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# Nitrogen transformation processes in relation to improved cultural practices for lowland rice

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Key words Ammonia volatilization Denitrification Nitrogen Rice

Summary Inappropriate method and timing of N fertilizer application was found to result in 50-60% N losses. Recent nitrogen transformation studies indicate that NH<sub>3</sub> volatilization in lowland rice soils is an important loss mechanism, causing a 5–47% loss of applied fertilizer under field conditions. Estimated denitrification losses were between 28 and 33%. Ammonia volatilization losses from lowland rice can be controlled by i) placement of fertilizer in the reduced layer and proper timing of application, ii) using phenylphosphorodiamidate (PPD) to delay urease activity in flooded soils, and iii) using algicides to help stabilize changes in floodwater pH.

Appropriate fertilizer placement and timing is probably the most effective technique in controlling denitrification at the farm level. The effectivity of nitrification inhibitors as another method is still being evaluated.

With 60–80% of N absorbed by the crop derived from the native N pool, substantial yield gains in lowland rice are highly possible with resources already in the land. Extensive studies on soil N and its management, and an understanding of soil N dynamics will greatly facilitate the decrease in immobilization and ammonium fixation in the soil and the increase in N availability to the rice crop. Critical research needs include greater emphasis on N transformation processes in rainfed lowland rice which is grown under more harsh and variable environmental regimes than irrigated lowland rice.

#### Introduction

The number of people to be fed in 1990 is likely to be about 25% higher than in 1980, even with the expected slow down of population growth in most of Asia. By the year 2000, it will be about 50% higher<sup>1</sup>. Modern rice varieties, increased area under irrigation and greater fertilizer use have dramatically increased rice production in the region. Traditional rice importing countries are faced with surplus and storage problems while rice exporting countries are looking for markets for their surpluses.

Past experience suggests that the use of nitrogenous fertilizers can substantially increase rice yields. Returns to producers, however, depend very much on the mode of fertilizer application. Unless high losses and low N fertilizer use efficiency are corrected, most of the potential benefits of increased N fertilizer use may not be realized.

Research results showed that N losses ranged from 50 to 60% when applied with inappropriate method and timing<sup>17</sup>. These include N lost to

the atmosphere via ammonia volatilization, through nitrification and denitrification, retained in the soil as a result of immobilization and ammonium fixation, and leached.

Nitrogen transformation processes in lowland rice soils were reviewed by Savant and De Datta<sup>46</sup> and Keeney and Sahrawat<sup>32</sup>. An understanding of these processes will greatly help minimize N losses from lowland rice soils to increase N availability to rice.

This paper deals with current information from basic and applied studies on increased N fertilizer efficiency in lowland rice soils.

# Nitrogen transformation processes

Even a slight improvement in N fertilizer efficiency will save energy costs and foreign exchange in N fertilizer-importing countries. Hence, the increased interest in N transformation processes in lowland rice in recent years.

The behavior of nitrogen in lowland soil markedly differs from that in upland soil. Flooding the soil results in ammonium accumulation, ni-



Fig. 1. Nitrogen transformations in submerged rice soils.<sup>13,46</sup>

trate instability, and low N requirement for organic matter decomposition. Ammoniacal nitrogen is subject to fixation by clay and loss by volatilization, nitrification and denitrification, leaching, runoff, and seepage. Significant inorganic N is assimilated into the organic fraction of lowland rice soil although its magnitude is lower than in an upland soil. Various fractions in the inorganic N pool of a lowland rice soil constitute an extremely dynamic N system in the soil, which is affected by physical, chemical, and microbiological reactions. These reactions are summarized by Savant and De Datta<sup>46</sup> in a schematic form (Fig. 1).

#### Ammonium dynamics

In lowland rice, 60–80% of N absorbed by the crop is derived from the native nitrogen pool<sup>5</sup>. Recent results suggest that approximately 60% of the rice yields, ranging between 2 and 4 t/ha, are produced without N fertilizer. With increased study on soil N and its management, substantial yield gains are possible with resources already on land<sup>2</sup>.

Ammonium nitrogen, the dominant form of mineral N in lowland soils, exists in three major fractions:

- Ammonium in soil solution
- Ammonium in exchange sites
- Ammonium in nonexchangeable forms

In a recent investigation, a highly significant correlation was recorded between the exchangeable soil NH<sub>4</sub><sup>+</sup> measured before the experiment was conducted and N uptake of rice<sup>49</sup>. Soil solution NH<sub>4</sub><sup>+</sup> tends to equilibrate with the exchangeable soil NH<sub>4</sub><sup>+</sup>, considered as the most important fraction for rice nutrition. Results of Schön *et al.*<sup>49</sup> fully supported the view that the initial exchangeable soil NH<sub>4</sub><sup>+</sup> behaved liked fertilizer N as shown in the linear relationship between N uptake by the crop and initial exchangeable NH<sub>4</sub><sup>+</sup> + fertilizer N. The coefficient of determination  $R^2 = 0.91$  suggests that other processes, such as ammonification, N<sub>2</sub> fixation, and denitrification during the growing season have only minor influence on N uptake in soils with different pH, organic N, and organic C.

In lowland rice, the nonexchangeable  $NH_4^+$  fraction plays an important role in N nutrition<sup>34</sup>. Subsequent studies by Keerthisinghe *et al.*<sup>34</sup> showed that exchangeable  $NH_4^+$  decreases to a very low level during the crop growing season. In most cases, this coincides with the highest rate of N uptake by the crop (Fig. 2). Some of the exchangeable  $NH_4^+$ , however, may be immobilized by soil microorganisms or lost through volatilization<sup>46</sup>.

Keerthisinghe *et al.*<sup>34</sup> reported that in some soils net release of exchangeable and nonexchangeable  $NH_4^+$  was higher than 50% of the total



Fig. 2. Effect of nitrogen fertilizer application on exchangeable  $NH_4^+$  in soil and nitrogen uptake by IR36 rice in Maligaya silty clay loam, 1981 dry season<sup>33</sup>. At the same N rate, means with common letters are not significantly different at the 5% level. DBT = days before transplanting, TPL = at transplanting, DT = days after transplanting. Reproduced from G. Keerthisinghe, S.K. de Datta and K. Mengel, Importance of exchangeable soil ammonium in nitrogen nutrition of lowland rice, *Soil Science*, Vol. 140, No. 3, pp. 194–201, by Williams and Williams Company, 1985.

N uptake of crop. It was concluded that the exchangeable  $NH_4^+$  and, in some soils, the nonexchangeable  $NH_4^+$  are the most important soil N fractions easily available to lowland rice at early to mid-crop stages. Moreover, organic soil N may contribute substantially to N supply at the spikelet-filling stage. In soils rich in vermiculite the nonexchangeable  $NH_4^+$  should also be considered for fertilizer N recommendation in lowland rice<sup>37</sup>.

# **Biological nitrogen fixation**

From extensive data, Watanabe *et al.*<sup>57</sup> found that a rice crop used an average of 40–50 kg N/ha from the soil pool, when no N fertilizer was applied. In most instances, soil N did not decrease, indicating that used N was compensated for by mechanisms among which biological nitrogen fixation (BNF) is most important. In a review by Lowendorf<sup>36</sup>, the ranges of fixed nitrogen per crop are: legumes, 25–61; blue–green algae (BGA), 0.2–39; azolla green manure, 25–121; azolla grown with rice, 2–7.5; and soil and rhizosphere fixers, 1.2–18.3 kg N/ha. Roger and

Watanabe<sup>42</sup> reported that only  $N_2$  fixing legume and azolla green manures are currently used. Straw incorporation, which enhances heterotropic  $N_2$  fixers, is not widely practiced in farmer's fields. BGA inoculation techniques have been developed and their use advocated, but adoption by farmers is still limited.

Green manures have been used in lowland rice in India and China for a long time. Some of the *Sesbania* and *Crotolaria* spp. are known to be high N producers. A considerable interest in *Sesbania rostrata*, a green manure crop from Senegal, has been aroused. It forms  $N_2$  fixing nodules on the roots and the stems, and has 5–10 times more nodules than most legumes. Because of its stem nodules, *S. rostrata* can fix N even under waterlogged conditions<sup>22</sup>.

### Mineralization-immobilization

Mineralization of organic N to  $NH_4^+$  is the key process in the N nutrition of lowland rice<sup>46</sup>. The important environmental factors affecting mineralization–immobilization are temperature, soil moisture regime, and soil drying; important soil characteristics include pH, organic matter, C/N ratio, and amount and quality of organic residues<sup>32</sup>.

Broadbent and Tusneem<sup>6</sup> reported that soil N mineralization was higher in the soil planted to rice than that unplanted, because the presence of active rice roots decreased N loss due to nitrification---denitrification.

Immobilization is important since it affects N availability and supply to rice. The ammonification-immobilization process assumes practical significance in the N nutrition of rice because rice plants heavily depend on soil N for their N requirement. However, information is lacking on ammonification-immobilization processes in actual lowland rice fields.

#### Nitrification

Nitrification or the biological oxidation of  $NH_4^+$  to  $NO_3^-$  in lowland soil is common but undesirable because it leads to N loss. Nitrification, strictly an aerobic process, occurs in the floodwater and in the thin, oxidized, surface soil layer. Studying nitrification *in situ* in a flooded soil system is difficult because as soon as  $NO_3^-$  is formed, it diffuses down to the reduced layer and is lost from the system by dentrification, or reduced to  $NH_4^+$  by dissimilatory  $NO_3^-$  reduction<sup>46</sup>. Nevertheless, nitrification is recognized as a mechanism of N loss via nitrification–denitrification in lowland soils. Nitrate has been established as an inefficient N source in lowland rice culture.

Occurrence of nitrification in the rhizosphere of a rice plant, which Savant and De Datta<sup>46</sup> referred to as Site II, is a subject of speculation since no data are available on *in situ* nitrification.

# Urea hydrolysis

Very few studies have emphasized urea hydrolysis in lowland rice soils. Sahrawat<sup>43</sup> found that the urease activity in 10 Philippine lowland rice soils was highly correlated with total N and organic C, but was not significantly correlated with other soil properties. Vlek *et al.*<sup>54</sup> studied urea hydrolysis in three flooded soils and reported that urea hydrolysis occurred at the floodwater-soil interface. Urease activity in the flooded soils was dynamic and was affected by the length of presubmergence period. The use of fertilizer additives to control urea hydrolysis in lowland rice soils is recently receiving increased attention. Delaying urea hydrolysis has been sought to minimize ammonia volatilization loss in lowland rice soils.

# Leaching

Nitrate produced in the oxidized surface layer of a flooded soil moves easily by diffusion and percolation into the underlying reduced layer, where it is rapidly denitrified.

Ammonium nitrogen is less subject to leaching than nitrate because of its adsorption on the cation exchange complex. Losses by leaching occur mainly in coarse-textured soils with low cation exchange capacity. Krishnappa and Shinde<sup>35</sup> found that when urea was incorporated into a flooded lowland soil under tropical field conditions, about 8% of N applied was lost through leaching.

# Surface runoff

Information is limited on the quantity of nutrient losses by runoff from lowland rice fields. Under certain situations, N losses through runoff were from 13 to  $16\%^{13}$ .

# **Denitrification**

Special soil and environmental conditions in a flooded rice field support the redox N processes, *i.e.*, nitrification (oxidation of  $NH_4^+$  to  $NO_3^-$ ) and denitrification (reduction of  $NO_3^-$  to  $N_2$ ). Potentially, these reactions occur in continuously flooded lowland and upland rice fields, the latter being subjected to alternate flooding and draining cycles.

Nitrification (k =  $3.18 \,\mu g \,$  N/cm<sup>3</sup> per day where K = kinetic constant) takes place in the surface aerobic layer. This results in a concentration gradient of NH<sub>4</sub><sup>+</sup> -N across the aerobic layer and anaerobic layer and causes the NH<sub>4</sub><sup>+</sup> present in the anaerobic layer to diffuse ( $\bar{D} = 0.216 \,$  cm<sup>2</sup>/day) into the aerobic layer where it is nitrified. The NO<sub>3</sub><sup>-</sup> -N formed diffuses back into the anaerobic layer ( $\bar{D} = 1.33 \,$  cm<sup>2</sup>/day) where it is easily denitrified (k = 15.0 mg N/cm<sup>3</sup> per day). Many factors governing denitrification were described earlier<sup>13</sup>.

In a lowland rice soil Savant and De Datta<sup>44,45</sup> and Savant *et al.*<sup>47</sup> studied the movement of N fertilizers, (prilled urea [PU], urea supergranules [USG], sulfur-coated urea [SCU], and urea placed in mudballs) placed in the root-zone (10 cm deep). The studies indicated that  $NH_4^+$  movement was downward > lateral > upward. However, when urea was surface applied, Savant and De Datta<sup>45</sup> measured a significant amount of  $NH_4^+$  at the 12–14 cm depth, 4 weeks after application. Thus, downward movement of plant available N can result in a significant loss from coarse-textured soils. Vlek *et al.*<sup>54</sup> measured significant loss in N fertilizer after USG placement in lowland soils with a percolation rate of 5 cm/day.

In soils with high organic matter content, the oxidized layer is thin. Under these conditions  $NH_4^+$  tends to diffuse into the floodwater. Nitrification is indicated by the significant concentration of  $NO_3^-$  formed in the floodwater of an organic soil<sup>41</sup>.

Under  $O_2$ -free conditions, many microorganisms utilize  $NO_3^-$  as a terminal electron acceptor. This process is called  $NO_3^-$  respiration or dissimilatory  $NO_3^-$  reduction. The pathway involving the  $NO_3^-$  reduction to gaseous end products ( $NO_3^- \rightarrow NO_2 \rightarrow HNO \rightarrow NO \rightarrow N_2O \rightarrow N_2$ ) is known as denitrification. Denitrification is a dominant process in soils with Eh values of 200–300 mV, while  $NO_3^-$  reduction to  $NH_4^+$  occurs in soils with Eh values of  $< -100 \text{ mV}^7$ .

Nitrogen loss due to denitrification was also found significant in soils planted to rice. However, the magnitude of N loss was lower compared to that for systems without plants<sup>40</sup>. Smith and De Laune<sup>52</sup> measured significantly greater  $N_2O + N_2$  production in the first 2 days after fertilizer application to lowland soil planted to rice as compared to non-planted lowland soil. The controlling factor of N loss from the rhizo-sphere is the competition for NO<sub>3</sub> uptake between denitrifying bacteria and rice roots.

Measurement of denitrification Several methods have been developed to measure denitrification losses from flooded soils. The most frequently used technique is to develop an <sup>15</sup>N balance then attribute the lost <sup>15</sup>N fraction to denitrification<sup>29</sup>. The gaseous products of denitrification, which include N<sub>2</sub>, N<sub>2</sub>O, and possibly NO, must directly be measured to distinguish denitrification from other losses. The elemental nitrogen gas produced from denitrification is difficult to measure against a background of 78% N in the atmosphere. However, nitrous oxide, the other product of denitrification, is normally only 300 parts/billion in the atmosphere and, therefore, losses as nitrous oxide can be measured easily. Figure 3 shows some measurements of nitrous oxide flux at the



Fig. 3. Effect of time and mode of N fertilizer application on  $N_2O$  flux. IRRI, 1979 dry season (adapted from Craswell and De Datta<sup>11</sup>) DT = days after transplanting, DBPI = days before panicle initiation.

IRRI farm. These measurements, the first in the tropics, prove that denitrification occurs in lowland rice fields<sup>11</sup>. The nitrous oxide fluxes are short-lived and occur soon after fertilizer application. Nitrous oxide seems to be only a minor product of nitrification–denitrification.

Freney et  $al.^{27}$  and Smith et  $al.^{51}$  attempted to measure N<sub>2</sub>O emission under field conditions to provide direct evidence for nitrification and denitrification. Nitrous oxide emissions amounted to less than 0.1% of the applied ammonium sulfate or urea.

Because of great demands for electron acceptors in the reduced zones of lowland soils,  $N_2O$  produced during denitrification is rapidly converted to  $N_2$  during microbial respiration. Since  $N_2O$  is only the minor and product of this process, the low evolution rate does not represent the total loss due to denitrification<sup>40</sup>.

Recently, Craswell *et al.*<sup>10</sup> developed a new method for measuring the <sup>15</sup>N content of mixture of N<sub>2</sub> and O<sub>2</sub> gases with a nonrandom N<sub>2</sub> isotopic distribution. The method involves a high voltage arc passed between a pair of tungsten electrodes sealed in a glass vessel to fix some of the N<sub>2</sub> as NO<sub>x</sub> species, thereby redistributing the N isotopes of the N<sub>2</sub> into an NO<sub>x</sub> pool. The NO<sub>x</sub> species are absorbed and oxidized by acidic permanganate, reduced to NH<sub>4</sub><sup>+</sup>, and distilled by routine procedures<sup>10</sup>.

This methodology was evaluated in a field study on flooded rice soil<sup>23</sup>. Only about 1% of the applied urea N was determined to be lost through denitrification.

# Ammonia volatilization

Nitrogen loss through ammonia volatilization from flooded soils was reported by various researchers and reviewed by Mikkelsen and De Datta<sup>38</sup> and Vlek and Craswell<sup>55</sup>.

Conditions in lowland rice field are conducive to ammonia volatilization loss. During the volatilization process, gaseous ammonia is formed:  $NH_4^+ \rightleftharpoons NH_3 + H^+$ . That is,  $H^+$  is released for each conversion of  $NH_4^+ \rightarrow NH_3$  (g). The pH and buffering capacity of oxidized, as well as reduced, soil layers, thus influence the process.

The overall inorganic ammonium nitrogen (equilibrium) system  $(N_t)$  in floodwater can be written as:

$$N_t = NH_3(aq) + NH_4^+$$

The concentration of  $NH_3(aq)$  changes in direct proportion with  $NH_4^+$ . It increases about tenfold per unit increase in pH of an aqueous system up to pH 9. Floodwater pH in lowland rice soils is markedly influenced by  $PCO_2$  and alkalinity, which in turn are determined by algal photosynthetic activity and respiration<sup>39</sup>. Wetselaar *et al.*<sup>58</sup> observed significant correlation in the relationship:

$$(pH) = \frac{(NH_3) \text{ volatilized}}{[NH_3(aq) + NH_4^+] \text{ floodwater}}$$

Other soil factors (pH, CEC, PCO<sub>2</sub>, buffering capacity, and alkalinity) and environmental factors (temperature, wind velocity, *etc.*) as well as the value and amount of N fertilizer applied and plant canopy size affect NH<sub>3</sub> volatilization loss in flooded soil<sup>46</sup>.

Summarized data of recent field studies on ammonia volatilization in lowland rice soils show a large variation (5–47%) in the amounts of ammonia volatilized (Table 1). The magnitude of losses are due to the different measurement techniques used by the researchers, the chemical nature of fertilizer, and the varying fertilizer application methods. Nevertheless, data from these recent field studies indicate that ammonia volatilization losses from lowland rice fields could be substantial. The advantages and disadvantages of these methods have been discussed by various workers but most recently by Vlek and Craswell<sup>55</sup>, Savant and De Datta<sup>46</sup>, and Fillery *et al.*<sup>25</sup>.

The aerodynamic and micrometeorological models suggest that the environmental parameters such as air temperature, wind speed (directly),

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Reference	Estimated ammonia lost % of N applied	Fertilizer material	Fertilizer rate (kg N/ha)	Method of measurement	Site
Mikkelsen <i>et al.</i> <sup>39</sup>	20	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> broadcast 10 DT	96	Chamber with enclosed acid trap and natural	IRRI farm, Phils. dry season
	ې	Urea broadcast	96	ventuation Chamber with enclosed acid trap and natural	IRRI farm, Phils. wet season
	۲	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> broadcast	06	Venturation Chamber with enclosed acid trap and natural	IRRI farm, Phils. wet season
Freney et al. <sup>27</sup>	5	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> broadcast and incorporated	80	venuauon Micrometeorological	IRRI farm, Phils. wet season
	11	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> topdressed at nanicle initiation	40	Micrometeorological	IRRI farm, Phils. wet season
Fillery <i>et al.</i> <sup>25</sup>	47 27	Urea, topdressed into the floodwater, 14 DT Urea, topdressed into	80 60	Micrometeorological Micrometeorological	Maligaya (Muñoz), Phils., dry season IRRI farm, Phils.
Simpson <i>et al.</i> <sup>50</sup>	=	the floodwater, 21 D1 Urea, broadcast evenly into the floodwater	80	Micrometeorological	dry season Griffith, N.S.W. Australia
Fillery and De Datta <sup>24</sup>	41-43	Urea or (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , topdressed into the floodwater. 10 DT	58	Micrometeorological	Maligaya (Muñoz), Phils., dry season
De Datta <i>et al.</i> <sup>18</sup>	27	Urea, broadcast into floodwater, 12DT	53	Simple micrometeorological	Calauan, Phils., dry season
	31	Urea, broadcast into floodwater, 12 DT	80	Simple micrometeorological	Calauan, Phils., dry season

Table 1. Field experiments measuring loss of N fertilizer via NH3 volatilization from lowland rice fields

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and solar radiation (indirectly) influence ammonia loss. Ammonia volatilization rate seems to follow the diurnal pattern of water temperature<sup>27</sup>. High wind speed or rapid air exchange at the water-air interface results in a marked decrease in  $\rho$ NH<sub>3</sub> in air, which is in immediate contact with the body of floodwater, and thus enhances ammonia volatilization<sup>3</sup>. Based on results of Bouwmeester and Vlek<sup>4</sup>, rice plant canopy, which modifies microclimate, will have a marked effect on ammonia volatilization from lowland rice fields. The two main effects of the rice plant canopy are (1) decreased transfer coefficient of NH<sub>3</sub> within the canopy due to restricted air movement and (2) reduced floodwater pH and temperature presumably due to shading<sup>46</sup>.

Ammonia volatilization measurement techniques Most of the studies which reported ammonia volatilization losses of 10% or lower were conducted in laboratory or greenhouse using distilled or deionized water and measurement techniques considered to retard NH<sub>3</sub> volatilization<sup>26</sup>. Mikkelsen *et al.*<sup>39</sup>, however, reported ammonia losses of up to 20% in field studies using closed systems with air exchange and acid trap.

Micrometeorological measurements are much preferred since they do not disturb the environmental or surface processes which influence gas exchange. They permit continuous monitoring, thus facilitating the measurement of environmental effects. Further, they provide a measure of the average flux density over a large area.

*Measurements of ammonia volatilization loss* Using micrometeorological technique and ammonium sulfate as N source (broadcast and incorporated), Freney *et al.*<sup>27</sup> reported a 5% ammonia volatilization loss. Losses could have been greater if the ammonium sulfate was surface applied into floodwater 2–3 weeks after transplanting using similar techniques.

Fillery *et al.*<sup>25</sup> reported a 47% loss in Muñoz, Central Luzon, Philippines when urea was surface broadcast into the floodwater. A lower rate of NH<sub>3</sub> loss, 27% of N applied, was found in a similar experiment conducted as Los Baños (IRRI farm) in the same season, primarily because wind speed was lower at Los Baños than at Muñoz.

From their studies in Australia, Simpson *et al.*<sup>50</sup> reported that some NH<sub>3</sub> loss (11% of N applied) occurred after applying urea to an 8-weekold direct-seeded rice crop, despite high pH values and elevated urea concentrations in floodwater, and high wind speeds. Low urease activity at the soil-floodwater interface and floodwater depth ( $\cong$  15 cm) may have retarded the ammoniacal N accumulation in floodwater. Ammonia loss measurements using simple techniques Wilson et al.<sup>59</sup>, Denmead<sup>19</sup>, and Freney et al.<sup>28</sup> recently discussed a micrometeorological technique more appropriate for smaller experimental areas, which have stringent measurement requirements.

With this area size the vertical ammonia flux density F (in  $\mu$ g N/m<sup>2</sup> per second) was calculated from

$$F = 0.91 \, \bar{u}_{0.8} \bar{c}_{0.8}$$

where  $\bar{u}_{0.8}$  is the mean wind speed at a height of 0.8 m and  $\bar{c}_{0.8}$  is the excess concentration of NH<sub>3</sub> (in  $\mu g \text{ N/m}^3$ ) over the background NH<sub>3</sub> concentration measured at a height of 0.8 m at the center of a fertilized circle of 25 m radius. Then fluxes were converted to kilogram per hectare per hour.

Using the above technique, high  $NH_3$  volatilization rates were recorded between 1400 and 1600 h in the 3 days following urea surface application into floodwater (Fig. 4).



Fig. 4. Ammonia fluxes from the circle as measured by simplified aerodynamic technique. Mabitac, Laguna, Philippines, 1985 dry season<sup>18</sup>.

Floodwater dynamics and potential ammonia volatilization loss Vlek and Craswell<sup>55</sup> found that aqueous  $NH_3$  content in floodwater increases about tenfold per unit increase in pH within the pH range of 7.5–9.0, and that it increases almost linearly with increasing temperatures at a given total concentration of ammoniacal N. In field systems, floodwater pH displays a diurnal pattern (Fig. 5) seemingly synchronized with the cycles of photosynthesis and net respiration or the depletion and addition of  $CO_2$  to floodwater<sup>39</sup>.

Cao et al.<sup>8</sup> reported that high pH and high total N (urea +  $NH_4^+$ -N) concentration in floodwater occurred after urea split application, indicating that greater  $NH_3$  volatilization and denitrification losses may result from this method. In contrast, urea supergranules (USG) point placement resulted in low floodwater pH and low total N concentration (5 mg/kg), indicating that this method can reduce N losses in lowland rice.

In a recent study<sup>14</sup>, the equilibrium vapor pressure of  $NH_3(\rho NH_3)$  in floodwater was used as an indicator of volatilized N. At each sampling time, water depth and floodwater pH and temperature were recorded. Relative potential N loss through ammonia volatilization was determined using the following equations:



Fig. 5. Diurnal fluctuations in floodwater pH in circle. Mabitac, Laguan, Philippines, 1985 dry season  $^{18}$ .

$$A = \frac{C}{1 + 10^{(0.09018 + 2729.92/T-pH)}} (Eq. 1, Denmead et al.20)$$
  
$$\rho NH_3 = \frac{0.00594 AT}{10^{(1477.8/T-1.6937)}} \times 100 (Eq. 2, Denmead et al.20,21)$$

where A = aqueous NH<sub>3</sub> (g N m<sup>-3</sup>), C = ammoniacal N (g N m<sup>-3</sup>), T = temperature (°K), and  $\rho$ NH<sub>3</sub> = partial pressure of ammonia (in pascal).

Results obtained by De Datta *et al.*<sup>14</sup> suggest that  $\rho$ NH<sub>3</sub> in the floodwater was lower when fertilizer was incorporated without standing water than when incorporated with 5 cm water. The equilibrium vapor pressure was high 1–4 days after urea was broadcast and incorporated into 5 cm water, suggesting that high volatilization loss occurred during this period.

Contribution of  $NH_3$  loss to total N loss Quantifying the ammonia volatilization loss in relation to total N loss in a lowland rice soil is critical when evaluating N fertilizer source and application techniques. From Australia, Simpson *et al.*<sup>50</sup> reported that NH<sub>3</sub> fluxes accounted for 24% of the <sup>15</sup>N lost. They attributed the balance of <sup>15</sup>N loss to nitrification-denitrification.

Fillery *et al.*<sup>25</sup> and Fillery and De Datta<sup>24</sup> reported that NH<sub>3</sub> volatilization accounted for about 92–100% N loss when urea or ammonium sulfate was topdressed into floodwater 15–20 days after transplanting in Muñoz, Philippines. In Los Baños, NH<sub>3</sub> fluxes from topdressed N accounted for 45% of the <sup>15</sup>N lost. Recent studies<sup>18</sup> in Mabitac, Philippines showed that the greatest total losses for 53 and 80 kg N/ha application rates were about 60% when urea was surface broadcast. Estimated denitrification losses were between 28–33% (Table 2).

Application method	Rate (kg/ha)	Water depth (cm)	Total N loss (%)	NH3 loss (%)	Estimated nitrification- denitrification loss (%) <sup>a</sup>
Researchers' split <sup>b</sup>	53	0	33	6	27
Researchers' split <sup>b</sup>	53	5	54	22	32
Farmers' split <sup>b</sup>	53	5	60	27	33
Researchers' split <sup>b</sup>	80	0	32	7	25
Researchers' split <sup>b</sup>	80	5	58	27	31
Farmers' split	80	5	59	31	28
Farmers' split <sup>d</sup>	80	5	55	31	24

Table 2. Relationship between total N loss and  $NH_3$  volatilization at the Mabitac site in Laguan, Philippines, 1985, late dry season<sup>18</sup>

<sup>a</sup> By difference. <sup>b</sup> 2/3 basal + 1/3 at 5–7 DBPI. <sup>c</sup> 2/3 at 10 DT + 1/3 at booting. <sup>d</sup> Circular plot.

# <sup>15</sup>N balance

Until recently, very few field studies reported on <sup>15</sup>N balance sheets for lowland rice. Such information is urgently needed to evaluate the performance of alternative fertilizer N materials and their application techniques most suitable to lowland rice culture. Further, earlier studies on N fertilizer rates in lowland rice were limited to ammonium sulfate. However, urea is currently more widely used than ammonium sulfate in lowland rice.

In field experiments using various application techniques, <sup>15</sup>N labelled urea was incorporated into puddled soil<sup>9</sup>. <sup>15</sup>N balance data showed that with deep point placement of urea supergranules, only 4-5% of applied N was unaccounted for after harvest of the dry and wet season crops. In contrast, when prilled urea was basally broadcast and incorporated and topdressed at panicle initiation, 11-35% of applied N was not recovered at harvest. This indicates substantial N fertilizer loss, especially when poor incorporation resulted in high floodwater mineral-N levels. The data further showed that 22–56% of the applied urea-N still remained in the soil after the final harvest.

In a recent study with broadcast-seeded flooded rice in Muñoz, Philippines (S.K. De Datta, R.J. Buresh, and M.I. Samson, IRRI, *unpublished data*), N losses were less with  $(NH_4)_2SO_4$  than with urea (Fig. 6). Basal deep placement of urea completely eliminated N loss.

Total <sup>15</sup>N balance Past results<sup>9,12</sup> suggest that significant amounts of applied N not taken up by the crop or lost by ammonia volatilization and denitrification remain in the soil and organic matter fraction. Schnier *et al.*<sup>48</sup> reported some of the recent work on the subject. Their results showed that the total amount of <sup>15</sup>N fertilizer recovered from the soil after 10 weeks of incubation varied between 61 and 66% in four soils. <sup>15</sup>N recovery from Maligaya silty loam (Vertic Tropaquept) from Central Luzon, Philippines was 52% of fertilizer applied. From total N uptake at maturity, only 20–30% were derived from N fertilizer.

### Cultural practices to minimize nitrogen losses

In recent years, a deeper understanding of the mechanisms causing poor N utilization helped develop cultural practices that improve N fertilizer use efficiency in lowland rice. Basic research results suggest that it is wasteful to apply N in the floodwater between transplanting and early tillering, as commonly practiced by farmers in Southeast Asia. Early N uptake is, however, essential for high tiller production.

Alternative technologies are therefore needed to improve N application efficiency. Improved nitrogen management should maximize N



Fig. 6. <sup>15</sup>N recovery in broadcast-seeded IR60 at flowering as affected by N source at 87 kg N/ha. Maligaya Rice Research and Training Center, Nueva Ecija, Philippines, 1985 dry season (S.K. De Datta, R.J. Buresh, and M.I. Samson, IRRI, *Unpublished data*). B & I = broadcast and incorporated; DBPI = days before panicle initiation.

uptake at critical growth stages and minimize transformation processes that lead to N losses or temporary losses from soil-water systems<sup>15</sup>. Ensuring that N absorbed by the rice plant is used for grain production is equally important.

# Timing of nitrogen application

Applying N when it is less vulnerable to high losses minimizes N loss and maximizes N use efficiency. Basal dressing without proper incorporation in the soil or early tillering stage leads to high N losses and should be avoided. In the 1986 dry season trials in three farmers' fields in the Philippines, researchers' timing at two N levels gave between 0.4 and 0.6 t/ha more grain yield than did farmers' timing (Table 3). These and other data<sup>14,15</sup> suggest that proper timing of urea application increases the potential for high N use efficiency.

Table 3. Effects of source and method of nitrogen application on grain yield of transplanted rice in farmers' fields, Nueva Ecija, Philippines, 1986 dry season

Treatment	N fertilizer	Grain yield <sup>a</sup>	
	applied (kg N/ha)	(t/na)	
No fertilizer N	0	4.3 e	
Farmers'split, PU <sup>b</sup>	58	5.6 c	
Researchers' split, PU <sup>c</sup>	58	6.0 b	
Point-placement, USG	58	6.1 b	
Press wedge, USG	58	5.3 d	
Plunger auger, PU	58	5.7 c	
Farmers' split, PU	87	5.7 c	
Researchers' split, PU	87	6.3 a	

<sup>a</sup> Av of 3 farms.

 $^{\rm b}$  1/2 topdressed at 15 days after transplanting, and 1/2 topdressed after panicle initiation.

 $^{\rm c}$  2/3 basal broadcast and incorporated without standing water, and 1/3 top dressed 5–7 days before panicle initiation.

# Effect of water depth and management on ammonia loss

Effects of water depth and fertilizer application method on floodwater urea-N +  $NH_4^+$  concentrations and pH were evaluated in a farmer's field in Nueva Ecija, Philippines<sup>30</sup>.

The yield response of IR58 to fertilizer was 2.6 t/ha with researchers' split (Table 4). Grain yield was significantly lower with 5 cm water than with no standing water or 2.5 cm water. In fact, the grain yield with point placement was similar to that with broadcast and incorporated (B & I) treatment without standing water and with 2.5 cm water.

Topdressing N at 10 days after transplanting (DT) gave similar grain yield at different water depths (as practiced by most rice farmers in Southeast Asia) but significantly lower than with B & I fertilizer (Table 4).

Application	Water depth	Yield*	
method	(cm)	(t/ha)	
No fertilizer N (control)	_	3.4 d	
Researchers' split <sup>b</sup>	0	6.0 a	
Researchers' split <sup>b</sup>	2.5	5.9 a	
Researchers' split <sup>b</sup>	5.0	5.3 b	
Farmers' split <sup>c</sup>	0	4.6 c	
Farmers' split <sup>e</sup>	5.0	4.6 c	
Farmers' split <sup>e</sup>	10.0	4.3 c	
Point placement			
(10 cm soil depth)	0	6.3 e	

Table 4. Effects of water depth and fertilizer application method at 87 kg N/ha on IR58 grain yield. San Jose City, Nueva Ecija, Philippines, 1984 dry season

<sup>a</sup> Means followed by a common letter are not significantly different at the 5% level by Duncan Multiple Range Test. <sup>b</sup> 2/3 basal plus 1/3 at 5–7 days before panicle initiation. <sup>c</sup> 2/3 at 10 days after transplanting plus 1/3 at booting.

#### Urea, modified urea materials, and their application methods

Urea is likely to remain the leading N source in the world until the end of the century. The large potential for new N capacity in Asia where rice is mostly grown primarily attests to this. However, some changes in the form of urea can be expected. Most urea is produced and sold as dry prills, yet recently production shifted towards that of granular urea. New granular urea production facilities are being built in Malaysia, Thailand, and Mexico<sup>53</sup>.

Because substantial N losses occur within 1 to 7 days after N fertilizer application, using slow release and slow dissolving N fertilizers, and enzymic or microbial inhibitors can possibly control these early losses.

In Japan, ureaform, mainly consisting of methyleneurea polymers such as methylenediurea with some free urea, has been developed. Also developed were isobutylidene diurea (IBDU) and 2-oxo-4-methyl-6 ureidohexahydropyrimidine (CDU). Of the coated materials, sulfur-coated urea (SCU) is the most widely tested and reported on<sup>14,16</sup>.

Chemists at the International Fertilizer Development Center (IFDC) developed a simple method of manufacturing ureaforms. It has the additional advantage of producing shorter molecular chains of urea as compared with those commercially processed. Results in a farmer's field in the Philippines showed that yield obtained with two ureaforms was comparable to that with researchers' split of urea.

Recently, several newly developed slow release N fertilizers were compared with SCU. Prilled urea mixed with 10% dicyandiamide (DCD) was also evaluated. A single or split dose of these modified urea products did not show a yield advantage over improved method and timing of N application<sup>31</sup>.

#### Urease inhibitor

The potential of urease inhibitor in reducing ammonia volatilization losses from broadcast urea in lowland rice was evaluated jointly by IRRI and IFDC. In earlier IRRI field studies, PPD (Phenylphosphorodiamidate) delayed the hydrolysis of urea broadcast into floodwater at 20 days after transplanting (DT). Although PPD retarded urea hydrolysis, it did not increase grain yield and total N uptake when compared with control without urease inhibitor<sup>15</sup>. Recently, Fillery and De Datta<sup>24</sup> reported that PPD was effective in reducing N loss, as determined by direct measurement of NH<sub>3</sub> loss using micrometerological technique (Fig. 7).

In an IRRI-IFDC joint project at IRRI, urea with and without 1% PPD was broadcast into the floodwater 18, 28, or 38 DT. PPD reduced N loss as determined by the <sup>15</sup>N balance. However, yields with or without



Fig. 7. Ammonia fluxes following the application of urea amended with PPD (1% wt/wt) to floodwater, Maligaya Rice Research and Training Center, Nueva Ecija, Philippines<sup>24</sup>. Reproduced from Soil Science of America Journal, Vol. 50, No. 1, Jan.–Feb. 1986 by permission of Soil Science of America, Inc.

PPD used at different times of N application, did not significantly increase beyond  $5.2 \text{ t/ha}^{31}$ .

# Deep placement

Cao *et al.*<sup>9</sup> critically evaluated the deep placement technology using <sup>15</sup>N-labelled urea. Rice crop efficiently used the applied N with deep placement resulting in low N fertilizer losses.

Table 5. Effect of urea source and method of application on the grain yield of a traditional variety Binato and a modern breeding line 1R29723-143-3-2-1. IRRI, 1986 dry season.

Urea source <sup>a</sup>	N rate (kg/ha)		Application method <sup>b</sup>	Grain yield <sup>c</sup> (t/ha)	
	Binato	IR29723- 143-3-2-1		Binato	IR29723- 143-3-2-1
_	0	0	No fertilizer N	3.7 a	4.8 d
PU	29	58	Farmers' split	4.1 a	5.5 c
PU	29	58	Researchers' split	3.8 a	6.4 ab
SCU	29	58	Basal, broadcast & incorporated	3.9 a	6.1 bc
USG	29	58	Point placement by hand	3.9 a	6.9 a
USG	30	58	Point placement by press wedge	4.0 a	5.6 c
PU	29	58	Band placement by plunger-auger	4.4 a	6.7 ab
PU	58	87	Researchers split	3.9 a	6.9 a

<sup>a</sup> PU = prilled urea, SCU = sulfur-coated urea, USG = urea supergranules.

<sup>b</sup> Farmers' split = equal split-doses at 10 days after transplanting and 10 days after panicle initiation. Researchers' split = 2/3 basal, broadcast and incorporated into mud plus 1/3 topdressed at 5–7 days before panicle initiation.

<sup>c</sup> In a column, means followed by a common letter are not significantly different at the 5% level by DMRT.

In a recent study with two rices, researchers' split of prilled urea (PU) with good water management gave grain yields similar with that of USG point placement with the modern breeding line IR29723-143. The traditional variety Binato lodged heavily and did not show any significant N response over nonfertilized control (Table 5).

*Machine deep placement* Several applicators developed for N fertilizer deep placement have been tested by IRRI and national programs in Asia. Although some progress has been made in machine deep placement of PU and USG<sup>14</sup>, results have not always been consistent (Table 5).

# Critical research needs

Considerable progress has been made in quantifying the magnitude of N losses as affected by various N sources and their management. It was clearly established that ammonia volatilization is an important loss mechanism in lowland rice system. If soil, water, and atmosphere conditions are favorable, ammonia volatilization loss could be serious (up to 50% loss). While ammonia volatilization losses are minimized by appropriate cultural practices, other losses, probably by nitrification and denitrification, are often substantial in irrigated rice. Quantifying ammonia volatilization loss in relation to total N losses from irrigated lowland rice fields is therefore critical in evaluating various N fertilizer sources and their application techniques.

While N transformation processes in irrigated lowland rice have been fairly well understood, hardly any research has been done on rainfed lowland rice. Rainfed conditions are more harsh and variable, so that denitrification losses may be high. Research should measure denitrification losses in relation to ammonia volatilization losses in rainfed lowland rice using simultaneous measurement techniques.

In recent years greater emphasis has been placed on N transformation processes and N fertilizer management in lowland rice. Likewise, more effort is warranted in studying soil N dynamics and their management which could result in substantial yield-gains with resources already on land. Biological nitrogen fixation (BNF) research should focus not only on sustaining N fertility but also on enhancing BNF in lowland rice fields by proper manipulation of ecology and cultural practices.

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