

Nitrogen Mineralization and Volatilization from Controlled Release Urea Fertilizers in Selected Malaysian Soils

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Summary: Controlled release urea fertilizers are usually used for extended duration in supplying nitrogen. The rate of urea hydrolysis could be efficiently minimized through these fertilizers. Various controlled released fertilizers *i.e* Uber-10 (30%N), Meister-20 (40%N), Meister-27 (40%N), Humate Coated Urea (45%N), Duration Polymer Coated Urea Type-V (43%N), Gold-N-Sulfur Coated Urea (41%N) and common urea (46%N) were applied to inland soil series of Malaysia. The soil series investigated were: Serdang (Typic Paleudult), Munchong (Typic Hapludox), Segamat (Typic Hapludox), Selangor (Typic Tropaquept), Rengam (Typic Kandiodult) and Holyrood (Typic Kandiodult). The maximum release of ammonium (NH₄-N) was noted in Gold-N-Sulfur Coated Urea, Humate Coated Urea and common Urea over 8 weeks of incubation. However, the release of NH₄-N under the influence of Duration Type-V and Uber-10 took 2nd place. The Meister-20 and Meister-27 had minimum release of NH₄-N. Munchong series was efficient in releasing higher NH₄-N compared to rest of soils during 8th week of incubation due to higher soil total carbon, low NH₄-N and total nitrogen. Ammonia (NH₃-N) loss progressively increased with unit increase in incubation week and was higher during 6th week of fertilizer application. The higher loss of NH₃-N was found in common Urea. However, Meister-20, Meister-27, Duration Polymer Coated Urea Type-V and Uber-10 had lower loss of NH₃-N due to slow release property and this character could be beneficial for supplying nutrients to next season crop.

Keywords: Urea, Nitrogen, Volatilization, Ammonia, Coated fertilizer

Introduction

Injudicious nitrogen (N) fertilizer in various cropping patterns has raised the concerns of environmental contamination and high input costs [1]. Nitrate could be lost through denitrification and leaching, if applied in the form of urea [2]. About 30 to 60% of N is lost in the form of ammonia [3]. Nitrogen present in the soil prior to crop uptake is subjected to loss by volatilization, immobilization, denitrification and/or leaching, with the magnitude and pathways influenced by environmental conditions such as temperature and soil moisture [4]. Thus, fertilizer N uptake efficiency from soil by cereal crops is usually less than 50% [5-7].

Controlled release urea (CRU) is an excellent way to minimize nitrogen losses, improve fertilizer uptake efficiency, reduce inorganic nitrogen accumulation in the soil and its associated risk of loss, and reduce seedling injury [8, 9]. They are efficient in perennial planting and long term cropping [10] by reducing concerned environmental issues. These fertilizers have the availability of N during the whole growth period and enhance crop N recovery [11, 12]. The nitrogen releases from CRU closely match the N requirements of the crop and apparent N use efficiency through CRU was higher than that of conventional urea fertilizer [13]. On the positive side,

controlled release urea does not seem to have any negative effect on the soil biological process [14]. Coated fertilizers are the major category of slow-release fertilizers [15], which are physically prepared by coating the granules of common Urea with various materials to reduce their dissolution or hydrolysis rate [16]. The release of nutrients is controlled by diffusion through the coating, and different materials have been reported to be used as coatings, such as polysulfone [17], polyvinyl chloride [18], and polystyrene [19]. Now days, the super-absorbent materials used as coatings in slow-release fertilizers have attracted more attention [20]. The polymer coated urea, would be an additional option to farmers for high crop productivity. The copper, zinc and sulphur as coating nutrient on urea was reported an efficient strategy in reducing rate of mineralization by 30% and ammonia volatilization by 50% in the acid soils where the pH was low [21].

Controlled release urea tested in different soil series with low pH in Malaysia increased soil pH. The rate of mineralization and ammonia volatilization reduced by 30 and 50% respectively in acid soils with positive effectiveness of coating material which had potential to control fast hydrolysis process and ammonia volatilization losses

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[21]. Controlled release urea releases nitrogen slowly and thus reduces nitrogen loss through leaching and volatilization compared with common urea [22]. Due to the concerns of fertilizer costs, nutrient losses, environmental pollution, this research therefore, was conducted to determine the effect of controlled release urea on nitrogen mineralization and volatilization from some Malaysian soils.

Experimental

The inland soil used in this experiment was brought from Serdang series (Typic Paleudult), Munchong series (Typic Hapludox), Segamat series (Typic Hapludox), Selangor series (Typic Tropaquept), Rengam series (Typic Kandiuult) and Holyrood series (Typic Kandiuult) in Malaysia. Their chemical properties are given in Table-1. The seven fertilizers viz. common urea (46%N), Uber-10 (30%N), Meister-20 (40%N), Meister-27 (40%N), Humate Coated Urea (45%N), Duration Polymer Coated Urea Type-V (43%N) and Gold-N-Sulfur Coated Urea (41%N) were purchased from authorized dealer of local market. The physico-chemical properties of soil were conducted at Soil Chemistry Laboratory, Department of Land Management, Universiti Putra Malaysia. For different determinations, the soil samples were air-dried, ground and passed from 2 mm sieve and stored at room temperature in moisture-proof containers. The soils soil pH measured from 1:2.5 ratio (soil: distilled water) slurry using glass electrode [23]. Organic carbon was determined by the potassium dichromate and H₂SO₄ digestion method [24], CEC by leaching with 1N ammonium acetate buffer (adjusted to pH 7.0). The mineral-N (NH₄⁺-N and NO₃⁻-N) through steam distillation technique [25] and total-N by the salicylic acid digestion-Kjeldahl procedure [26]. Mechanical analysis of the soils was done using pipette method and USDA Textural Triangle to determine soil texture. Nitrogen mineralization was estimated by establishing incubation experiments of soil samples under controlled conditions and constant temperature in aerobic incubation method was maintained. The air dried soil (20 g) was filled in each container with volume of 254.6 cm³. The soils were then wetted to 40% moisture content and equivalent of 400 µg N g⁻¹ of each fertilizer was added. The soils were incubated for eight weeks under room temperature. The containers were weighed once in a week (randomly) and distilled water was added to compensate the water loss due to evaporation. Extraction was done every week up to eight weeks. After the incubation period, the shaking was done with 2M potassium chloride solution, containing urease inhibitor, phenyl mercuric acetate

(PMA) mixtures at 150 rpm for one hour. The extract was filtered through filter paper. The 10 mL of the soil extract was pipetted into a distillation flask. About 0.5 g of dry magnesium oxide powder (MgO) was added and distilled on a micro Kjeldahl steam distillation unit. The distillate was absorbed in 10 mL boric acid. The collected distillate was back titrated against 0.01 N HCl to determine the NH₄⁺-N content in the soils. After the distillation of NH₄⁺-N, the distillation flask was removed and 0.2 g Devarda alloy was added to determine the NO₃⁻-N content in soils. The distillation flask was reconnected. The rest of procedures were followed as NH₄⁺-N distillation analyzed for NH₄⁺-N and NO₃⁻-N using the steam distillation technique [25]. Ammonia volatilization was determined using the force-draft technique for ten weeks. A closed-dynamic (aerobic) air flow system, marginally modified from Fenn and Kissel [27] was used to collect volatilized NH₃-N. The system comprised an air exchange chamber (ground-glass Erlenmeyer 500 mL) and trapping flask (ground-glass Erlenmeyer 250 mL), both stopped and fitted with an inlet/outlet facility. The inlet of the chamber was connected to a heavy duty air pump while the outlet connected by polyethylene tubing to the trapping flask fitted with a glass distribution rod immersed in trapping solution. The chamber was filled with soil equivalent to 300 g of air-dried soil. The soil is wetted to 40% moisture content and equivalent of 400 µg of each fertilizer was added. In this method, each volume of soil was placed in the air exchange chamber leaving some volume above the soil surface for air exchange to take place. The chamber was weight every two days interval and distilled water was added to compensate for the water loss due to evaporation. Air was pumped using air-pump and the flow rate was adjusted to an appropriate rate (2.5-3.5 volume/minute). Air was passed through the chamber and subsequently through the trapping flask containing 75 mL of 2% boric acid-mixed indicator (bromocresol green and methyl red) to capture NH₃-N release. When the colour of the indicator changes from purple to green, it was titrated using a 0.1 N HCl acid solution. The end point is reached when the color changes from green to purple (color as the blank). The amount of the urea lost by volatilization of NH₃-N was then determined. Titration with 0.1 N HCl was done to determine the percentage of NH₃-N volatilized. Finally, statistical analyses were performed using variance technique and Tukey's test at P ≤ 0.05 to compare the differences among treatments means [28] using Statistical Analysis System software version 9.2.

Table 1. Chemical characteristics of soils.

Soil Series	Serdang	Munchong	Segamat	Selangor	Rengam	Holyrood
pH (H ₂ O)	5.1	4.0	4.3	4.0	4.7	4.9
Total Carbon (%)	2.1	3.7	2.4	2.9	1.3	1.6
CEC (+) (cmol kg ⁻¹)	5.4	8.7	8.9	19.9	5.4	3.0
<i>Mineral N</i>						
NH ₄ -N (ug g ⁻¹)	11.9	9.0	10.1	18.9	18.5	16.4
NO ₃ -N (ug g ⁻¹)	3.6	9.0	12.7	13.2	5.2	7.7
<i>Exchangeable</i>						
K (cmol kg ⁻¹)	0.3	0.4	0.9	1.5	0.2	0.2
Mg (cmol kg ⁻¹)	4.2	3.6	4.4	4.1	3.5	3.5
Ca (cmol kg ⁻¹)	1.1	0.8	1.0	0.7	0.4	0.1
Total N (%)	0.1	0.3	0.2	0.3	0.1	0.1

Table 2. Release of NH₄-N and NO₃-N from urea and controlled release urea across incubation weeks.

Treatment	NH ₄ -N (µg/g)	NO ₃ -N
Common Urea	308.0 a (± 8.21)	50.8 a (± 3.62)
Uber-10	114.5 b (± 7.63)	31.6 bc (± 2.24)
Meister-20	69.7 c (± 4.23)	33.8 bc (± 2.92)
Meister-27	47.2 d (± 2.46)	28.1 c (± 2.40)
Humate Coated Urea	309.2 a (± 8.49)	39.4 b (± 3.10)
Duration Polymer Coated Urea Type-V	123.2 b (± 8.62)	27.4 c (± 1.98)
Gold-N-Sulfur Coated Urea	316.7 a (± 8.05)	40.1 b (± 3.14)

Different alphabets in column indicate significant difference between means using Tukey's test at P ≤ 0.05. *(± Standard error)

Table 3. Release of NH₄-N and NO₃-N from controlled released urea in various soils of Malaysia

Treatment	NH ₄ -N (µg/g)	NO ₃ -N
Serdang	176.4 c (± 7.35)	31.0 c (± 1.94)
Munchong	241.5 a (± 11.09)	49.2 b (± 2.36)
Segamat	193.6 c (± 10.70)	75.9 a (± 3.49)
Selangor	218.4 b (± 11.85)	19.7 d (± 1.52)
Rengam	155.1 d (± 8.25)	11.6 d (± 0.64)
Holyrood	121.9 e (± 5.18)	16.2 d (± 1.79)

Different alphabets in column indicate significant difference between means using Tukey's test at P ≤ 0.05. *(± Standard error)

Results and Discussion

Release of NH₄-N and NO₃-N from fertilizers

The significant difference in NH₄-N release was noted in different soil series during the incubation period treated with CRU fertilizers. The higher release of NH₄-N was found in Gold-N-Sulfur Coated Urea and (316.7 ± 8.05 µg/g), Humate Coated Urea (309.2 ± 8.49 µg/g) and common Urea (308.0 ± 8.21 µg/g). All these treatments were statistically non-significant with each other. The release of NH₄-N under the influence of Duration Type-V and Uber-10 was 123.2 ± 8.62 and 114.5 ± 7.63 µg/g

respectively. However, Meister-20 and Meister-27 had lowest NH₄-N concentration in soil with 69.7 ± 4.23 and 47.2 ± 2.46 µg/g respectively after 8th week of incubation. The maximum release of NH₄-N across different soil series indicates the availability of nutrient due to coated fertilizers specially Sulfur Coated Urea (Gold-N) and Humate Coated Urea (Table-2). The extended release of coated fertilizers could be the reason that upon soil application a slow bacterial degradation takes place, becoming available for plant uptake after slow hydrolysis process. Although, NH₄-N releasing values of Gold-N-Sulfur Coated Urea were statistically non-significant, but it had greater NH₄-N release in 8th week of incubation.

Similarly, Subbarao *et al.* [29] reported that coated urea fertilizers are usually designed with chemical and physical properties that regulate the process of releasing nitrogen into the soil solution to meet plant needs by reducing NH_4 availability to nitrifying bacteria and thus, subsequently reduction of NO_3 leaching or gaseous loss as N_2O or NO occurs. Sulfur coating material is generally costs less than other slow release fertilizers. It also supplies essential elements and tends to decrease soil pH. However, conventional fertilizers especially common Urea or any uncoated Urea fertilizer have tendency of leaching, volatilization and plant burn. In this study, Duration Polymer Coated Urea Type-V also had greater release of NH_4 -N, which might be the effect of reduced leaching and runoff as well as release of N in time [30]. Thus, slow-release mineral fertilizers can minimize potential leaching losses and maximize fertilization return and efficiency [31]. In case of common Urea, it also released higher NH_4 -N in 8th week of incubation, but it is well known fact that upon application to soil, urea is rapidly hydrolyzed by urease enzymes to form ammonia and thus, the accumulation of excess ammonia can result toxicity to plants as well as leaching and volatilization in the environment [32]. Therefore, splitting the application of urea into three or more doses are recommended compared to single application of coated fertilizers throughout the growing season [33].

Nitrate is one of the mineral-N found in soils and is available for plant uptake. However, NO_3 -N form is not stable and more mobile than NH_4 -N and easily lost through leaching and denitrification. The findings showed that common Urea produced higher soil NO_3 -N compared to coated urea fertilizers. The lower NH_4 -N produced by the controlled released fertilizers resulted in lower nitrification which indicates that most of the urea was transformed in to NH_4 -N especially at early incubation period and subsequently NO_3 -N released slowly up to latter incubation weeks (Table 2). For example, Shoji [34] compared the patterns of nitrate leaching with use of polymer-coated urea (PCU) and common Urea and, they observed higher nitrate leaching in the earlier growing season in common Urea.

Release of NH_4 -N and NO_3 -N from soil

The higher release of NH_4 -N (241.5 ± 11.09 $\mu\text{g/g}$) was found in Munchong series during the 8th week of incubation. The amount of NH_4 -N present in these soils in descending order was: Munchong series > Selangor series > Segamat series > Serdang series > Rengam series > Holyrood series (Table-3). The higher concentration of NH_4 -N in Munchong series

could be a possible reason that urea hydrolysis was rapid and thus, higher NH_4 -N concentration was found in the soil. The availability of N in soils increased the soil N content. However, Holyrood series had low concentration of NH_4 -N because due to low carbon content in this soil as well as this soil series had sandy loam texture which is more prone to N loss processes through NH_3 -N volatilization. Similarly, Wang and Alva [35] observed large reductions in N due to leaching losses in sandy soils and further reported that this type of soil could be amended with slow-release fertilizers (IBDU, isobutylidene diurea), and polyolefin resin-coated urea (Meister) as compared to applications of ammonium nitrate fertilizer. Accumulation of ammonium in soils is not desired because it is prone to ammonia loss [36]. In this study, the ammonium concentrations were lower in most of the soil series. However, the results are evident in the reduction of NH_4 -N accumulation in coated urea treated soils due to inhibitory activity of urease inhibitors especially coating material, slow release of N with increases in soil pH. The retention of NH_4 -N can be beneficial in improving urea efficiency because a high level of soil ammonium-N without retention does not guarantee the plant N use efficiency [3].

The NO_3 -N concentration was low in Selangor, Holyrood and Rengam soil series with 19.7, 16.2 and 11.6 $\mu\text{g/g}$ respectively. Segamat series showed the highest concentration of NO_3 -N in the soil with 75.9 $\mu\text{g/g}$, followed by Munchong (49.2 $\mu\text{g/g}$) and Serdang series (31.0 $\mu\text{g/g}$). The amount of NO_3 -N present in these soils in descending order was: Segamat series > Munchong series > Serdang series > Selangor series > Holyrood series > Rengam series (Table 3).

Volatilization of NH_3 -N

Bi-weekly observation showed that ammonia loss progressively increased with a unit increase in incubation week and was higher during 6th week. Urea had the highest NH_3 -N losses followed by, Gold-N-Sulfur Coated Urea and Humate Coated Urea fertilizers. The Meister-20 followed by, Meister-27, Duration Polymer Coated Urea Type-V and Uber-10 fertilizers has lower loss of ammonia across soil series (Fig. 1). The maximum rate of NH_3 -N loss generally corresponded to the higher soil pH. In Holyrood series, the volatilization rate of ammonia correspondingly increased right from 2nd week of urea application, while in rest of soil series, the volatilization rate steadily increased over time. Maximum volatilization rates of ammonia also have been reported to occur during the initial period of

fertilizer application [37]. Ammonia volatilization losses due to surface application in common urea could range from 5 to 20% and even as high as 50% under extreme conditions [38]. Conditions favouring ammonia volatilization from urea or urea-based fertilizers include surface-application of the fertilizer, relatively high surface soil pH, high amounts of surface residue, warm and windy weather, high relative humidity, and soil water content. The

additional possible benefits of use of urease inhibitors to delay urea hydrolysis include possible reductions in nitrate leaching losses when conditions for nitrate leaching are high [39]. The lower N_2O losses, and less damage to germinating seeds and seedlings is caused by released ammonia and nitrite in higher quantities when urea is band placed close to seed [40].

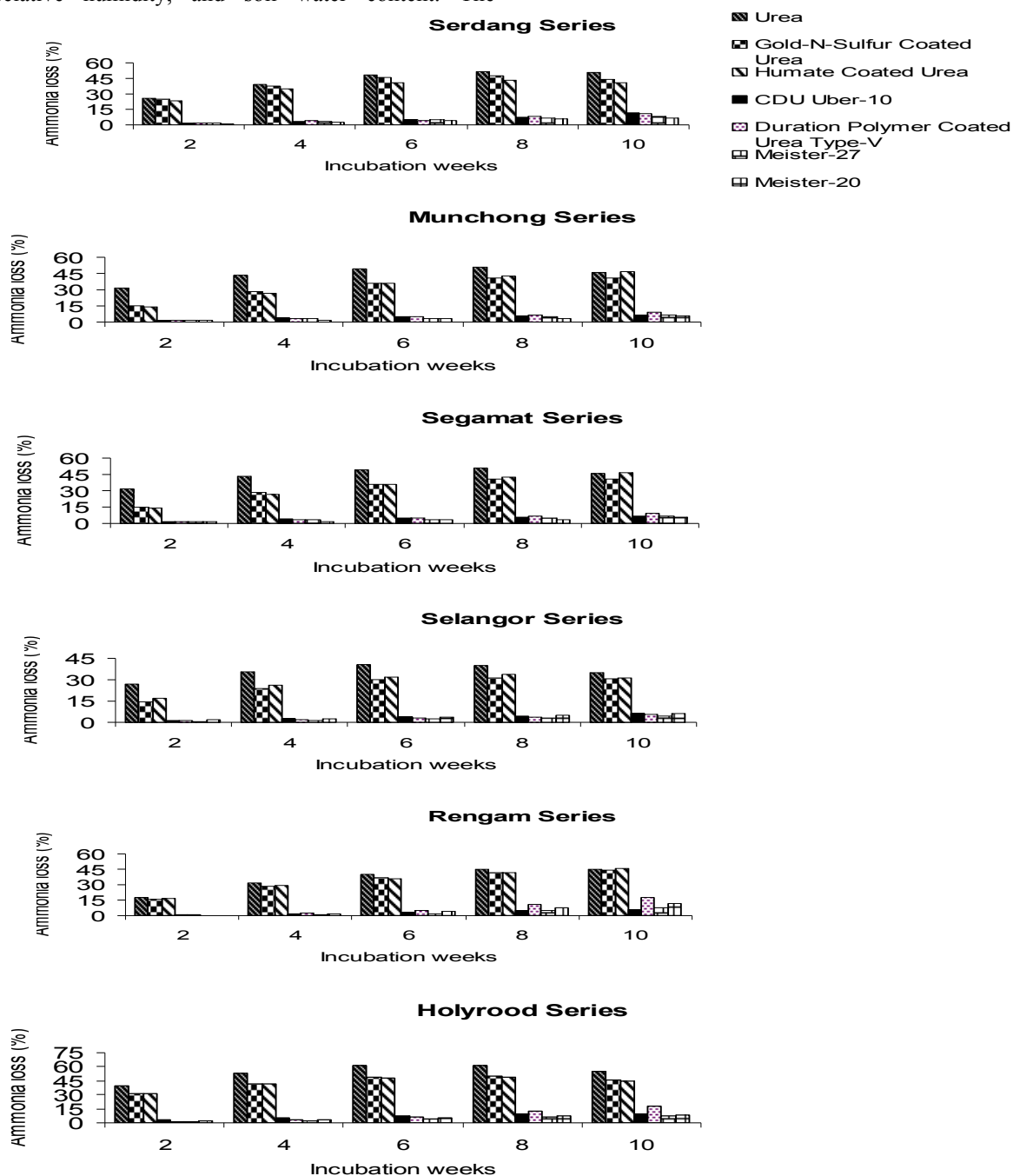


Fig. 1: Cumulative ammonia volatilization in different incubation weeks from urea controlled release urea fertilizers in various soil series of Malaysia.

Conclusion

Controlled release urea fertilizers particularly Gold-N-Sulfur Coated Urea, Humate Coated Urea and common Urea released maximum $\text{NH}_4\text{-N}$ during 6 to 8 weeks of incubation due to their quick response for hydrolysis in the soil. However, release of $\text{NH}_4\text{-N}$ was very slow in Meister-20 and Meister-27. Among the tested soil series, Munchong had higher $\text{NH}_4\text{-N}$ release due to higher total carbon, low $\text{NH}_4\text{-N}$ and total nitrogen in soils. Ammonia loss progressively increased with unit increase in incubation week. Some controlled release fertilizers *i.e.* Gold-N-Sulfur Coated Urea and Humate Coated Urea had greater ammonia ($\text{NH}_3\text{-N}$) loss as in common Urea. Whereas, Meister-20, Meister-27, Duration Polymer Coated Urea Type-V and Uber-10 due to slow release character minimized the loss of $\text{NH}_3\text{-N}$ which could be beneficial for next season crop.

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