Effects of Nitrogen Inhibitors and Slow Nitrogen Releasing Fertilizers on Crop Yield, Nitrogen Use Efficiency and Mitigation of Nitrous Oxide (N_2O) Emission

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Abstract: *Improving the production and productivity of crops through appropriate nutrient management including nitrogen fertilizer is one of the most important means to satisfy the food demand of the ever increasing world's population. Consequently, intensive use of nitrogen fertilizers increase cost of production and cause environmental pollution through different forms of nitrogen losses such as nitrate (NO^-_3) leaching, ammonia (NH_3) volatilization and nitrous oxide (N_2O) emission. The main aim of this paper is, therefore, to review the effects of nitrogen inhibitors and slow nitrogen releasing fertilizers on crop yield, nitrogen use efficiency and mitigation of N_2O emission. Various research results showed that application of nitrification inhibitors (DCD, DMPP, thiosulfate, neem, and N-serve), urease inhibitors such as agrotain, PPD, NBPT and hydroquinone, and slow nitrogen releasing fertilizers like polymer and sulfur coated urea substantially improved nitrogen use efficiency and yield of crops as well as significantly mitigating GHG (N_2O) emission. Therefore, application of such technologies has great contribution to reduce environmental pollution caused by intensive utilization of nitrogen fertilizers while increasing crop yields.*

Keywords*: Nitrogen fertilizer, leaching, nitrogen loss, agrotain, mineralization*

1. Introduction

Nitrogen is required by all living organisms for the synthesis of proteins, nucleic acids and other nitrogen-containing compounds (the James Hutton Institute, 2014). Although 78 % of the air is nitrogen gas (N_2), it is not directly available to plants. In order to become available to plants, nitrogen must be fixed to form ammonium (NH_4^+) or nitrate (NO_3^-) through the process of making industrial fertilizers (Haber-Bosch process) and/or through nitrogen-fixing bacteria associated with the roots of legumes (Clark, 2014).

Leguminous plants and soil microorganisms contribute significant amounts of nitrogen in the soil that can be used by crops. However, high crop yields require more nitrogen than provided by natural means (Ribaudo *et al*., 2011). Therefore, nitrogen is usually supplied in the form of artificial fertilizer, which is produced through a chemical process (Haber-Bosch process) that converts atmospheric nitrogen into ammonium(NH_4^+) using very high quantities of energy (James Hutton Institute, 2014).

Chemical fertilizer has played a major role in the global food production over the past 60 years. It supplies about 50 % of total N required by crops. However, its use efficiency in crop production is low (10-50 %) mainly due to loss of N through nitrate (NO_3) leaching, volatilization of ammonia (NH_3) and nitrous oxide (N_2O) emission resulting in pollution of groundwater and atmosphere (Zhaohui *et al*., 2012; Galloway *et al*., 2003). Moreover, the production cost of nitrogen fertilizer is very high. These scenarios lead to the use technologies such as nitrogen inhibitors and slow nitrogen releasing fertilizers given as fertilizer additives to increase nutrient uptake, fertilizer use efficiencies and yields of crops (Frame and Reiter, 2013). Slow released fertilizers, nitrification and urease inhibitors are the three possible types of products that control nitrogen loses and consequently improve nitrogen use efficiency (Schwab and Murdock, 2010). Therefore, the main aim of this paper is to review the effects of nitrogen inhibitors and slow nitrogen releasing fertilizers on crop yield, nitrogen use efficiency and mitigation of N_2O emission.

2. Nitrogen Inhibitors, Slow Releasing Fertilizers and their Effects on Crops

Nitrification and urease inhibitors are called nitrogen inhibitors. Nitrification inhibitors are substances that inhibit biological oxidation of ammonium to nitrate (Schwab and Murdock, 2010). Some of nitrification inhibiting products includes dicyandiamide (DCD), 3,4-dimethyl-1H-pyrazoliumdihydrogen (DMPP), thiosulphate, neem, karanjin, and nitrapyrine (N-serve) (Khan *et al.,* 2013). Exudates of some plant species have also the capacity to inhibit nitrification process in the soil (Al-Ansari and Abdulkareem, 2014). Urease inhibitors are substances that inhibit conversion/hydrolysis of urea to ammonia and carbon dioxide and hence minimize ammonia volatilization losses (Schwab and Murdock, 2010). The common urease inhibitor products are phenyl phosphorodiamidate (PPD), hydroquinone (HQ), N-(n-butyl) thiophosphorictriamide (NBPT), phenyl mercuric acetate (PMA), and catechol. Controlled-released fertilizers are fertilizers such as urea that are coated with a polymer or sulfur (Khan *et al.,* 2013).

2.1 Effects of Nitrogen Inhibitors on Crop Yield

The results of various researches showed that treating of fertilizers with nitrogen inhibitors improves yields of various types of crops. Significantly higher yields of maize were for example obtained when urea is treated with agrotain or NBPT (N-butyl thiophosphoric triamide). It increased yield of maize by 6.6% at 87 kg N ha-1and by 9.1% at the dose of 115 kg N ha^{-1} compared to untreated once (Khan *et al*., 2014). Similarly Dawar *et al*. (2011) found that urea treated with agrotain increased grain and biomass yield of maize by 27% and 30%, respectively, compared with urea alone. Agrotain also increased biological and grain yield of wheat by 25.2% and 37.5%, respectively, at 60 kg N ha^{-1} as indicated in Table 1. Whereas at 120 kg N ha^{-1} it increased the biological and grain yield by 17.4% and 22.6%, respectively, compared to untreated urea (Khan *et al*., 2013).

Table 1. Increase in biological and grain yield of wheat by urease (Agrotain) and super-urea inhibitors

Treatment	Biological yield (kg/ha)	Increase by inhibitors (%)	Grain yield (kg/ha)	Increase by inhibitors (%)
Urea at 60 kg N/ha	7231	-	2794	-
Agrotain treated urea at 60 kg N/ha	9668	25.2	4470	37.5
Supper urea (agrotain + DCD) 60 kg N/ha	10365	30.2	4897	42.9
Urea at 120 kg N/ha	8806	-	3826	-
Agrotain treated urea at 120 kg N/ha	10666	17.4	4942	22.6
Supper urea (agrotain + DCD) at 120 kg N/ha	11743	25.0	5282	27.6

Source: Khan *et al*., 2013

Research results also confirmed the potential of neem (*Azadirachta indica*) as nitrogen inhibitor. Based on the results of their research, Joshi *et al*., (2014) have been recommended to apply neem coated urea at 100 kg/ha in 3 splits to achieve higher growth and yields of maize with better monetary returns. Neem coated urea resulted 6.2% yield increment of maize compared to non-coated urea (Figure 1).

Similarly, Makinta *et al*. (2014) showed that the application of 150 kg N ha^{-1} treated with 30% crushed neem seed was superior and most economical for maize production. Such treatment produced the highest total dry matter (5,808 kg ha^{-1}) and grain yields (1,501 kg ha^{-1}) of maize.

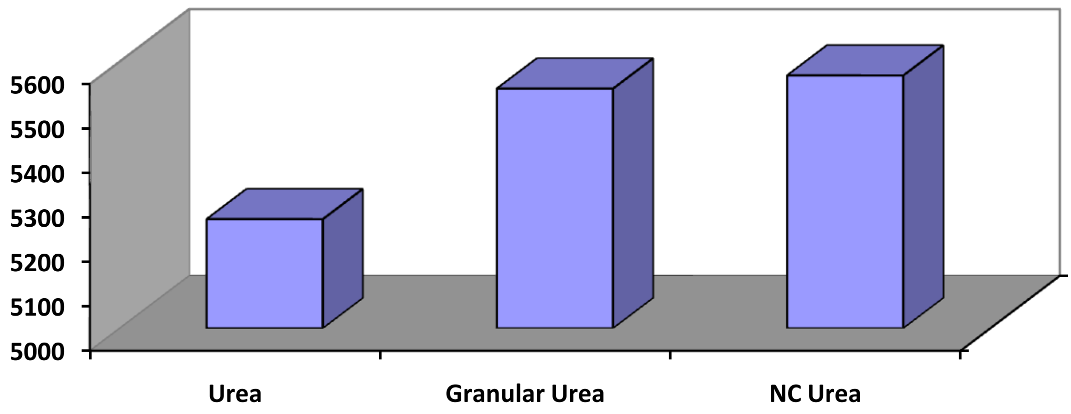

Figure 1. Effects of neem as nitrogen inhibitor on yield of maize (kg ha^{-1})

NC= neem coated; **Source:** Joshi *et al*. (2014)

According to Arafat *et al*. (1999), treating urea with 0.04% neem cake increased rice yield by 26% compared to urea alone. Besides amonium sulfate treated with 0.02% and 0.04% neem cake increased rice yield by 14.4 and 25.6% , respectively, over that of amonium sulfate alone (Table 2). Coating of urea with tar and engine oil also increased rice yield compared to uncoated urea (Sannagoudra *et al*. (2012).

Table 2. Effects of nitrogen inhibitors on rice yield

Treatments	**Yield (g/pot)**	**Treatments**	**Yield (g/pot)**
Control	26.60 [e]	Control	26.60 [e]
Urea	49.40 [d]	**Amonium Salfate (AS)**	51.12[c]
Urea +N serve	62.10 [b]	AS +N serve	59.80 [b]
Urea + 0.02% neem cake	52.00 [c]	AS + 0.02% neem cake	59.00 [b]
Urea + 0.04% neem cake	63.70[a]	AS + 0.04% neem cake	64.60[a]
Urea + 0.02%tea waste	50.70 [c]	AS + 0.02%tea waste	50.40[cd]
Urea + 0.04%tea waste	51.30 [c]	AS + 0.04%tea waste	49.90 [d]
LSD (0.05)	*1.22*	*LSD (0.05)*	*1.58*

Source: Arafat *et al*. (1999)

Not only the individual use of urease and nitrification inhibitor but also their combination hampers the loss of nitrogen and improves its utilization. Zhang *et al.* (2010) found that amending urea with combination of urease and nitrification inhibitors improve maize yield, while saving urea fertilizer by 30% and protecting the environment. Application of 126 kg N ha^{-1} treated with combination of NBPT and DMPP gave comparable biomass and grain yield of maize to that of 180 kg N ha^{-1} without treatment. Similarly, Khan *et al*. (2013) found that the highest grain yield (5,282 kg ha^{-1}) of wheat was obtained by application of super-urea, urea treated with the combination of agrotain and DCD), at 120 kg N ha^{-1}. Super-urea increased wheat yield by 42.9% at 60 kg N ha^{-1} and by 27.6% at 120 kg N ha^{-1} compared to respective untreated urea as indicated in Table 1.

Similarly, blending of urea with the combination of neem cake and tar has increased grain yield of rice (Figure 2) significantly. These results indicated the potential benefit of combined use of urease and nitrification inhibitors than single inhibitor alone.

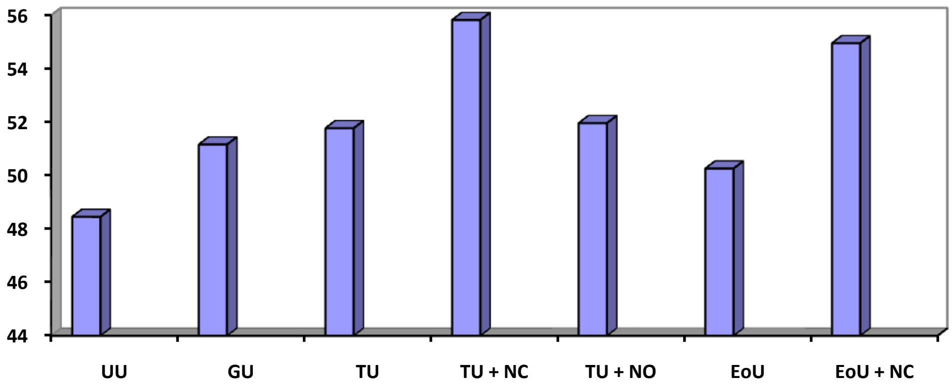

Figure 2. Effects of nitrogen inhibitors on the yield of rice (qt ha^{-1})

UU= uncoated urea, GU = Granular urea, TU = Tar coated urea, NO = neem oil, EoU = Engine oil coated urea, NC = Neem coated urea

Source: Sannagoudra *et al*. (2012)

2.2 Effects of Slow Nitrogen Releasing Fertilizers on Crop Yields

Research results revealed that slow nitrogen releasing fertilizers improved crop yields appreciably. According to Wang *et al*. (2013), control released urea (CRU) and combination of 60% CRU and 40% urea gave 12.4% and 4.5% higher cotton yield compared to that of urea without treatment as basal and split application (Figure 3). Other research results showed that applying controlled release fertilizer and its combination with urea at the ratio of 3:7 increased rice yields by 7.8% and 9.8%, respectively, compared to urea alone (Ji *et al*., 2011). Similar research result showed compared to basal application of untreated one, polymer-coated urea increased rice yields by 15.1%–51.4%, while compared with split application of untreated urea it increased the yield by 7.9%–31.7% (Xi-shengYe *et al*., 2013). Fu-liang *et al*. (2012) also observed that sulfur-and polymer-coated urea increased wheat yield, protein and starch contents by 6.5-10.4%, 5.8-18.9%, 0.3-1.4%, respectively, compared with that of untreated urea fertilizer application methods.

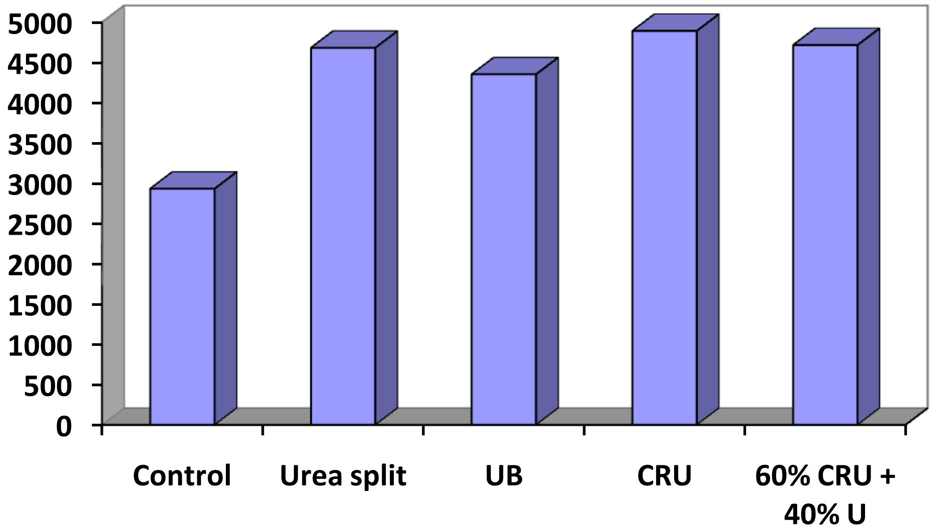

Figure 3. Effects of controlled-release urea on yield of cotton (kg/ha)

CRU = controlled release urea, UB = base application of urea

Source: Wang *et al*. (2013)

3. Effects of Nitrogen Inhibitors and Slow Nitrogen Releasing Fertilizers on Nitrogen Uptake and Use Efficiency

In addition to the increment of crop yields, results of various researches have also shown positive effects of nitrogen inhibitors and slow nitrogen releasing fertilizers on nitrogen uptake and use efficiency of plants. For instance, significantly higher nitrogen uptake of rice was recorded by treating urea with neem cake + tar (Sannagoudra *et al*., 2012) and treating with 0.02% neem cake (Arafat *et al*., 1999). According to Khan *et al*. (2013), the highest nitrogen uptake of wheat (108.9 kg ha^{-1}) was obtained from urea treated with the combination of urease and nitrification inhibitor (supper-urea) at 120 kg N ha^{-1} followed by super urea at 60 kg N ha^{-1} (104.0 kg ha^{-1}). Super-urea increased the nitrogen uptake by 45.1 % at 60 kg N, while agrotain, (urease inhibitor) at 60 kg N $ha^{-1}$and 120 kg N ha^{-1} increased nitrogen uptake by 38.0 % and 29.2 %, respectively (Table 3).

Controlled released urea (CRU) increased cotton nitrogen uptake by 13.01% and 52.03% compared to urea applied by split application and 60% CRU + 40% urea treatment, respectively (Wang *et al*., 2013). Placement of blended urea with CRU at the rate of 225 kg N ha^{-1} improved wheat N uptake efficiency by 28.5% compared to urea alone at the same dose (Yang *et al*., 2011).

Generally, super-urea performed better than agrotain in terms of increasing nitrogen use efficiency. The use of inhibitors with low level of urea (60 kg N ha^{-1}) was better than with high (120 kg N ha^{-1}) level of urea (Khan *et al*., 2013). Apparent nitrogen recovery of applied nitrogen increased from 35% for prilled urea to 55.0, 52·5 and 37·5% for super granules urea, neem-cake-coated urea and DCD coated urea, respectively (Chauhana and Mishraa, 1989).

Table 3. Effect of agrotain and super urea on wheat N uptake

Treatment	N-uptake (kg/ha)	Nitrogen uptake increase by inhibitors (%)
60 kg/ha N without inhibitors (2splits)	57.1	-
60 kg/ha N with agrotain inhibitor (2splits)	92.3	38.0
60 kg/ha N with supper urea inhibitor (2splits)	104.0	45.1
120 kg/ha N without inhibitors (2splits)	77.1	-
120 kg/ha with agrotain inhibitor (2splits)	108.9	29.2

Source: Khan *et al*. (2013)

Compared with the conventional urea, the slow released urea significantly increases apparent nitrogen efficiencies by 63.3%–139.9%. Compared with the conventional urea split, the polymer-coated controlled released urea and the 70% sulfur-coated controlled released urea combined with 30% conventional urea increased the agronomic nitrogen efficiencies by 2.2%–17.6% (Xi-shengYe *et al*., 2013). Polymer-coating improved urea-nitrogen use efficiency of wheat by 58.2-101.2% (Fu-liang *et al*., 2012).

4. Effects of Nitrogen Inhibitors and Slow Nitrogen Releasing Fertilizers in N_2O Emission and Other Forms of Nitrogen Losses

Nitrous oxide is one of the most important greenhouse gases produced at different level of nitrogen cycle. Both nitrification and denitrification reactions in the soil produce the intermediate gaseous nitrous oxide (N_2O), which is ultimately released into the atmosphere (Kanyama and González, 2007). The N_2O concentration in the atmosphere is increasing by 0.25% per annum (IPCC 1997). This in turn causes global warming and stratospheric ozone layer depletion, which shields the earth from biologically harmful ultra-violet radiation (IPCC, 1997; Johnston, 2005). The global warming potential of N_2O is 300 times more damaging than CO_2 (Clark, 2014). Reducing N_2O emission from agricultural soils using nitrification inhibitors is very important. One of the potential mitigation methods to reduce these emissions from the agricultural soils is to use nitrification inhibitors that slow down the conversion of NH^+_4 to NO^-_3 in the soil.

In line with this, various research results revealed that application of nitrogen inhibitors significantly reduced N_2O emission and other N losses. When urea was applied without nitrification inhibitors, 72 to 84% of applied nitrogen was lost from the soil of cotton field, but treating urea with acetylene, phenylacetylene, and nitrapyrin reduced nitrogen losses to 57%, 52%, and 48%, respectively (Chen *et al*., 1994). Application of urea together with formaldehyde, dicyandiamide & hydroquinone, hydroquinone & thiosulphate and hydroquinone & DCD in different crops reduced N_2O emissions by 42%, 33-63%, 5%-31% and 7% -29%, respectively as indicated by research results of Jianga *et al*. (2010) and Malla *et al*. (2005).

As reported by Sanz-Cobena *et al*. (2012), a two-year field experiment using irrigated maize showed that N_2O emissions were effectively abated by NBPT (urease inhibitor) and its combination with DCD (nitrification inhibitor). It was found that treating urea with NBPT alone and with combination of NBPT + DCD reduced N_2O emission by 54 and 24%, respectively (Sanz-Cobena *et al*., 2012). Similarly, Shojia *et al*. (2001) observed that dicyandiamide and polyolefin treated urea in barley field reduced N_2O emissions by 81 % and 35 %, respectively.

Application of DCD on grazed pasture soils was also found to be very effective in reducing N_2O emissions. Total N_2O emission was reduced by 61-73% when the animal urine was applied with DCD in pastureland (Cameron *et al*., 2007). Similarly, Di and Cameron (2003) reported that treating the soil with DCD decreased N_2O emissions by 76% in 6 autumn months of experimental periods, whereas in 3 months of spring N_2O flux was decreased by 78% with the same treatment. Other study indicated that applying a combination of Agrotain and DCD at the ratio of 1:7 w/w 5 days prior to urine application significantly decreased NH_3 volatilization by 38% in autumn and by 28% in spring compared to urine alone. Moreover, DCD treatment significantly reduced NO_3^{-1} leaching by 43% (Zamana and Nguyen, 2012).

Research results indicated that nitrification inhibitors reduced volatilization of ammonia and nitrates leaching. In sunflower field trial, it was found that when urea was treated with NBPT, the total NH_3 los was 5.9 % compared to 10.1% NH_3 loss of untreated urea (Sanz-Cobena *et al*., 2008). Combined application of NBPT and DCD increased soil $NH4^+$ by 2%-53% and decreased soil NO_3 concentration (Jiao *et al*., 2004). Combination of hydroquinone and DCD effectively inhibited oxidation of the $NH4^+$, which decreases the accumulation of NO_3^- in soil and hence the potential leaching of NO_3 (Chen *et al*., 2005). In two years rice-rape rotation experiment, it was also found that urea treated with DMPP increased $NH4^+$ concentrations by 19.1–24.3% and reduced NO_3^- concentrations by 44.9–56.6% compared to the urea alone (Li *et al*., 2008). Controlled released fertilizer and its combination with urea at the ratio of 3:7 decreased N_2O emission during rice growth season by 59.6% and 40.4%, respectively compared with urea alone (Ji *et al*., 2011).

5. Conclusion

Use of nitrification and urease inhibitors as well as their combination in the application of nitrogen fertilizer appreciably improved yield, nitrogen uptake and its use efficiency by various crops. In addition, treating urea fertilizer with polymer and sulfur coating materials increased crop yields by reducing nitrogen loss through volatilization, nitrification and leaching. Furthermore, such treatments reduced nitrous oxide emission, a greenhouse gas that has a great contribution to global warming. Therefore, the use of such new technologies may contribute to the reduction of environmental pollution caused by intensive application of nitrogen fertilizers in agriculture while increasing the crop yield.

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