International Journal of Manures and Fertilizers Vol. 2 (8), pp. 355-358, August, 2013. Available online at www.internationalscholarsjournals.org

Full Length Research Paper

Advancing formulated nitrogen, phosphorus and potassium compound fertilizer using zeolite

Nolan Yore, Ipah Kalpana and Tan Saya

Department of Plant Protection, Faculty of Agriculture, Universiti Putra Malaysia, Serdang, Selangor, Malaysia.

Accepted 1 July, 2013

Ammonia volatilization from urea and ammonium containing compound fertilizers cause higher cost of fertilization in agriculture. In this study, an incubation experiment was carried out to compare the effect of different ratios of compound fertilizer amended with clinoptilolite zeolite on NH_3 volatilization, soil exchangeable NH_4 and available NO_3 contents on Bekenu Series (Tipik Tualemkuts) with surface-applied urea without additives. Treatments with zeolite significantly reduced NH_3 loss when compared with urea without addictives. They also improved retention of exchangeable NH_4 and NO_3 and this was possible because zeolite favoured formation of ammonium and nitrate over ammonia. There is a potential for compound fertilizer with zeolite to improve nitrogen efficiency by lowering ammonia volatilization and increasing accumulation of exchangeable NH_4 and NO_3.

Key words: Ammonia volatilization, compound fertilizers, clinoptilolite zeolite, soil exchangeable ammonium, available nitrate.

INTRODUCTION

Compound fertilizers supply nutrients to plants. Ammonia volatilization from urea and ammonium containing compound fertilizers cause higher cost of fertilization in agriculture (Hanafi et al., 1999). About 1 to 60% of NH_3 volatilize (Christianson, 1989), hence causing low N use efficiency. Many laboratory studies such as coating urea with polymers (Hanafi et al., 1999; Junejo et al., 2011), urease inhibitors (Khalil et al., 2009) and acidifying materials to reduce NH_3 volatilization have been conducted. Technical processes with relatively high cost may lead to a risk of soil pollution (Watson, 2000; Ahmed et al., 2006; Junejo et al., 2011). In recent years, clinoptilolite zeolite approach has attracted much attention in the fertilizer industry.

According to Payra and Dutta (2003), clinoptilolite zeolite is a hydrated aluminosilicate having three-dimensional rigid crystalline networks that are 10^{-9} m in size containing internal exchange sites that have high affinity for ammonium ion exchange. Clinoptilolite zeolite serves as excellent carrier regulator and stabilizes mineral fertilizer and is a source of nutrients such as K, Ca and Mg (Bagdasarov et al., 2004). In various studies, clinoptilolite zeolite has proven to reduce NH_3 volatilization. In an incubation experiment, Ahmed et al. (2006) found that treatments with larger amounts of humic acid and zeolite had the greatest effect when compared with urea alone in improving soil retention of NH_4 as well as minimizing the conversion of NH_4 to NO_3. In their study, Junrungreang et al. (2002) reported that chemical fertilizer with zeolite improved soil chemical properties, sugarcane growth and yield. Combination of higher dose of chemical fertilizer and higher dose of zeolite showed the highest effect on height, diameter and yield of sugarcane. However, according to Bernardi et al. (2010), amending urea with zeolite requires a relatively small increase in dry matter. Yet, by blending the compound fertilizer with clinoptilolite zeolite where clinoptilolite zeolite acts as supplementary nutrients could be an alternative way of formulating desired fertilizers in

*Corresponding author. E-mail: N_yore19@yahoo.com

Table 1. Selected chemical and physical properties of Bekenu Series and clinophtilolite zeolite.

Property	Soil (0 to 15 cm)		Clinophtilolite zeolite
	Value obtained	Standard data range	(Value obtained)
pH(water)	4.70	4.6-4.9	7.03
pH(0.01M KCl)	3.43	3.8-4.0	6.37
Total organic carbon (%)	3.6	0.57-2.51	Nd
CEC(cmol kg^{-1})	12.8	3.86-8.46	75.4
Exchangeable K (cmol kg^{-1})	0.174	0.05-0.19	22.29
Exchangeable Ca (cmol kg-1)	0.717	0.05-0.19	50.06
Exchangeable Mg (cmol kg-1)	0.525	0.07-0.021	2.21
Texture	SL	SL	Nd
Bulk density(gm^{-3})	1.01	Nd	Nd

CEC, Cation exchange capacity; SL, sandy loam; SCL, sandy clay loam; nd, not determined; standard data range (Paramananthan, 2000).

agriculture. In this study, an incubation experiment was conducted to compare the effect of different ratios of compound fertilizer incorporated with zeolite on NH_3 volatilization, soil exchangeable NH_4 and available NO_3 contents of an acid soil.

MATERIALS AND METHODS

The soil used in this study was a Tipik Tualemkuts (Bekenu Series). Soil samples were taken at 0 to 15 cm depth using an auger, air dried and ground to pass a 5 mm sieve. The clinoptilolite zeolite used was in powder form. Soil and clinoptilolite zeolite were analyzed for their selected physio-chemical properties using standard procedures. The pH of soil and clinoptilolite zeolite were determined in a ratio of 1:2.5 soil : distilled water suspension and 1 M KCl solution using a glass electrode (Peech, 1965). Soil organic carbon was determined using Walkley and Black (1934). Soil CEC was determined by leaching with ammonium acetate buffer adjusted to pH 7.0 followed by steam distillation (Bremner, 1965) and exchangeable K, Ca and Mg using by atomic absorption spectrophotometry (AAnalyst 800, Perkin Elmer Instruments, Norwalk, CT). The CEC of clinophtilolite zeolite was determined using CsCl method (Ming and Dixon, 1986). Exchangeable K, Ca and Mg of the clinophtilolite zeolite were extracted using Ming and Dixon (1986) and their concentrations determined as previously outlined. The soil texture was determined using hydrometer method (Tan, 2005).

Eight treatments were used to compare the percent of ammonia volatilization loss in sandy loam soil. The treatments per 250 g of soil evaluated were:

1. 14.88 g commercial compound fertilizer with ratio of 15:15:15 (control) (T1);
2. Compound fertilizer with ratio of 15:15:15 (4.85 g urea + 4.85 g TSP + 3.72 g MOP) mixed with 1.46 g clinoptilolite zeolite (T2);
3. Compound fertilizer with ratio of 13:15:13 (4.85 g urea + 5.61 g TSP + 3.73 g MOP) mixed with 3.01 g clinoptilolite zeolite (T3);
4. Compound fertilizer with ratio of 10:10:10 (4.85 g urea + 4.85 g TSP + 3.73 g MOP) mixed with 8.92 g clinoptilolite zeolite (T4);
5. Compound fertilizer with ratio of 8:8:8 (4.85 g urea + 4.85 g TSP + 3.71 g MOP) mixed with 14.46 g clinoptilolite zeolite (T5);
6. Compound fertilizer with ratio of 5.5:5.5:5.5 (4.85 g urea + 4.85 g TSP + 3.72 g MOP) mixed with 27.04 g clinoptilolite zeolite (T6);
7. 2.425 g urea without additives (control) (T7);
8. Soil alone (T8).

The amount of compound fertilizer used was calculated from the standard recommendation for mature Masmadu maize (Malaysian Agricultural Research and Development Institute, 1990). Only treatment 7 (urea alone) was scaled down to half, the other treatments (1 until 6) had 4.85 g of urea. Ammonia volatilization from soil was measured by a closed dynamic airflow system (*Siva* et al., 1999) with modifications. The treatments were applied on soil surface. Air was passed through the chambers at a rate of 3.5 L min^{-1} and released NH_3 captured in the trapping solution containing 75 ml of boric acid with bromocresol green and methyl red indicator. Rate of air flow was maintained throughout the incubation period using a Gilmont flow meter (Gilmont Instrument, Great Neck, NY, USA) to measure and adjust air flow at room temperature. Boric acid was replaced 24 h and back titrated with 0.01 or 0.1 M HCl to estimate NH_3 released. Measurement was continued until the loss declined to 1% of the N added in the urea (Ahmed et al., 2008).

After incubation, the soil samples were taken and pH, exchangeable NH_4 and available NO_3 were determined. The exchangeable NH_4 and available NO_3 were extracted from the soil by the method of Keeney and Nelson (1982), and their amounts were determined using steam distillation method. The experimental design was fully randomized with three replications for all treatments. Analysis of variance (ANOVA) was used to test the treatment effects and means of treatments were compared using Tukey's test.

RESULTS AND DISCUSSION

The selected physio-chemical properties of Bekenu Series and clinophtilolite zeolite are summarized in Table 1. Values obtained for pH (water), exchangeable K and texture were consistent with those reported by Paramananthan (2000). Total organic carbon, CEC, exchangeable Ca and Mg contents were higher than the standard range probably due to cultivation.

The daily loss of ammonia (NH_3) recorded during the experiment is shown in Figure 1. The NH_3 started on the first day of incubation for T1 and T7 only. For T2, T3, T4, T5 and T6, NH_3 loss occurred on third day of incubation.

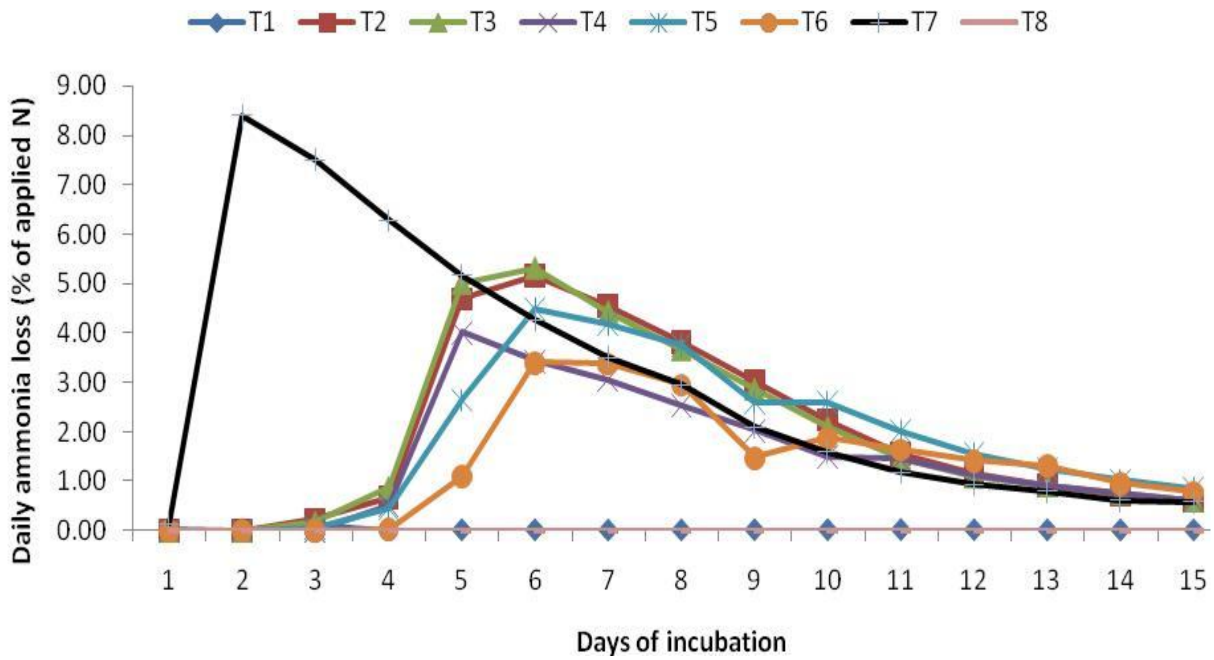

Figure 1. Daily loss of ammonia from incubation. For key to treatments see materials and methods.

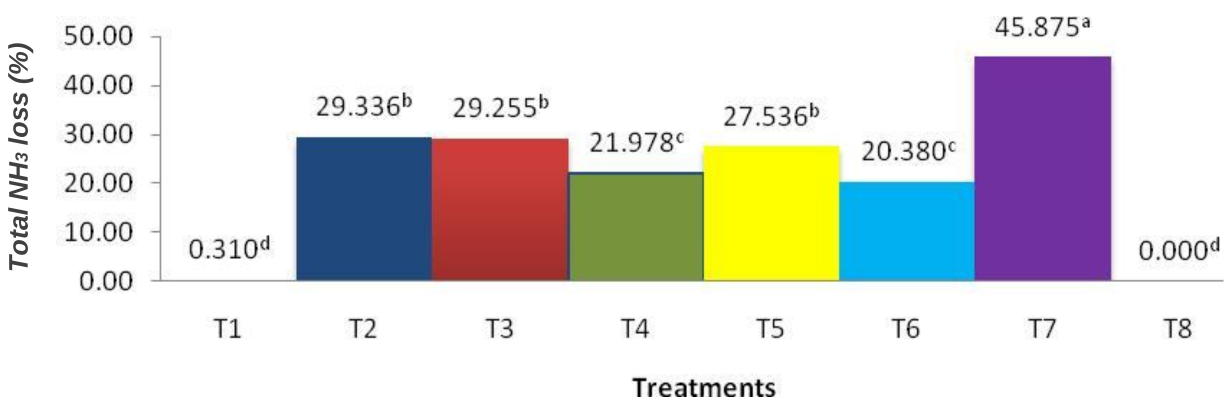

Figure 2. Total amounts of ammonia lost over 15 days of incubation. Different letters (within column) indicate significant difference between means using Tukey's test at P = 0.05. For key to treatments see materials and methods.

Treatments T1, T2, T3, T4, T5, T6 reduced maximum of NH_3 loss from 8.4 to 0.12, 5.16, 5.31, 4.02, 4.5 and 3.41% (of the N added as urea), respectively (Figure 1). The maximum NH_3 loss of the treatments occurred on days 2 (T7), 3 (T1), 4 (T4) and 5 (T2, T3, T5 and T6) of incubation after which there was a general decline until day 15 when the NH_3 loss was about 1% of the N added as urea (Figure 1). All the treatments (T2, T3, T4, T5 and T6) significantly reduced NH_3 loss when compared with urea without addictives (T7) but lower than T1. The total amounts of NH_3 lost at the end of the incubation period as a percentage of urea-N were 0.310, 29.336, 29.255, 21.978, 27.538, 20.380, 45.875 and 0 (note: mean of values with different letters are significantly different at $p \leq 0.05$ as determined by Tukey's test) for T1, T2, T3, T4, T5, T6, T7 and T8, respectively (Figure 2). All the treatments with clinoptilolite zeolite (T2, T3, T4, T5 and T6) significantly reduced NH_3 loss as compared to urea without additives (T7). T6 and T4 with greater amounts of clinoptilolite zeolite had the greatest effect on ammonia loss. The amount of N applied based on treatments (T2, T3, T4, T5 and T6) were twice that of urea only (T7); however the treatments significantly minimized total NH_3 loss as compared to urea only. The significant reduction of ammonia volatilization could be due to the retention of NH_4 on the cation-exchange sites of the zeolite and as

Table 2. Soil pH during 15 days of incubation.

Treatment	pH (H_2O)	pH (0.01 M KCl)
T1	5.13^{c}	4.92^{c}
T2	6.84^{b}	6.76^{ab}
T3	6.86^{b}	6.70^{ab}
T4	6.79^{b}	6.69^{ab}
T5	6.76^{b}	6.76^{ab}
T6	6.89^{b}	7.06^{a}
T7	7.72^{a}	6.41^{b}
T8	4.48^{d}	3.34^{d}

Different letters (within column) indicate significant difference between means using Tukey's test at P=0.05. For key to treatments see materials and methods.

Table 3. Effect of treatments on exchangeable ammonium and nitrate accumulation at 15 days of incubation.

Treatment	Exchangeable NH_4-N (mg L^{-1})	NO_3-N (mg L^{-1})
T1	15.64^{a}	0.21^{b}
T2	6.75^{b}	0.17^{b}
T3	6.55^{b}	0.04^{b}
T4	6.90^{b}	0.11^{b}
T5	7.07^{b}	0.21^{b}
T6	8.24^{b}	0.63^{a}
T7	3.07^{c}	0.07^{b}
T8	0.19^{d}	0.03^{b}

Different letters (within column) indicate significant difference between means using Tukey's test at P=0.05. For key to treatments see materials and methods.

CEC of the zeolite (75.4 cmol kg^{-1}) was substantial. Clinoptilolite zeolite may have served as a slow release fertilizer. Similar observation has been reported by Latifah et al. (2011) and Ahmed et al. (2008).

On the 15th day of incubation, soil pH (H_2O and KCl) of all treatments were significantly different (Table 2). This was because NH_3 loss varied much among treatments (Figure 2). The phosphoric acid produced by hydrolysis of acidic phosphates may have acidified the soil surrounding the acid zeolite mixture (Fan and Mackenzie, 1993).

There was significant difference in accumulation of exchangeable NH_4 for all treatments (Table 3). T1 had the highest accumulation of exchangeable NH_4, while T6 had the highest accumulation of available NO_3. Treatments amended with zeolite (T2, T3, T4, T5 and T6) caused higher accumulation of exchangeable NH_4 as compared to urea only (T7). For accumulation of NO_3, all treatments except T6 were not significantly different. The high accumulation of exchangeable NH_4 could be because of the high CEC of clinoptilolite zeolite (75.4 cmol kg^{-1}) as clinoptilolite zeolite effectively absorbs exchangeable NH_4 ions and releases it slowly. A similar finding has been reported by Latifah et al. (2011). This could be one of the reasons why there was loss of ammonia for urea without additives.

Conclusion

There is a potential for compound fertilizer with zeolite to improve nitrogen efficiency by lowering ammonia volatilization and increasing accumulation of exchangeable NH_4 and NO_3.

ACKNOWLEDGEMENTS

The researchers acknowledge the financial support of this research by the Ministry of Higher Education, Malaysia and Universiti Putra Malaysia, Malaysia.

REFERENCES

Ahmed OH, Aminuddin H, Husni MHA (2006). Reducing Ammonia loss from urea and improving soil-exchangeable ammonium retention through mixing triple superphosphate, humic acid and zeolite. Soil Use Manage. 22:315-319.

Ahmed OH, Aminuddin H, Husni MHA (2008). Ammonia volatilization and ammonium accumulation from urea mixed with zeolite and triple superphosphate. Acta Agric. Scandinavica Sect. B Soil Plant Sci. 58:182-186.

Bagdasarov VR, Kazachenko AA, Rustambekov MK, Uspenskij BG, Kuznetsova VV, Efremov EN (2004). Prolonged-activity nitrogen-zeolite fertilizer, Russia.

Bernardi ACDC, Mota EPD, Souza SDCHD, Cardodo RD, Oliviera PPA (2010). Ammonia volatilization, dry matter yield and nitrogen levels of Italian ryegrass fertilized with urea and zeolite. 19th World Congress of Soil Science, Soil solutions for a changing world. August, 1-6, 2010. Australia.

Bremner JM (1965). Total Nitrogen. In, Method of soil analysis, Part 2, Black CA, Evants DD, Ensminger LE, White JL, Clark FE, Dinauer RC (eds.), Am. Soc. Agron., Madison, Wisconcin pp. 1149-1178.

Christianson CB (1989). Ammonia volatilization from urea nitric phosphate and urea applied to the soil surface. Fert. Res. 19:183-189.

Fan MX, Mackenzie AF (1993). Urea and phosphate interactions in fertilizer microsites: Ammonia volatilization and pH changes. Soil Sci. Soc. Am. J. 57:839-845.

Hanafi MM, Eltaib SM, Ahmad MB (1999). Physical and chemical characteristics of controlled release compound fertilizer. Eur. Polym. J. 36(2000):2081-2088

Malaysian Agricultural Research and Development Institute (MARDI). (1990). Jagung Manis Baru, Masmadu. Serdang, Malaysia.

Junejo N, Khanif MY, Hanfi MM, Dharejo KA, Wan ZWY (2011). Reduced loss of NH_3 by coating urea with biodegradable polymers, palm stearin and selected micronutrients. Afr. J. Biotechnol. 10(52):10618-10625.

Junrungreang S, Limtong P, Wattanaprapat K, Patsarayeangyong T (2002).17th WCSS Symposium 2002. Effect of zeolite and chemical fertilizer on the change of physical and chemical properties on Lat Ya soil series for sugar cane. August 14-21, 2002. Thailand.

Keeney DR, Nelson DW (1982). Nitrogen-inorganic forms. In, Method of Soil Analysis, Part 2 (2nd ed), Page Al, Keeney DR, Baker DE, Miller RH, Ellis R, Rhoades JD (eds.). Agron. Monogr., 9. ASA and SSSA, Madison, Wisconsin.

Khalil MI, Gutser R, Schmidhalter U (2009). Effects of urease and nitrification inhibitors added to urea on nitrous oxide emissions from a loess soil. J. Plant Nutr. Soil Sci. 172:651-660.

Latifah O, Ahmed OH, Nik Muhamad AM (2011). Reducing ammonia loss from urea and improving soil exchangeable ammonium and available nitrate in non waterlogged soils through mixing zeolite and sago (*Metroxylon sagu)* wastewater. Int. J. Phys. Sci. 6(4):866-870.

Ming DW, Dixon JB (1986). Clinoptilolite in South Texas soils. Soil Sci. Soc. Am. J. 50:1618-1622.

Paramananthan S (2000). Soil of Malaysia: Their characteristics and identification. Academy of Science Malaysia, Kuala Lumpur, Malaysia, Vol. 1.

Payra P, Dutta PK (2003). Handbook of zeolite science and technology. Ohio, USA.

Peech HM (1965). Hydrogen-ion acticity. In: Method of soil analysis, Part 2. Black CA, Evants DD, Ensminger LE, White JL, Clark FE, Dinauer RC(eds.), Am. Soc. Agron., Madison, Wisconsin, pp. 914-926.

Siva KB, Aminuddin H, Husni MHA, Manas AR (1999). Ammonia volatilization from urea as affected by tropical-based palm oil effluent (pome) and peat. Comm. Soil Sci. Plant Anal. 30:785-804.

Tan KH (2005). Soil sampling, preparation, and analysis (2nd ed). Boca raton, Florida, USA.

Walkley A, Black IA (1934). An examination of Degtjaref method for determination of soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37:29-28.

Watson CJ (2000). Urease activity and inhibition-principles and practice. Proceedings. Publ., The Int. Fertiliser Soc. York, UK 454:40.