Effects of Natural Zeolite and Urea on NH_3 Emission and Nitrogen Uptake in Rice Soils

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Abstract- The research was aimed at investigating the effect of natural zeolite of Taskmalayan deposit and urea fertilizer on ammonia (NH_3) emission, nitrogen uptake and rice yield. The researh was a pot experiment using Eutrudept soil type conducted in a green house in the Agriculture Faculty, Jenderal Soedirman University. The experiment was factorially arranged in a randomized block design. The factors were composed of three levels of natural zeolite (equivalent to 0, 1000 and 2000 kg/ha, respectively) and two types of urea fertilizers with levels equivalent to 0, 100, 200 kg N prilled urea/ha and 0, 100, 200 kg N supergranule urea/ha, respectively. Ammonia emmited was determined using Sulfuric Acid Entrapment System, whereby each experimental pot was covered with a transparent plastic chamber into which N-free air was transferred. NH_3 emitted was trapped in by dilute sulfuric acid solution. The results of the experiment indicated that application of natural zeolite could reduce N volatilized by 46 %, from 78,78 to 42,11 mg N/pot. The highest N volatilized was observed at the application of prilled urea at 200 kg N/ha (197.23 mg/pot). The applications of natural zeolite did not significantly affect nitrogen uptake by rice plants.

Keywords : Zeolite, ammonia emission, rice

1. Introduction

It has long been known that ammonium-based nitrogen (N) fertilizers applied to rice fields tend to have a very poor efficiency. The main cause of this is the loss of applied N through ammonia (NH_3) emission or volatilisation, denitrification and leachings processes. Through these mechanisms, the loss of applied N can be as high as 80 percent ((Lin *et al.*, 2007; Freney, 1997). N loss through emission of NH_3 is of significant importance, especially when ammonium-based fertilizers like urea are applied by broadcasting, which can reach 50% (Freney, 1997) . In rice soil, high N losses through volatilization was mainly due to the reduced conditions leading to the accumulation NH_4^+, which is the potential source for NH_3 gas. The high soil pH in rice soils also stimulate the conversions of NH_4^+ to gaseous NH_3.

Numerous efforts have been made to minimize the loss of N. One of the efforts is to modify the N fertilizers like the use super granules urea (SGU) or commonly known as tablet urea. This type of fertilizer is considered adequately effective in suppressing the rate of NH_3 volatilization. However, utilization of SGU is facing some obstacles, especially related to technical applications in the field that are considered difficult and require a lot of manpower. Another disadvantage is that SGU has been known less effective when applied to the soils having low cation exchange capacity (CEC).

Mineral zeolite is deemed to able to overcome this weaknesses. It is widely known that zeolite minerals have great ability to adsorb positively charged ions as they have a very high cation exchange capacity (van Straaten, 2007). Therefore, the ammonium ions released from urea hydrolysis or other mechanisms like mineralization of crop residues can be captured temporarily by the zeolite. Bernal *et al.* (1993) reported that the use of zeolite at 53 g kg^{-1} compost (5%) could reduce N losses by 80%. It has also been reported that zeolite is capable of capturing 76 g N for every kg zeolite (Park and Komarneni, 1998).

Zeolites are aluminosilicate minerals that have unique tridimensional crystal structures forming channels and cage-like frameworks resulting in a very high surface area. The central ion Si^{4+} in tetrahedral structure is generally replaced by tri-valence Al^{3+} generating negative charges in the zeolite structure. This negatively charged surface is neutralized by alkali metals or alkaline earth ions like Na^{+}, K^{+}, Ca^{2+} and Mg^{2+}. This unique character allows the zeolite to provide essential properties such as adsorption, cation exchange, molecular filtration and catalytic properties (Kharisun and Budiono, 1999; van Straaten, 2007). Research conducted by Khitome *et al.* (1998) also concluded that zeolites were able to effectively adsorb NH_4^{+}, thus it could act as a controlled-release N fertilizer. The purpose of this study was to determine the effects of natural zeolite of Tasikmalaya deposit on ammonia volatilization and nitrogen fertilizer efficiency in rice fields applied with 2 types of urea fertilizers.

2. Research Method

This research was a pot experiment conducted in the Greenhouse of the Faculty of Agriculture, Unsoed using Eutrudept soil. The experiment was laid out in a split-plot arrangement based on the randomized complete block design (RCBD) with three replications. The treatments were composed of factorial combinations of zeolites (diameter <2 mm) at 3 levels (0, 1000 and 2000 kg Ha^{-1}), and prilled and super granule urea (SGU) or commonly known as tablet urea applied at 3 levels (0, 100 and 200 kg N Ha^{-1}, respectively). The pot dimension was 394 cm^2 x 30 cm containing 15 kg of air-dried soil (ø < 2 mm). Prior to planting, the soil was flooded and incubated for 2 weeks. The natural zeolite and prilled urea were applied before transplanting by broadcasting. SGU was placed at a depth of 10cm from surface of the soil. Each pot was planted with 4 21-day old rice seedlings with a plant spacing of 20cm x 20cm. A transparent plastic chamber (ø 15 cm, 18 cm-high) was placed in between the rice clumps. Top of the chamber had an inlet and an outlet. The chamber inlet and outlet were connected to an electric air pump and a flask (containing 0.05N H_2SO_4 solution), respectively, using flexible plastic tubing. Air flown from the electric compressor was passed through a flask containing 0.5 N H_2SO_4 to capture the NH_3 gas. The NH_3-free air was then flown to the chamber. The NH_3 emitted from the soil was then transferred to a flask containing 0.05N H_2SO_4 solution. Captured NH_3 was measured using a titration method using 0.05 N NaOH solution. Variables observed included volatilization of NH_3, soil pH and N uptake by rice plants. Measurements of emitted NH_3 were taken every 24 hours for the first 40 days and every 3 days thereafter. The lay-out of the NH_3 capturing system is depicted in figure 1.

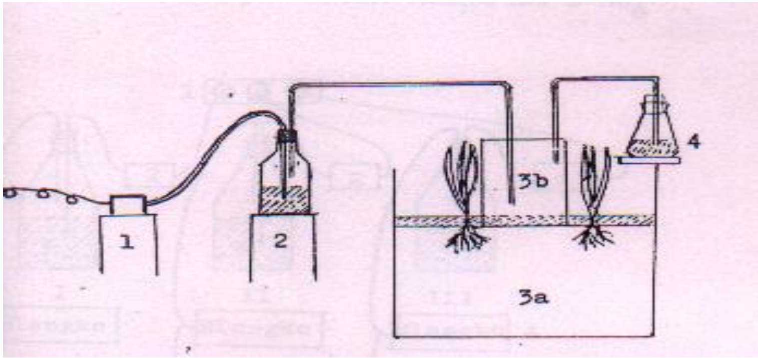

Figure 1. Lay out of NH_3 trapping system (Note: 1. The electric air pump; 2. Flask containing 0.5N H_2SO_4; 3a. Flooded soil; 3b. plastic chamber; 4. Flask containing 0.05N H_2SO_4 Solution)

3. Results and Discussion

The results indicated that the type and level of urea fertilizer as well as applications of zeolite gave a significant effect on NH_3 volatilization. As can be seen from Table 1, gaseous NH_3 emitted on prilled urea treatments was remarkably high. The highest NH_3 emission was observed on the prilled urea treatment applied at the highest rate (200 kg N ha^{-}). The NH_3 emitted on the application of prilled urea at a level of 100 kg N ha^{-} and 200 kg N ha^{-} was 70.49 and 197.23 mg N/pot, respectively, which was significantly much higher than NH_3 emission from the SGU treatments. The NH_3 emitted from the applications of SGU at levels of 100 kg ha^{-1} and 200 kg ha^{-1} was only 12.96 and 20.13 mg N/pot, respectively. It was observed that the NH_3 emitted from SGU treatments was not significantly different from the control plot (without urea application). The high ammonia emission on the prilled urea treatments might have been attributable to two factors. First, the high surface area of prilled urea resulted in the higher amount of NH_4^+ ion released to the soil solution. Second, the broadcast applications of prilled urea has caused more NH_4^+ released to remain in the standing water, not in contact with soil particles leading to increased concentrations of NH_4^+ in the standing water. The high concentration of NH_4^+ in the standing water favoured by high pH conditions (Figure 2) has resulted in higher ammonia emission.

Table 1. Average amounts of NH3 emitted resulted from the applications of urea fertilizers and natural zeolite

Treatment	Description	**Emitted NH_3 (mg N / pot)**
Urea		
No.	Without urea	11.40 A
NP1	Prilled urea 100 kg N ha^{-1}	70.49 b
NP2	Prilled urea 200 kg N ha^{-1}	197.23 c
NT1	SGU of 100 kg N ha^{-1}	12.96 A
NT2	SGU of 200 kg N ha^{-1}	20.13 A
Natural Zeolite		
Z0	Without zeolite	78.78 A
Z1	1000 kg zeolite ha^{-1}	42.11 b
Z2	2000 kg zeolite ha^{-1}	66.41 ab

Notes: Values followed by the same letter on the treatment and the same column are not significantly different according DMRT (confidence level $P < 0.05$).

The application of SGU up to the rate of 200 kg N ha^{-} was able to suppress the formation of NH_3 gas (Table 1.). Deep placement of SGU into the reduced zone of rice soil allowed a significant amount of released NH_4^+ ions to be retained by negatively charged soil colloids. The bigger particle size of SGU had also contributed to less NH_3 emission as it would reduce the rate of urea solubilisation providing more chances of NH_4^+ being retained by soil particles (Kabir *el al.*, 2009; Hussaini *et al.*, 2010; Xu et *al.* 2012).

Gaseous N losses through ammonia emission with the applications of urea fertilizer could be significantly high in the rice soils. Table 2 shows the average proportion of urea being emitted as NH_3 gas at different rates of natural zeolite applications. The values of proportions were calculated using the difference method, whereby the amount of NH_3 emitted in the unfertilized pot (control) was subtracted from the amount of NH_3 emitted in the fertilized pot. As can be seen from table 2, as high as 53.39 percent of applied urea was lost through NH_3 volatilization as prilled urea applied by broadcasting, particularly when urea applied at a high rate (200 kg N Ha^{-1}). The results of the experiment also showed that the NH_3 emitted was profoundly reduced when natural zeolite was added. Table 2 shows that the applications of natural zeolite at a rate of 1000 kg ha^{-1} reduced the NH_3 emmited from prilled urea application by 46.5%.

The reduction of ammonia volatilization by zeolites was also obtained with the applications of SGU. With the addition of zeolit at a rate of 1000 kg ha^{-1} , the proportion of urea lost through ammonia emission was reduced from 3.76 % to 0.73% with the applications of SGU at 100 kg N ha^{-1}. At a higher rate of SGU applications (200 kg N Ha^{-1}), the additions of natural zeolites at rate of 1000 kg ha^{-1} was able to reduce proportions of urea volatilized from 5.20 % to 0.45%. The proportions of urea loss through ammonia emission were not significantly different with the SGU treatments of 1000 kg ha^{-1} and 2000 kg ha^{-1} (Table 2).

The reduction of NH_3 emission could be attributed to the ability of zeolite minerals to adsorb cations into their adsorption complex. With the presence of zeolite minerals NH_4^+ released from the hydrolysis of urea fertilizer could be immediately adsorbed by negatively-charged adsorption complex of zeolite. Thus it would suppress the formation of gaseous NH_3. Park and Komarneni (1998) reported that zeolite minerals were capable of capturing 76 g N / kg zeolite.

Table 2. The average proportion of urea being emitted as NH_3 gas at different rates of natural zeolite applications (%).

Treatments	100 kg N ha^{-1}		200 kg ha^{-1}	
	Prilled urea	SGU	Prilled urea	SGU
Z0	37.57 aB	3.76 aC	53.39 aA	5,20 aC
Z1	22.46 bA	0.73 AB	25.09 bB	0.45 aB
Z2	24.09 bA	1.11 AB	53.56 bA	0.46 aB

Notes: Values followed by the same small letters (in the same column) or capital letters (on the same row) are not significantly different according DMRT (confidence level P> 0.05)

The experiment indicated that there was a tendency that ammonia emitted was higher with the applications of higher rate of natural zeolite (2000 kg ha^{-1}). This phenomenon could be related to the higher pH of the soil with the increased zeolite rates (Figure 2). Increased pH is presumably due the release of the base cations (such as

K $^{+,}$ Na $^{+}$ and Ca $^{2+}$) contained in zeolite adsorption complex into the soil solution as compensation for the adsorption of ion NH_4^+ .

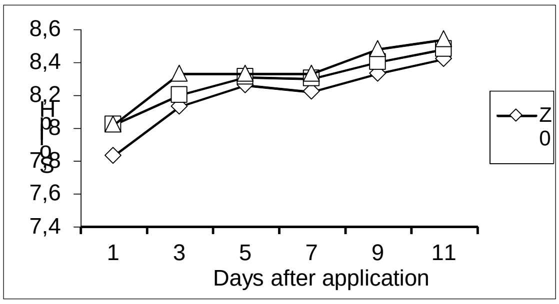

Figure 2. Soil pH values after 11 days of application of zeolites measured at 14.00. (Z0 = without zeolites; Z1 = 1000 kg ha^{-1} zeolites; Z2 = 2000 kg ha^{-1} zeolites)

The applications of urea fertilizers in the forms of prilled urea and SGU increased N uptake, growth and yield parameters (Table 3). The highest N uptake was achieved by the application of SGU at a rate of 200 kg N ha^{-1}. The applications of SGU gave significantly higher shoot and root weigh as compared to prilled urea applications applied at the same rate. SGU at a rate of 100 kg N ha^{-1} showed N uptake comparable to the treatment of prilled urea at the rate of 200 kg N ha^{-1} indicative of more N loss in the prilled urea treatment. However, further addition of SGU (200 kg N ha^{-1}) did not effectively promote growth and yields rice.

Results of the experiment also showed that even though natural zeolite was capable of suppressing ammonia volatilization, It could not increase the N uptake, plant growth and yields. This was an indication that NH_4^+ ions adsorbed on the zeolite minerals could not be utilized effectively by the plant, as shown by the high residual soil N (Table 3). The uptake efficiency of applied urea is depicted in figure 3.

Table 3. N uptake by rice plant, soil residulal N, and the rice growth parameters and yield as affected by applications of urea and natural zeolites

Treatment	N uptake (mg/clump)	**Bbt straw (g/clump)**	**Root weight (mg/clump)**	**Weight of grain (mg/clump)**	**Soil residue N (%)**
Urea					
No.	158 a	5.87 a	6.03 a	5.34 a	0.02 a
NP1	327 b	8.57 b	9.06 b	9.94 b	0.08 b
NP2	442 c	11.22 d	15.84 d	11.42 b	0.15 c
NT1	402 c	9.87 c	11.97 c	11.29 b	0.17 c
NT2	527 d	12.071 e	15.76 d	11.72 b	0.18 c
Natural Zeolite					
Z0	336 a	933 a	11.73 A	9.99 a	0.11 a
Z1	374 a	981 a	11.97 A	9.95 a	0.13 a
Z2	373 a	954 a	11.49 A	9.89 a	0.13 a

Notes: Values followed by the same letter on the treatment and same column are not significantly different according DMRT (confidence level P <0.05).

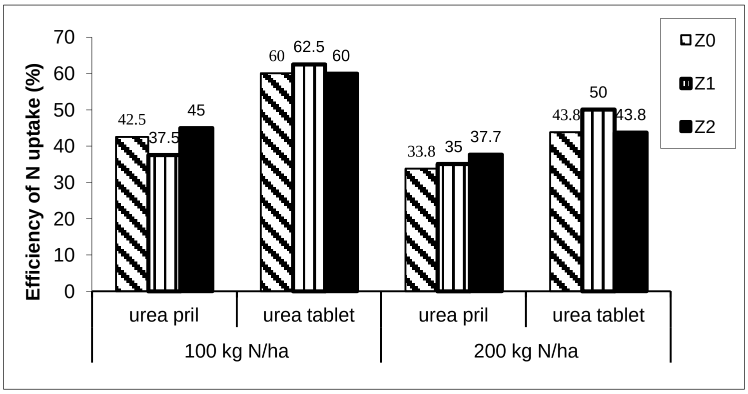

Figure 3. N uptake efficiency of different types and rates of urea as combined with zeolite application

4. Conclusions

- Applications of prilled urea at high rate (200 kg N/ha) result in highest rates of ammonia emission.
- Application of natural zeolite could reduce N volatilized by 46 % N when N fertilizer is applied as prilled urea.
- The applications of natural zeolite did not significantly affect nitrogen uptake and rice yields

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