

COMPARATIVE ANALYSIS OF ZEOLITE AND PHOSPHOGYPSUM USE FOR CATTLE MANURE PH AND AMMONIA EMISSIONS CONTROL

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SUMMARY

The aim of the present study was to perform a comparative analysis of zeolite and phosphogypsum application for cattle manure pH and ammonia emissions control. Cattle manure mass prepared by mixing equal parts of urine and faeces was supplemented with 5 and 10% zeolite or phosphogypsum. Its pH values were monitored for 12 hours at one-hour intervals and compared with those of control samples without minerals. For analysis of ammonia emissions, control and experimental samples supplemented with 5% of either zeolite or phosphogypsum were prepared. The measurement was done in the modified flux chamber of Burgos et al. (2010) over 8 hours, and average values were used to evaluate the effect of tested minerals. The analysis of manure pH showed that until the 2nd hour, the addition of either zeolite or phosphogypsum did not alter significantly the environmental pH. After hour 2, phosphogypsum reduced manure pH with values under 8 by hour 6 and thereafter. Zeolite samples showed lower manure pH than controls, but with values over 8.5 or by more than 1 unit vs pH values detected after phosphogypsum addition. Unlike phosphogypsum, zeolite exhibited a tendency for better pH control when used at higher concentration. The data about ammonia emissions showed that both tested minerals were able to reduce ammonia emissions although the differences were not statistically significant. After addition of zeolite, average 8-hour ammonia emission from manure was 0.061 mg/m³ or by 0.019 mg/m³ lower than control. After addition of phosphogypsum, the average ammonia emission was 0.069 mg/m³ (by 0.011 mg/m³ lower than control).

Key words: *zeolite, phosphogypsum, manure mass, ammonium*

Introduction

Livestock breeding is a branch of agriculture providing mankind with essential nutrient sources of amino acids, vitamins and minerals. Along with the valuable foodstuffs and supplies for technical products, the branch is a source of waste products and gases which pose a serious threat for pollution of the environment. Earning a living and at the same time protecting nature's ecological balance from adverse consequences of livestock farming is a real challenge for men.

The use of animal manure for soil fertilisation with regard to ecological norms is an extensively discussed topic. The principal chemical elements in manure important for soil fertility are nitrogen, phosphorus and potassium (Petrov et al., 1983). Investigations on animal manure used as soil fertilizer have shown a considerable deviation in the proportions of elements and the needs of plants (Beegle, 1999; Sharpley et al., 1998). The data reported by authors demonstrate nitrogen to phosphorus ratio in manure from 3:1 to 5:1, whereas the optimum needs of plants are satisfied at N/P ration of about 8:1. Therefore, the utilisation of manure from farm animals to meet the nitrogen needs of crops results in excess of phosphorus in soils and increased concentrations of this element (Lefcourt and Meisinger, 2001).

The high levels of phosphorus established after analysis of soils showed a tendency towards accumulation in tap water sources through direct erosion of the sediment with high phosphorus content. This is the cause for accumulation of phosphorus in water basins located in regions with developed agriculture (Sharpley et al., 1998; Sims, 1993; Snyder et al., 1993). Two main factors for low manure N/P ratio have been identified – the loss of nitrogen by evaporation as ammonia and dietary phosphorus excess in animal rations (Lefcourt and Meisinger, 2001).

A well known and adopted practice is the processing of manure by addition of enhancers such as acidifying agents (alum, iron salts, inorganic acids), inactivating substances (zeolites,

flocculants) or substances for extraction of phosphorus (alum, calcium salts). The factors important for application of one or another method for manure processing are the cost of the supplement, as well as the possible benefits with all side environmental effects. So far, according to Lefcourt and Meisinger (2001) two compounds are potentially compliant to these requirements – alum and zeolite. Alum is usually used to remove phosphorus in sewage cleaning, as it is readily available and low-cost. The substance is extensively added to poultry farming wastes, mostly for phosphorus removal (Moore and Miller, 1994). It is shown that alum could reduce ammonia emissions in poultry houses when added in litter as well (Moore, 1998). Zeolite is a powdered silica mineral, widely spread in many countries at a global scale (Lefcourt and Meisinger, 2001). It is an intermediate cationic product used for reduction of ammonia in water (Kithome et al., 1998), in poultry litter (Maurice et al., 1998), in anaerobic tanks for cattle manure treatment (Borja et al., 1996), and poultry manure composting (Kithome et al., 1999).

Alum is still a very good means of control of ammonia wastes through manure acidification but its use is yet not broad due to several reasons. The primary one is the real hazard for soil pollution with aluminum. Zeolite is a good means of control of ammonia emissions from animal manure and its use is most popular in poultry farming. A serious flaw is its high price, due mainly to high production and transportation costs. Both science and practice are still in quest of a means of control, which should be cheap, able to control manure ammonia emissions and at the same time not altering the chemical structure of the soil with harmful elements.

The aim of the present study was to perform a comparative analysis of the use of zeolite and phosphogypsum as means of control of cattle manure pH and ammonia emissions.

Material and methods

Zeolite used in this study was produced in Bulgaria near to the Beli plast village, and phosphogypsum is a waste product of the air filters cleaning exhaust gases of the Maritsa Iztok Thermal Power Plant. Individual urine and faecal samples were obtained from dairy cows and transported to the lab in a cooling bag. Cows were fed a ration with 18% crude protein. Urine and faeces were brought to room temperature before being mixed in equal proportion (1:1) as per statements of Burgos et al. (2010) for urine and faeces amounts excreted by cows fed a similar ration. From the prepared slurry, three control and three experimental samples were collected for each experiment, as followed:

Experiment I – the slurry was supplemented with 5% (w/v) zeolite.

Experiment II – the slurry was supplemented with 10% (w/v) zeolite.

Experiment III – the slurry was supplemented with 5% (w/v) phosphogypsum.

Experiment IV – the slurry was supplemented with 10% (w/v) phosphogypsum.

Manure pH was measured at one-hour intervals for 12 hours with a pH meter Lab 850 Schott instruments®.

Parallely, samples for measurement of ammonia emissions from the slurry and for evaluation of the potential of zeolite and phosphogypsum for their reduction were prepared. For this purpose, a modification of the flux chamber described by Burgos et al. (2010) (Fig. 1) was made. The flux chamber was created by using excicators with a lid vent, and the modification consisted in the lack of the oxygen bottle supplied to the chamber.

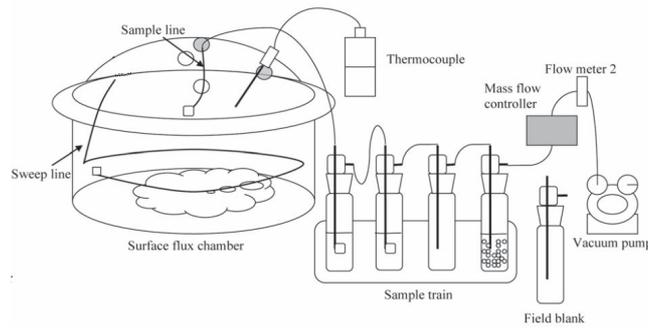


Fig 1. Modified flux chamber of Burgos et al. for quantitation of ammonia emissions

The manure in the container was supplemented with 5% (w/v) either zeolite or phosphogypsum.

The measurements were performed at a flow rate of 9 m³/min over one hour. Afterwards, the ammonia was quantitated by titration of the solution in tube absorbers. For each container with slurry (control and experimental), eight measurements were made at one-hour intervals. Measurements were done at 22 °C and pressure 94.6 kPa. Absorbing devices were filled with equal parts of 0.1 N HCl and distilled water and then, titrated with 0.1 N NaOH. The air aspirated by the vacuum pump was brought to normal conditions (0 °C and 101.3 kPa). Ammonia concentration was calculated by the formula:

$$X = F \cdot a \cdot m / V_0 \cdot 1000$$

where:

X – ammonia concentration in mg/m³

a – amount of ammonia-bound 0.1 N HCl, cm³

F – binding factor between ammonia and HCl, equal to 0.466;

m – amount of HCl, mg; in 1 cm³ 0,1 n HCl m= 3.65

V₀ – air volume when brought to normal conditions

1000 – coefficient for conversion ammonia concentration in mg/m³.

The results for ammonia emissions of control and both experimental samples were presented as mean values.

Data were statistically processed with Statistica 6 software.

Results and discussion

The comparative analysis of zeolite and phosphogypsum as potential means for control of cattle manure pH is presented on Fig. 2

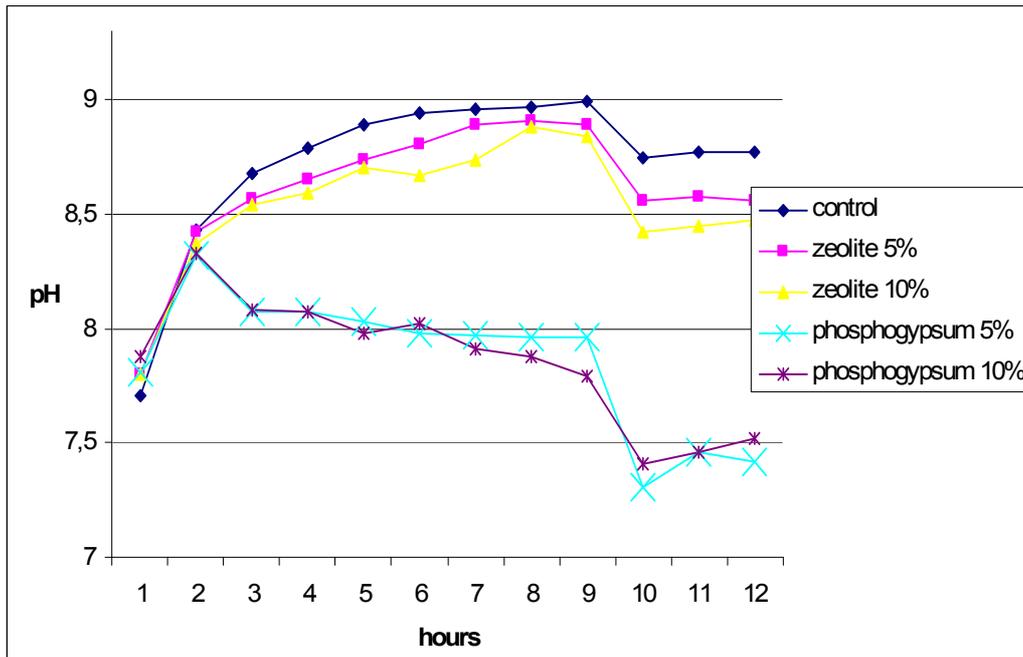


Figure 2. Comparative analysis of manure pH supplemented with zeolite and phosphogypsum at 5 and 10%

Data on Fig. 2 demonstrated that by the time of the first measurement of the active reaction of slurry, it was alkaline with values between 7.5 and 8. The measurement performed a hour later showed increase of pH by one unit both in control and all experimental samples. It could be affirmed that there were no statistically significant differences between manure pH of control and experimental specimens, although pH values of samples supplemented with 5 and 19% zeolite or phosphogypsum were lower. After the 2nd hour, phosphogypsum added at 5% or 10% decreased manure pH up to 8, and after the 6th hour – to even lower values. This confirmed the ability of phosphogypsum to control chemical reactions in manure, resulting in considerable release of ammonia in the atmosphere. At a constant temperature, manure pH determines the balance between $\text{NH}_4\text{-N}$ and $\text{NH}_3\text{-N}$. Being non-volatile, ammonium N ($\text{NH}_4\text{-N}$) could be volatilised from manure only under the form of $\text{NH}_3\text{-N}$. In an aqueous medium, the equilibrium between both forms ($\text{NH}_4\text{-N}$ and $\text{NH}_3\text{-N}$) is controlled at a time by environmental pH and temperature (Hristov et al., 2011). Lower pH is favourable for nitrogen retention as $\text{NH}_4\text{-N}$ and therefore decrease the volatilisation of NH_3 . When pH increases, the equilibrium shifts towards $\text{NH}_3\text{-N}$, i.e. towards evaporation. The greatest increase of ammonia emissions occurs at pH between 7 and 10. The release of ammonia decreases gradually with environmental pH 7 or lower, and at pH 4.5 no detectable free NH_3 could be found (Ndegwa et al., 2008). This showed that tested zeolite and phosphogypsum could not stop completely the chemical reactions in cattle manure, but only slow them down and reduce the nitrogen wastes from manure. Thus, the value of manure as plant fertilizer becomes higher.

The insignificant difference in manure pH of samples supplemented with 5% and 10% phosphogypsum should be noted, demonstrating the high efficacy of this energy production waste product. This is important, because the lower concentration of used phosphogypsum would alter at a lesser extent the physical and chemical composition of the slurry. The changes in manure chemical composition is the main disadvantage of the application of some minerals i.e. alum for animal manure acidification (Lefcourt and Meisinger, 2001). The physical properties of cattle manure are also important with regard to its potential use as soil fertilizer. The large amounts of dry acidifiers reduce the water content of manure and thus impede its use on agricultural lands via deep injection. These reasons support the utilisation of phosphogypsum as means of manure pH and ammonia

emissions control. Prior to recommend the application of phosphogypsum as a supplement to manure, a chemical analysis of treated manure should be done to exclude a potential pollution of soils.

The results from the analysis of manure pH confirmed the effect of zeolite as a means of pH reduction and this, nitrogen waste control. Substantial differences between manure pH (more than 1 unit) could be noted after addition of zeolite and phosphogypsum. With increasing zeolite concentration, the pH of the environment decreased, which is another essential inconvenience of this mineral's use, as the efficient control of chemical events occurring in manure by adding zeolite would require the use of larger amounts, hence with higher costs and last but not least, alteration of the physical structure of manure. These are the main reasons for the limited application of zeolite in dairy cattle farming for control of manure pH and ammonia emissions.

Data about the ammonia emissions from control and experimental samples are presented in Table 1.

Table 1. Average ammonia emissions from cattle manure supplemented with zeolite and phosphogypsum

Parameter mg/m ³	Number (n)	Control x ± SE	Zeolite x ± SE	Phosphogypsum x ± SE
Amonia	8	0.080 ± 0.016 ^{ns}	0.061 ± 0.012 ^{ns}	0.069 ± 0.014 ^{ns}

a, b, c – statistically significant differences at $p < 0.05$; ns – not significant

The analysis of results showed that ammonia emissions from the control exceeded those of experimental samples. Although phosphogypsum was a significantly better acidifier of manure than zeolite, the comparison with regard to ammonia emissions control showed the superiority of the latter. There was no statistically significant difference between ammonia emissions from manure with added zeolite or phosphogypsum. Also, a substantial reduction of ammonia between control and treated samples was neither observed. Nevertheless, there was a clear tendency towards lower ammonia emissions from manure treated with the tested minerals. This fact requires additional studies on the effect of zeolite and phosphogypsum on the profile and amount of volatile compounds emitted from manure. The present study provides a rationale for extension of the research on the potential application of phosphogypsum in animal farming. This waste product from the energy production in southern Bulgaria is extremely low-cost and available at sufficient amounts. More detailed studies on manure chemical composition alteration are needed with respect to its safe use as fertilizer of agricultural land.

Conclusion

The comparative analysis of zeolite and phosphogypsum showed the superiority of phosphogypsum as cattle manure acidifier at concentration of 5%. Zeolite is a possible alternative for manure acidification, but its effect is largely dependent on the amount used. This makes it a less preferred alternative due to needed amounts and occurring physical changes in manure. As ammonia emissions are concerned, both tested minerals tended to reduce them without statistically significant difference. This fact deserves additional more detailed studies on the composition of emissions after use of minerals. Before recommending the use of phosphogypsum as a means of manure pH and harmful emissions control, it is mandatory to carry out a chemical analysis of treated manure in order to certify the protection of soil ecological balance and soil pollution with chemical elements.

References

1. Beegle, D., 1999. Integrating phosphorus and nitrogen management at the farm level. Pages 159–168 in *Agriculture and Phosphorus Management: the Chesapeake Bay*. A. N. Sharpley, ed. Lewis Pub., Boca Raton, FL.
2. Borja, R., E. Sanchez, and M. M. Duran, 1996. Effect of the clay mineral zeolite on ammonia inhibition of anaerobic thermophilic reactors treating cattle manure. *J. Environ. Sci. Health*. A31:479–500.
3. Burgos, S. A., N. M. Embertson, Y. Zhao, F. M. Mitloehner, E. J. DePeters and J. G. Fadel, 2010. Prediction of ammonia emission from dairy cattle manure based on milk urea nitrogen: Relation of milk urea nitrogen to ammonia emissions. *Journal of Dairy Science*, 93 :2377–2386.
4. Hristov, A. N., M. Hanigan, A. Cole, R. Todd, T. A. McAllister, P. M. Ndegwa and A. Rotz, 2011. Review: Ammonia emissions from dairy farms and beef feedlots. *Canadian Journal of Animal Science*, 91:1-35.
5. Kithome, M., J. W. Paul, and A. A. Bomke, 1999. Reducing nitrogen losses during simulated composting of poultry manure using adsorbents or chemical amendments. *J. Environ. Qual.* 28:194–201.
6. Kithome, M., J. W. Paul, L. M. Lavkulich, and A. A. Bomke, 1998. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. *Soil Sci. Soc. Am. J.* 62:622–629.
7. Lefcourt, A. M. and J. J. Meisinger, 2001. Effect of Adding Alum or Zeolite to Dairy Slurry on Ammonia Volatilization and Chemical Composition. *Journal of Dairy Science*, 84:1814–1821.
8. Maurice, D. V., S. F. Lightsey, E. Hamrick, and J. Cox, 1998. Alum sludge and zeolite as components of broiler litter. *J. Appl. Poult. Res.* 7:263–267.
9. Moore, P. A., 1998. Best management practices for poultry manure utilization that enhance agricultural productivity and reduce pollution. Pages 89–124 in *Animal Waste Utilization: Effective Use of Manure as a Soil Resource*. J. L. Hatfield and B. A. Stewart, ed. Ann Arbor Press, Chelsea, MI.
10. Moore, P. A., Jr., and D. M. Miller, 1994. Decreasing phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. *J. Environ. Qual.* 23:325–330.
11. Ndegwa, P. M., A. N. Hristov, J. Arogo and R. E. Sheffield, 2008. A review of ammonia emission mitigation techniques for concentrated animal feeding operations. *Biosystem Engineering*, 100: 453-469.
12. Petrov, P., A. Bozhilov, I. Vankov, I. Mladenov, G. Petrov, S. Marinova, N. Bildirev, 1983. Liquid manure – treatment and utilisation in agriculture. *Zemizdat, Sofia*, p. 303.
13. Sharpley, A. N., J. J. Meisinger, A. Breeuwsma, J. T. Sims, T. C. Daniel, and J. S. Schepers. 1998. Impacts of animal manure management on ground and surface water quality. Pages 173–242 in *Animal Waste Utilization: Effective use of Manure as a Soil Resource*. J. L. Hatfield and B. A. Stewart, ed. Ann Arbor Press, Chelsea, MI.
14. Sims, J. T., 1993. Environmental soil testing for phosphorus. *J. Prod. Agric.* 6: 501–507.
15. Snyder, C. S., S. L. Chapman, W. H. Baker, W. E. Sabbe, and Y. S. McCool. 1993. Changes in Arkansas' sampled acreage testing low and high in soil phosphorus over the last 30 years. *Soils and Fertility Information Article* 1–93. Univ. of Arkansas Cooperative Extension Service, Little Rock, AR.