

## **Nitrogen Fertilizer Losses from Rice Soils and Control of Environmental Pollution Problems**

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**Abstract:** Nitrogen (N) requirements of rice crop are met from both the soil and fertilizers. Because of acute N deficiency in most rice soils, fertilizer N must be applied to meet the crop demand. N fertilizer applied to rice crops is partially lost through different mechanisms, including ammonia volatilization, denitrification, and leaching. These losses may cause environmental problems such as polluting the atmosphere, aquatic systems, and groundwater. These problems cannot be alleviated completely. However, they can be reduced a considerable extent by various techniques. Research has been conducted around the world to minimize N fertilizer losses. This paper reviews this information on N fertilizer losses, indicating management practices for minimizing these losses from the soil-water system.

**Keywords:** Nitrogen losses, rice soils, environmental pollution

### **INTRODUCTION**

Rice is the main food crop of an estimated 40% of the world's population (Buresh and De Datta 1990). The rice crop removes large amounts of N for its growth and grain production. The estimated amount of N removal ranges from 16 to 17 kg for the production of one ton of rough rice, including

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straw (Choudhury et al., 1997; Ponnampereuma and Deturck 1993; Sahrawat, 2000). Total N uptake by rice plant per hectare varies among rice varieties (Table 1). Most of the rice soils of the world are deficient in N, and biological nitrogen fixation by cyanobacteria and diazotrophic bacteria can only meet a fraction of the N requirement (Baldani, Baldani, and Döbereiner 2000; Hashem 2001; Trân Van et al. 2000). Fertilizer N applications are thus necessary to meet the crop's demands. Generally urea is the most convenient N source for rice. The efficiency of the urea-N in rice culture is very low, generally around 30–40%, in some cases even lower (Cao, De Datta, and Fillery 1984; Choudhury and Khanif 2001, 2004; Choudhury et al. 2002).

The low N-use efficiency is attributed mainly to ammonia volatilization, denitrification, leaching, and runoff losses (Cho 2003; Freney et al. 1990; Ponnampereuma 1972; Singh, Singh, and Sekhon 1995). However, the magnitude of N loss by different ways varies depending on environmental conditions and management practices. Volatilization and denitrification cause atmospheric pollution through the emission of gases like nitrous oxide, nitric oxide, and ammonia (Azam et al. 2002; Reeves et al. 2002). Nitrous oxide absorbs infrared radiation contributing to the greenhouse warming and the depletion of the stratospheric ozone layer (Bohloul et al. 1992). Nitric oxide contributes to the formation of tropospheric ozone, a major atmospheric pollutant that affects human health, agricultural crops, and natural ecosystems (Chameides et al. 1994). Nitric oxide is also a precursor to nitric acid, a principal component of acid deposition (Kennedy 1992). The deposition of nitric oxide and ammonia in terrestrial and aquatic ecosystems can lead to acidification, eutrophication, shifts in species diversity, and effects on predators and parasite systems (Reeves et al. 2002; Vitousek et al. 1997). Leaching of nitrate causes groundwater toxicity (Shrestha and Ladha 1998). Excess amounts of nitrate in drinking water and food may cause methemoglobinemia in infants, respiratory illness, and decreased content of vitamin A in the liver (Bohloul et al. 1992; Phupaibul et al., 2002). This paper discusses these environmental problems and possible ways to minimize these problems.

**Table 1.** Nitrogen uptake by four rice varieties

Rice variety	Yield (t ha <sup>-1</sup> )		N uptake (kg ha <sup>-1</sup> )			N uptake (kg) for the production of one ton of rough rice		
	Grain	Straw	Grain	Straw	Total	Grain	Straw	Total
Niger Sail	3.3	6.5	30	26	56	10	7	17
BR22	4.3	6.8	43	31	74	10	7	17
Pajam	4.8	7.1	53	22	75	11	5	16
BR25	5.1	6.8	57	28	85	11	5	16

Source: Choudhury et al. (1997).

## AMMONIA VOLATILIZATION

About 85% of the world's rice-cropped area is under wetland culture. In the wetland rice soils, rice plants take N mainly as ammonium ( $\text{NH}_4^+$ ), requiring less energy to assimilate into amino acids than nitrate (Kennedy 1992). Ammonia volatilization losses occur in flooded rice soils in moderately to slightly acid soils, although losses are higher in alkaline soils (De Datta 1978). Utilization of carbon dioxide by algae and other aquatic biota for their photosynthetic activities increases the floodwater pH, which leads to substantial losses of N by ammonia volatilization (Broadbent 1978). Ammonium fertilizers dissociate directly to  $\text{NH}_4^+$ , while urea may decompose by catalytic hydrolysis to produce  $\text{NH}_4^+$  ions (De Datta 1981). Ammonium ions are loosely bound to the water molecules, and convert to nonionized ammonia ( $\text{NH}_3$ ), which may escape from the water as gas. Ammonia volatilization losses in the flooded soils range from negligible to almost 60% of the applied N (De Datta 1985; Xing and Zhu 2000). Factors affecting ammonia volatilization are pH and temperature of the floodwater, algal and aquatic weed growth, crop growth, and soil properties (De Datta 1987).

## POLLUTION PROBLEMS DUE TO AMMONIA VOLATILIZATION

Ammonia emitted from agricultural systems may be transported and deposited in gaseous or dissolved forms to downwind terrestrial and aquatic ecosystems causing eutrophication (Matson et al. 1997). Eutrophication (overenrichment in nutrients) brings many undesirable changes, including proliferation of algae and aquatic macrophytes, depletion of the dissolved oxygen in the bottom water, and a decrease in water clarity (Keeney 1982).

## WAYS OF REDUCING AMMONIA VOLATILIZATION

There are several ways to reduce ammonia volatilization in the soil-water system. These include application of soluble salts of calcium, potassium, and magnesium; use of urease and algal inhibitors; deep placement of nitrogen fertilizers; and use of modified forms of urea and slow-release fertilizers.

### Soluble Salts of Calcium, Potassium, and Magnesium

Ammonia ( $\text{NH}_3$ ) volatilization can be reduced by coapplication of calcium ( $\text{Ca}^{++}$ ), magnesium ( $\text{Mg}^{++}$ ), or potassium ( $\text{K}^+$ ) salts (chloride or nitrate) with urea (Fenn and Kissel 1973; Khanif and Wong 1987; Rappaport and

Axley 1984). When urea is applied to soil, it is converted to ammonium carbonate, which is susceptible to  $\text{NH}_3$  volatilization loss. If nitrate or chloride salt of calcium or magnesium is applied with urea, it reduces volatilization by forming ammonium chloride or nitrate (Fenn, Taylor, and Matocha, 1981).

Potassium ( $\text{K}^+$ ) reduces  $\text{NH}_3$  volatilization loss indirectly by increasing calcium carbonate precipitation by replacing  $\text{Ca}^{++}$  from the exchange complex in high  $\text{Ca}^{++}$  soil. Precipitation or loss of exchangeable calcium enhances ammonium occupancy on the exchange complex, resulting in a reduction in  $\text{NH}_3$  volatilization losses (Fenn, Matocha, and Wu 1982). This study showed that either potassium nitrate ( $\text{KNO}_3$ ) or potassium chloride (KCl) could be used to reduce  $\text{NH}_3$  volatilization losses. Investigations showed that addition of KCl with urea reduced ammonia volatilization loss significantly and consequently increased N use efficiency significantly (Khanif and Wong 1987). Experimental results at the University of Maryland, United States, indicated that either addition of KCl with urea or KCl-coated urea reduced  $\text{NH}_3$  volatilization significantly over urea alone (Gameh, Angle, and Axley 1990). Studies conducted at University Putra Malaysia with the  $^{15}\text{N}$  labeled urea showed that fertilizer N recovery increased considerably due to addition of KCl (Khanif and Pancras 1992).

Laboratory and greenhouse experimental results indicated that addition of Mg salts effectively reduced  $\text{NH}_3$  volatilization loss from the surface applied urea and thus increased N recovery (Fenn et al. 1981a, 1981b; Foster and Zakaria 1986). Experimental results showed that ammonia loss from urea decreased with increasing cation/N ratio when Mg, Ca, or K was applied with urea (Khanif and Wong 1987). In that study, ammonia losses by volatilization were 28.9% to 35.8% with cation/N ratio of 0.25 and decreased less than one-third to 8.4% to 13.1% with cation/N ratio of 2.00.

### **Urease and Algal Inhibitors**

When urea is applied to the soil, it is converted to ammonium carbonate after hydrolysis by the urease enzyme. This conversion leads to the availability of high concentrations of ammonium ions in the floodwater, which are lost through ammonia volatilization when the pH of the floodwater rises due to the photosynthetic activity of algae. Application of urease inhibitors limits urease activity at the soil surface and allows urea to move into the deeper soil layer before hydrolysis. Ammonium released then remains in the cation exchange complex in the soil (Freney et al. 1995). In some laboratory and greenhouse experiments, the urease inhibitors phenylphosphorodiamidate (PPD) and N-(n-butyl)thiophosphoric triamide (NBPT) performed successfully in reducing ammonia volatilization loss (Byrnes et al. 1983; Cai et al. 1989). Laboratory and field experimental results demonstrated that application of urease inhibitors like hydroquinone and phenylendiamine

increases agronomic efficiency of urea-N due to reduced ammonia volatilization loss in flooded rice soils (Abdel-Bary and Metwally 2001). Algal inhibitors can retard the growth of algae, which contribute to the rise of soil pH, and thus can reduce the ammonia volatilization loss. Freney et al. (1995) found that application of an algal inhibitor (copper sulfate + terbutryn) decreased ammonia volatilization loss resulting an increase in rice yield by 0.3–0.6 t ha<sup>-1</sup>.

Rawluk, Grant, and Racz (2001) reported that ammonia volatilization loss was decreased by 28–88% due to NBPT application with granular urea. Phongpan and Byrnes (1990) also reported similar results. Experimental results at the International Rice Research Institute (IRRI) reveal that addition of the urease inhibitor PPD along with urea reduced the ammonia loss by 12–22 kg N ha<sup>-1</sup> (De Datta 1985). The beneficial effects of other urease inhibitors (thiourea, hydroquinone, 2–4 dinitro phenol, and boric acid) were also reported (Bayrakli 1990).

### **Deep Placement of Nitrogen Fertilizers and Use of Modified Forms of Urea**

Deep placement of N fertilizers into the anaerobic soil zone is an effective method to reduce volatilization loss (Mikkelsen, De Datta, and Obcemea 1978). Field experimental results using the <sup>15</sup>N as tracer at IRRI demonstrated that N use efficiency was higher when fertilizer was placed at 10-cm soil depth (De Datta 1981). Urea can be placed deep into the reduced soil layer at 8–10-cm soil depth by an instrument called “pneumatic urea injector” developed in the Netherlands. Field experimental results conducted at Bangladesh Rice Research Institute (BRRI) showed the superiority of this method of urea application over the conventional split broadcast method (Choudhury and Bhuiyan 1994). In this study, apparent recovery of applied N increased considerably due to deep placement of urea (Table 2). Another instrument called “liquid urea injector” is used to inject dissolved urea into the upper soil layer at 5–6 cm soil depth as band placement between alternate rice rows (Schnier et al. 1988, 1993). This method of N application was found effective in reducing ammonia volatilization loss resulting in increase in grain yield and fertilizer N recovery of the <sup>15</sup>N labeled urea in several field experiments (Schnier 1995; Schnier et al. 1990).

Different sources and forms of N fertilizer are now available in the market for commercial use. The most commonly used N fertilizer for rice crop is prilled urea (PU). Mean diameter of PU is 1.5 mm. Urea super granule (USG) is a modified form of urea having an average diameter of 11.5 mm. It has been developed at the International Fertilizer Development Centre, United States. The superiority of USG over PU in rice culture has been found in many investigations (Craswell et al. 1985; Kannaiyan 2002; Roy 1988). Field studies using <sup>15</sup>N-labeled urea at IRRI showed that fertilizer N

**Table 2.** Effects of rates and methods of nitrogen fertilizer application on grain yield of BR3 rice, total N uptake, agronomic efficiency, and apparent recovery of added N

N rate (kg ha <sup>-1</sup> )	Method of application <sup>1</sup>	Grain yield (t ha <sup>-1</sup> )	Total N uptake (kg ha <sup>-1</sup> )	Agronomic efficiency (kg grain per kg added N)	Apparent recovery of added N (%)
0	—	2.7	35.9	—	—
29	SB	3.3	44.3	20.7	29
58	SB	3.6	49.8	15.5	24
87	SB	4.0	55.9	14.9	23
29	I	3.7	51.4	34.5	53
58	I	4.0	59.2	22.4	40
87	I	4.6	69.9	21.8	39
LSD (0.05)		0.42	3.3	—	—

<sup>1</sup>SB = Surface Broadcasting, I = Injection.

Source: Choudhury and Bhuiyan (1994).

recovery with USG point placement was 65–96% while it was only 32–55% with the conventional PU broadcasting due to lower amount of ammonia volatilization loss (Cao et al. 1984; Schnier et al. 1990). Urea large granule (ULG), another modified form of urea having an average diameter of 7 mm, has been developed in the Netherlands. This modified form of urea, because of its larger granule size, may go deeply into the mud simply by force throwing, and thus may be expected to be more efficiently used than PU. Azollon, a slow-release nitrogen fertilizer, has been developed in Germany. It is a urea-formaldehyde condensation product containing 38% N. The relative performances of PU, ULG, USG, and Azollon in wetland rice culture were evaluated in a field experiment at BRRI (Choudhury et al. 1994). Considering grain yield, USG was significantly superior to PU and azollon, whereas ULG had a slight edge over PU but was not statistically different (Table 3). Total N uptake increased significantly in ULG- and USG-treated plots compared to the conventional PU-treated plots. Agronomic efficiency and apparent recovery of added N were considerably higher with USG and ULG compared to PU (Choudhury et al. 1994).

### Use of Slow-Release Fertilizers

Ammonia volatilization loss can be reduced considerably by using slow-release fertilizers like sulfur-coated urea (SCU), neem-cake blended urea (NBU), and lac-coated urea (LCU). Earlier literature indicates that SCU reduces ammonia volatilization loss considerably, resulting in higher fertilizer N efficiency (De Datta, 1985; Keeney 1982). Several other investigations

**Table 3.** Effects of forms and sources of nitrogen fertilizer on grain yield of BR3 rice, total N uptake, agronomic efficiency, and apparent recovery of added N

N rate (kg ha <sup>-1</sup> )	N fertilizer form/source	Grain yield (t ha <sup>-1</sup> )	Total N uptake (kg ha <sup>-1</sup> )	Agronomic efficiency (kg grain per kg added N)	Apparent recovery of added N (%)
0	—	2.9 d	36.7 e	—	—
87	Prilled urea	4.0 b	62.6 c	12.6	29.8
87	Urea large granule	4.4 ab	70.3 b	17.2	38.6
87	Urea super granule	4.6 a	91.0 a	19.5	62.4
87	Azollon	3.6 c	53.0 d	8.1	18.7

Values followed by different letters within a column are significantly different at 5% level by Duncan's Multiple Range Test.

Source: Choudhury et al. (1994).

proved the superiority of SCU over PU for increasing N use efficiency (De Datta 1981; Reddy and Mittra 1985; Roy 1988). Prilled urea (PU) can be blended with neem-cake to make it slow release for increasing N use efficiency (Sharma and Prasad 1980). Several investigations revealed the superiority of NBU over PU in increasing grain yield of rice (Kannaiyan 2002; Sharma and Prasad 1990). Similarly, PU is coated with lac to make it slow release. Investigations showed the superiority of LCU over PU in increasing grain yield of rice (Patil et al. 1987; Roy 1988).

## DENITRIFICATION

Denitrification occurs in the flooded rice soils following the nitrification of ammonium into nitrate (NO<sub>3</sub><sup>-</sup>). Nitrification occurs at a distance of 0–2 mm from root surface while denitrification occurs at a distance of 1.5–5.0 mm (Arth and Frenzel 2000). In this process, NO<sub>3</sub><sup>-</sup> is reduced by a series of steps to nitric oxide (NO), nitrous oxide (N<sub>2</sub>O), and nitrogen (N<sub>2</sub>) gases, which are then released into the atmosphere (Reddy and Patrick 1986). In wetland rice soils, denitrification primarily occurs in the reduced soil layer devoid of oxygen (O<sub>2</sub>). In the absence of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> is used as an electron acceptor by the facultative anaerobes during the oxidation of soil organic matter and other organic materials (Kennedy 1992). The magnitude of denitrification loss, as estimated by the <sup>15</sup>N tracer technique at IRRI, may vary from negligible to 46% of the applied N depending on urea application and crop establishment methods (Buresh and De Datta 1990). Fillery and Vlek (1982) reported that denitrification losses of fertilizer N were 5–10% in

continuously flooded rice-cropped soils, while in the fallow soil the loss was around 40% of the applied N.  $^{15}\text{N}$  studies indicate that denitrification rate is higher in underground saturated soils under rice cultivation compared to soils under wheat cultivation (Xing et al. 2002).

## **POLLUTION PROBLEMS DUE TO DENITRIFICATION**

Nitric and nitrous oxides are emitted through the denitrification process. Nitric oxide contributes to the formation of tropospheric ozone, a major atmospheric pollutant that affects human health, agricultural crops, and natural ecosystems (Chameides et al. 1994; Matson et al. 1997, 1998). Nitric oxide is also a precursor to nitric acid, a principal component of acid deposition (Kennedy 1992). Nitrous oxide absorbs infrared radiation contributing to the greenhouse warming and the depletion of the stratospheric ozone layer (Bohlool et al. 1992). Nitrous oxide, because of its absorption spectrum and long half-life in the atmosphere, is considered to have 300 times the global warming impact of carbon dioxide (Baggs et al. 2002; Xing 1998).

## **WAYS OF REDUCING DENITRIFICATION LOSSES**

The reduction of ammonia volatilization loss by different means as discussed in the previous section may not be effective in reducing nitrogen losses. The ammonium ion retained in the soil-water system is readily converted to nitrite, then to nitrate through the nitrification process. The nitrate ion is subject to losses through denitrification and leaching. Denitrification follows the nitrification process. So if the nitrification of ammonium into nitrate is delayed or reduced, denitrification loss will be reduced. As a result, denitrification losses can be reduced by using nitrification inhibitors like dicyandiamide (DCD), iron pyrite, nitrapyrin, phenylacetylene, encapsulated calcium carbide, terrazole, etc. (Blaise, Amberger, and Tucher 1997; Carrasco et al. 2004; De Datta 1981; Freney et al. 1995). Field experimental results conducted by CSIRO (Commonwealth Scientific & Industrial Research Organization) using  $^{15}\text{N}$  as the tracer at Griffith showed that use of encapsulated calcium carbide reduced denitrification significantly (Keerthisinghe et al. 1996). Denitrification losses can also be decreased by deep placement of urea fertilizer (Ding et al. 2002; Fillery and Vlek 1982). Slow-release fertilizers like sulfur-coated urea can reduce denitrification losses considerably (Keeney 1982; Keeney and Sahrawat 1986). Nitrous oxide emitted from the agricultural soils due to denitrification loss is one of the major three greenhouse gases (methane, carbon dioxide, and nitrous oxide). Application of plant residues having high polyphenol content and high protein binding capacity may reduce nitrous oxide emissions (Baggs et al. 2002).

## LEACHING

Both ammonium and nitrate forms of nitrogen are lost through leaching. However, nitrate form is lost easily due to its negative charge while the positively charged ammonium form is usually adsorbed to the negatively charged soil clay lattice. Marko et al. (2002) reported that more than 98% of the leached N was in the form of  $\text{NO}_3\text{-N}$  in soybean cultivation. The leached nitrate joins the groundwater through percolation of water through the soil column under gravity. The magnitude of fertilizer-N leaching varies depending on soil condition and the method of fertilizer application (Velu and Ramanathan, 2001; Vlek, Byrnes, and Craswell 1980; Xing and Zhu 2000).

## POLLUTION PROBLEMS DUE TO NITRATE LEACHING

The leached nitrate accumulates in the groundwater. When the groundwater is used for drinking, it causes human health problems, particularly if nitrate is reduced to nitrite. Again, when this groundwater is used for irrigating crops, the accumulated nitrate can be returned to the food chain through plant uptake. Excess nitrate consumption through food is also hazardous. Drinking water containing more than  $10 \text{ mg L}^{-1}$  of  $\text{NO}_3\text{-N}$  is considered unsafe for human consumption (Shrestha and Ladha 1998). Nitrate and nitrite also participate in the formation of nitrogenous carcinogenic compounds (nitrosamines), which may lead to human gastric cancer (Phupaibul et al. 2002).

## WAYS OF REDUCING LEACHING LOSSES

Nitrate leaching can be reduced by increasing water use efficiency of the rice crops. Nitrate is leached into the ground through percolating water. By increasing the efficiency of water use, it may be possible to reduce the leaching loss of nitrate (Keeney 1982). Use of slow-release fertilizers and nitrification inhibitors and puddling of the rice fields are also ways of reducing leaching losses (Keeney and Sahrawat 1986; Rao and Prasad 1980). Catch crops like maize and indigo can be grown in a rice-cropping pattern to reduce leaching losses. These deep-rooted crops can be grown in the transition period of two rice crops. Due to the deep root systems, these crops can uptake nitrate from the deep soil layer and thus prevent leaching of nitrate into the groundwater. Field experimental results conducted at IRRI showed that these catch crops are effective in reducing leaching losses in the groundwater (Shrestha and Ladha 1998). Cover crops can be grown in rice-cropping patterns to scavenge soil residual N for decreasing leaching losses of N. Field experimental results in Japan indicated that cover crops

like rye and crimson can prevent N leaching losses (Komatsuzaki and Gu 2002). Use of crop residues in situ in the field after harvesting crops can add a substantial amount of organic carbon into the soil, which immobilizes the residual  $\text{NO}_3\text{-N}$  from fertilizer applications, and thus minimizes nitrate leaching (Keeney 1982).

## USE OF PLANT-GROWTH PROMOTING MICROORGANISMS IN REDUCING NITROGEN LOSSES

Nitrogen fertilizer losses through different mechanisms can be minimized by reducing the amount of applied fertilizer N with an efficient use of N by the rice plant. Plant growth promoting microorganisms like *Rhizobium* and *Azospirillum* can reduce the use of urea-N by growth promotion through the production of auxins, cytokinins, gibberellins, and ethylene (Dobbelaere, Vanderleyden and Okon 2003). The use of plant-growth promoting microorganisms can increase plants' capacity to utilize fertilizer N efficiently. Hence, use of these organisms can reduce N losses (Choudhury and Kennedy 2004; Kennedy, Choudhury, and Kecskés 2004). *Azospirillum* inoculation can increase ammonium uptake by rice plants (Murty and Ladha 1988). *Rhizobium* can also increase N uptake by rice plants (Biswas et al. 2000a, 2000b). The increased N uptake by rice plant will result in the reduction of N losses by different ways. So if plant-growth promoting microorganisms like *Rhizobium* and *Azospirillum* are used in rice cultivation, obviously there will be a reduction in the environmental pollution problems due to N losses.

## CONCLUSIONS

Nitrogen fertilizer losses through ammonia volatilization, denitrification, and leaching may cause environmental pollution and health problems. Although these problems cannot be alleviated completely, there are enough research findings that indicate that these problems can be minimized by certain management practices. Ammonia volatilization losses can be reduced by (1) applying soluble chloride or nitrate salts of calcium, magnesium, and potassium; (2) using urease and algal inhibitors; (3) deep placement of N fertilizers and use of modified forms of urea; and (4) use of slow-release fertilizers.

Denitrification losses can be reduced by (1) use of nitrification inhibitors, (2) deep placement of N fertilizers, (3) use of slow-release fertilizers, and (4) application of plant residues having high polyphenol content and high protein binding capacity.

Leaching losses can be reduced by (1) increasing water-use efficiency, (2) using slow-release fertilizers and nitrification inhibitors, (3) puddling the

rice fields, (4) planting catch and cover crops, and (5) using crop residues in situ.

The use of plant-growth promoting microorganisms in rice culture can reduce the need of N fertilizer by efficient N use by the rice crop and can thus reduce the environmental pollutions due to N losses.

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