's alloy (Lu, 2000).

The nutrient value of maize harvested at cutting time was determined with the subsamples collected for dry matter (DM) yield. The maize samples were analyzed for crude protein (CP) according to the methods of the Association of Official Analytical Chemists (AOAC, 1990). The neutral detergent fiber (NDF) and acid detergent fiber (ADF) were determined by the method of Van Soest et al. (1991) using a Dosi-Fiber extractor (Dosi-fiber, Barcelona). TDN was estimated by the ADF-based equation: TDN = 88.9 – (0.779 × % ADF).

5. Statistical analysis

Duncan's multiple range tests were used to compare the means of three replications between treatments. Unless otherwise stated, conclusions are based on differences between the means, with the significant level at p 0.05 by using SAS 9.1.3 software.

Ⅲ. RESULTS AND DISCUSSION

The application of pig slurry into the grassland and crop is a meaningful practice to recycle organic resources, however it accompanies with emission of hazardous gas and nitrogen loss. In the present study, we attempt to estimate the effectiveness of zeolite in mitigating NH_3 and N_2O emission. The total NH_3 emission throughout the experimental period in the plots applied with pig slurry was 5.32-fold higher than that of non-N fertilized control (Fig. 1). In the plots applied with pig slurry, higher emission which includes the highest emission within 3 days occurred dominantly up to 14 days after application of pig slurry (Fig. 1). When pig slurry is applied to maize field, a large portion of NH_3 volatilization is occurred at the early period (Rochette et al., 2001; Sommer and Hutching, 2001). Li and Li (2014) reported that most of NH_3 emitted within 7 days in laboratory aerobic incubation from chicken, pig and cattle manure. In this study, total NH_3 emission through whole period of measurement was 0.31, 1.33, and 1.14 kg ha^{-1}, respectively, in the non-N fertilized control, pig slurry alone and treated pig slurry with zeolite (inlet of Fig. 1). This results reflected the mitigation of NH_3 emission by zeolite application during the early 14 days (-20.1%) when a larger proportion NH_3 emission occurred. Similarly, several studies have reported that the reduction of NH_3 emission was decreased by adsorption in zeolite (He at al., 2002; Park et al., 2014; Kim, 2016). Lee at al. (2000) also reported that the NH_3 emission in cattle manure composting was decreased by 54~70% by application of artificial zeolite, in addition the more zeolite applied, the less ammonia was emitted. These alleviatory effects of zeolite application on NH_3 emission would be possibly associated with the property of zeolites which have a porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others and these positive ions are rather loosely held and can readily be exchanged for others as known as "molecular sieves" (Pabalan and Bertetti, 2001).

The N_2O emission occurs mainly through both aerobic nitrification, in which NH_4^+ is oxidized NO_2^- and further NO_3^-, and anaerobic microbial denitrification, in which NO_3^- is reduced to gaseous nitrogen compounds (Gilsanz et al., 2016). Therefore, the factor of determination of N_2O emission are the amount of NH_4^+-N available for nitrification to NO_3^--N and soluble organic C available for denitrification. In this study, daily N_2O emission

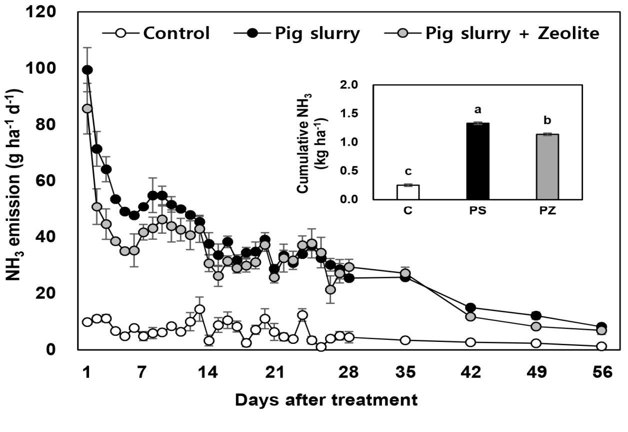

Fig. 1. Changes in daily emission of ammonia (NH_3) and total cumulative NH_3 emission throughout the whole period of measurement (inlet of Fig. 1) in the plot of non-N fertilized control (C), only pig slurry (PS), and pig slurry mixed with zeolite (PZ). Data are mean ± SE (n=3). Different letters indicate significantly different at $p < 0.05$ according to the Duncan's multiple range test.

in both plots of pig slurry treated with or without zeolite was always higher within a range of 2.8 – 7.0 g ha^{-1}, while 1.3 – 2.4 g ha^{-1} in the non-N fertilized control (Fig. 2). As a time-course kinetics, daily N_2O emission was the highest at 21 days after pig slurry treatment and then it slightly decreased (Fig. 2.). This later peak of N_2O emission, comparing to that of NH_3 pattern, reflected the process of nitrification from to NH_4^+ to NO_3^-, which is the initial required substrate for denitrification to produce N_2O (Subbarao et al., 2006; Gilsanz et al., 2016). Total N_2O emission throughout whole period of measurement 38.8, 94.7, and 82.0 g N ha^{-1}, respectively, in the non-N fertilized control, pig slurry alone and treated pig slurry with zeolite (inlet of Fig. 2). This result indicated that zeolite reduced the N_2O emission by 13.4% from pig slurry applied to forage corn cultivation. Ates et al. (2011) reported that natural zeolite and iron exchanged natural zeolites decreased the nitrous oxide decomposition activity.

Forage yield and nutrient composition as affected by pig slurry application with/without zeolite are summarized at Table. 3. Forage DM yield was significantly higher in both plots applied pig slurry, with an increase of 64% in the Zeolite treated and 57% in pig slurry alone compared to non-N fertilized control. Pig slurry application also increased ear yield by 35% on average. These results were consistent with the results of Cairo et al. (2017) who reported a positive effect of zeolite and organic fertilizer on sugarcane yield. In addition, CP and TDN content was also higher in both plots applied with pig slurry than non-N fertilized control, whereas NDF and ADF were not significantly affected (Table 3). However, the effect of zeolite overall on the variables of yield and nutrient composition was statistically poor or not significant.

The results obtained indicated that a proper utilization of zeolite in the pig slurry application for the forage production may represent an effective means to mitigate the emission of ammonia and nitrous oxide without disturbing forage corn growth and yield.

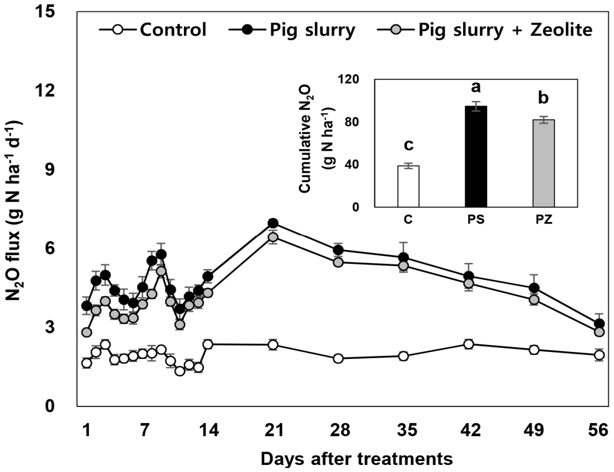

Fig. 2. Changes in daily emission of nitrous oxide (N_2O) and total cumulative N_2O emission throughout the whole period of measurement (inlet of Fig. 2) in the plot of non-N fertilized control (C), only pig slurry (PS), and pig slurry mixed with zeolite (PZ). Data are mean ± SE (n=3). Different letters indicate significantly different at $p < 0.05$ according to the Duncan's multiple range test.

Ⅳ. ACKNOWLEDGMENTS

This study was financially supported by the National Research Foundation of South Korea (NRF-2019R1A6A3A01092319).

Ⅴ. REFERENCES

AOAC. 1990. Association of official analytical chemists (15th ed.). Official Methods of Analysis. Arlington, Virginia.

Ates, A., Reitzmann, A., Hardacre, C. and Yalcin, H. 2001. Abatement of nitrous oxide over natural and iron modified natural zeolite. Applied Catalysis A: General. 407:67-75.

Table 3. The effects of pig slurry applied without or with zeolite on herbage, ear yield, neutral detergent fiber (NDF), acid detergent fiber (ADF), crude protein (CP) and total digestible nutrients (TDN)

	Total herbage yield (t ha^{-1})	Ear DM (t ha^{-1})	NDF (%)	ADF (%)	CP (%)	TDN (%)
Control (non-N fertilized)	7.5 ± 0.2^b	2.25 ± 0.33^b	46.8 ± 1.4^a	26.4 ± 0.5^a	6.7 ± 0.2^b	68.1 ± 0.4 ^{b}
Pig slurry	12.3 ± 0.9^a	3.04 ± 0.23^a	45.3 ± 1.3^a	23.5 ± 0.6^b	7.5 ± 0.3^a	70.3 ± 0.5^a
Pig slurry + Zeolite	11.7 ± 0.8^a	3.08 ± 0.23^a	43.0 ± 1.1^a	22.9 ± 0.3^b	7.9 ± 0.3^a	70.8 ± 0.2^a

Values are mean ± SE of three replicates.
Different letters in horizontal row indicate significantly different at $p < 0.05$ according to the Duncan's multiple range test.

Bernal, M.P., Roig, A., Madrid, R. and Navarro, A.F. 1992. Salinity risk on calcareous soils following pig slurry applications. Soil Use and Management. 8:125-130.

Birkmose, T. and Vestergaard, A. 2013. Acidification of slurry in barns, stores and during application:Review of Danish research, trials and experience. In Proceedings from the 15th RAMIRAN Conference, Versailles, France.

Bittman, S. and Mikkelsen, R. 2009. Ammonia emissions from agricultural operations: Livestock. Better Crops. 93:28-31.

Bremner, J.M. 1996. Nitrogen-total. In D.L. Sparks, A.L. Page, P.A. Helmke, R.H. Loeppert, P.N. Soltanpour, M.A. Tabatabai, C.T. Johnston and M.E. Sumner (Eds.), Methods of soil analysis. Part 3: Chemical methods. SSSA Book Series 5 (pp. 1085-1121). SSSA and ASA. Madison.

Cairo, R.C., Armas, J.M., Artiles, P.T., Martin, B.D., Carrazana, R.J. and Lopez, O.R. 2017. Effect of zeolite and organic fertilizers on soil quality and yield sugarcane. Australian Journal of Crop Science. 11:733-738.

Di, H.J. and Cameron, K.C. 2002. The use of nitrification inhibitor, dicyandiamide (DCD), to reduce nitrate leaching from cow urine patches in a grazed dairy pasture under irrigation. Soil Use and Management. 18:395-403.

Fanguerio, D., Maibritt, H. and Gioelli, F. 2015. Acidification of animal slurry-a review. Journal of Environmental Management. 149:46-56.

Gilsanz, C., Báez, D., Misselbrook, T.H., Dhanoa, M.S. and Cárdenas, L.M. 2016. Development of emission factors and efficiency of two nitrification inhibitors, DCD and DMPP Agriculture. Ecosystems and Environment. 216:1-8.

Guo, Y., Li, B., Di, H., Zhang, L. and Gao, Z. 2012. Effects of dicyandiamide (DCD) on nitrate leaching, gaseous emissions of ammonia and nitrous oxide in a greenhouse vegetable production system in northern China. Soil Science and Plant Nutrition. 58:647-658.

He, Z.L., Calvert, D.V., Alva, A.K., Li, Y.C. and Banks, D.J. 2002. Clinoptilolite zeolite and cellulose amendments to reduce ammonia volatilization in a calcareous sandy soil. Plant and Soil. 247:253-260.

Houghton, J.T., Jenkins, G.J. and Ephraums, J.J. (Eds.) 1990. Climate change: The IPCC assessment. Cambridge University Press, Cambridge, p. 365.

Keith, P.S., Jan, S.F., Kinfe, H. and Nicola, S. 2005. Alternatives to the global warming potential for comparing climate impacts of emissions of greenhouse gases. Climate Change. 68:281-302.

Kim, C.G. 2016. Removal of ammonium and nitrate nitrogens from wastewater using zeolite. Journal of the Korea Organic Resource Recycling Association. 24:59-63.

Kim, T.H. and Kim, B.H. 1996. Ammonia microdiffusion and colorimetric method for determining nitrogen in plant tissues. Journal of Korean Society Grassland and Forage Science. 16:253-259.

Kithome, M., Paul, J.W. and Bomke, A.A. 1999. Reducing nitrogen losses during simulated composting of poultry manure using adsorbents or chemical amendments. Journal of Environmental Quality. 28:194-201.

Lee, Y., Kim, S.J. and Parise, J.B. 2000. Synthesis and crystal structures of gallium- and germaniumvariants of the fibrous zeolites with the NAT, EDI and THO structure types. Microporous and Mesoporous Materials. 34:255-271.

Li, L.L. and Li, S.T. 2014. Nitrogen mineralization from animal manures and its relation to organic N fractions. Journal of Integrative Agriculture. 13:2040-2048.

Lu, R. 2000. Soil agricultural chemical analysis methods. China Agricultural Science and Technology Press, Beijing.

Moiser, A.R. 2001. Exchange of gaseous nitrogen compounds between agricultural system and the atmosphere. Plant and Soil. 228:14-27.

Ndegwa, P.M., Vaddella, V.K., Hristov, A.N. and Joo, H.S. 2009. Measuring concentration of ammonia in ambient air or exhaust air steam using acid traps. Journal of Environmental Quality. 38:647-653.

Pabalan, R.T. and Bertetti, F.P. 2001. Cation-exchange properties of natural zeolites. Reviews in Mineralogy and Geochemistry. 45:453-518.

Park, J.H., Park, S.J., Seo, Y.J., Kwon, O.H., Choi, S.Y., Park, S.D. and Kim, J.E. 2014. Effect of mixed treatment of urea fertilizer and zeolite on nitrous oxide and ammonia emission in upland soil. Korean Journal of Soil Science and Fertilizer. 47:368-373.

Park, S.H., Lee, B.R. and Kim, T.H. 2016. Effect of dicyandiamide and hydroquinone on ammonia and nitrous oxide emission from pig slurry applied to Timothy (*Pheleum pretense* L.) sward. Journal of the Korean Society of Grassland and Forage Science. 36:199-204.

Park, S.H., Lee, B.R., Jung, K.H. and Kim, T.H. 2018. Acidification of pig slurry effects on ammonia and nitrous oxide emissions, nitrate leaching, and perennial ryegrass regrowth as estimated by 15N-urea flux. Asian-Australasian Journal of Animal Science. 3:457-466.

Rochette, P., Chantigny, M.H., Angers, D.A., Bertrand, N. and Côté, D. 2001. Ammonia volatilization and soil nitrogen dynamics following fall application of pig slurry on canola crop residues. Canadian Journal of Soil Science. 81:515-523.

Rodhe, H. 1990. A comparison of the contribution of various gases to the greenhouse effect. Science. 248:1217-1219.

Rotz, C.A. 2004. Management to reduce nitrogen losses in animal production. Journal of Animal Science. 82:119-137.

Sommer, S.G. and Hutchings, N.J. 2001. Ammonia emission from field applied manure and its reduction. European Journal of Agronomy. 15:1-15.

Subbarao, G.V., Ito, O., Sahrawat, K.L., Berry, W.L., Nakahara, K., Ishikawa, T., Watanabe, T., Suenaga, K., Rondon, M. and Rao, I.M. 2006. Scope and strategies for regulation of nitrification in agricultural systems-challenges and opportunities. Crit. Rev. Plant Sci. 25:303-335.

Van Soest, P.J., Robertson, J.B. and Lewis, B.A. 1991. Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. Journal of Dairy Science. 74:3583-3597.

(Received : October 8, 2020 | Revised : November 11, 2020 | Accepted : November 14, 2020)