2. Nitrogen transformations in flooded rice soils

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Abstract. A review is made of the recent literature pertaining to the reactions and processes that soil and fertilizer N undergo in lowland rice soils in relation to the improved N management and overal N economy of lowland rice soils. Topics discussed include: nitrogen leaching, ammonium fixation and release, ammonia volatilization, N_2 fixation, mineralization-immobilization, nitrification-denitrification, dissimilatory nitrate reduction, urea hydrolysis, critical pathways for control of nitrogen loss.

Flooded soils differ considerably from their arable counterparts in several characteristics. Perhaps the characteristic that makes the flooded soils markedly different from arable soils, and which also greatly affects N transformations and fertilizer use by rice is their low supply of O_2. Thus, they are reduced most of the season, the anaerobic metabolism is dominated by bacteria, and the products of metabolism differ markedly from the arable soils [42, 67, 93, 112, 113].

The presence of oxidized and reduced soil layers (see Figure 1) makes the flooded soils a unique system where both aerobic and anaerobic N metabolism can occur in close proximity. Thus N is markedly susceptible to losses in these soils (Table 1).

Several reviews are available that discuss various aspects of the N cycle in flooded soils and sediments [7, 8, 22, 42, 59, 60, 67, 71, 75, 92, 93, 105, 112, 113]. We will focus on N transformations and transport processes in flooded soils that have relevance to improved N management and overall N economy of lowland rice soils. The interest in N transformations in flooded soil ecosystems stems from the fact that rice, which is the staple food for half of the world population [15, 22], does not use fertilizer N very efficiently [16, 69, 75, 89].

Nitrogen is the nutrient element limiting growth in most rice-growing soils [92]. Further, increased yields due to improved management involves use of fertilizer N. Better understanding of the availability of N from the soil organic N and the fate of added N fertilizer should aid in development of innovative N management technology. Even a small increase in the efficiency of fertilizer

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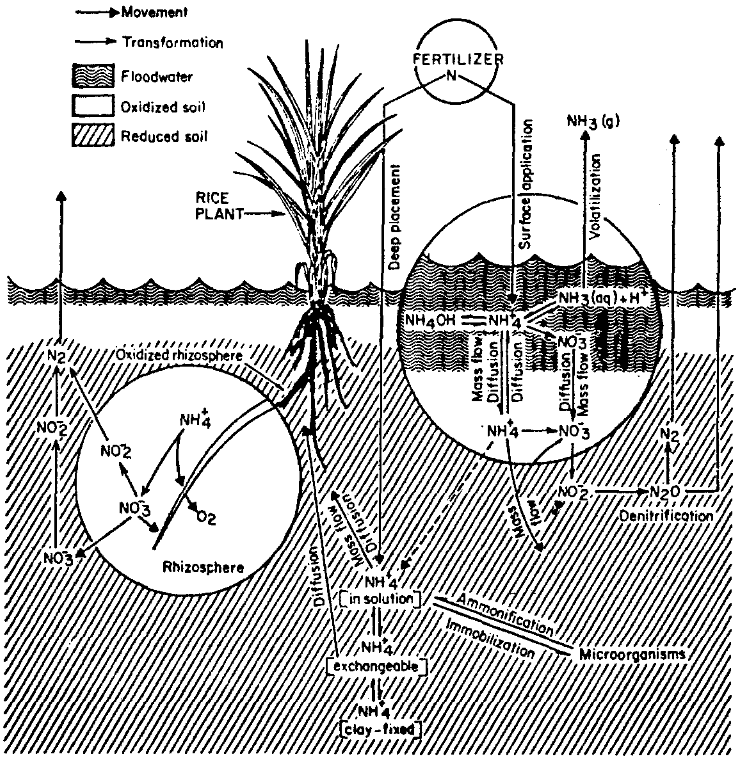

Table 1. Biochemical nitrogen transformation reactions that occur in the different redox zones of an idealized flooded soil-water system

Zone	Redox state	Dominant nitrogen transformation reactions
Floodwater	Oxidized	N_2 fixation by algae, aerobic bacteria; nitrification, ammonia volatilization
Oxidized surface face layer	Partially oxidized	Ammonification, nitrification, immobilization, N_2 fixation by algae, bacteria
Reduced soil	Reduced	N_2 fixation, ammonification, immobilization, denitrification, (reductive deamination), dissimilatory nitrate reduction
Rhizosphere	Partially oxidized	N_2 fixation, ammonification, nitrification, (oxidative deamination), defitrification

N will save energy costs and foreign exchange spent by countries where N fertilizer must be imported.

Physical/metabolic zones of flooded soils

A flooded soil is a dynamic heterogeneous soil-water system that has three distinct soil layers established mainly by the prevailing oxidation-reduction or redox potential (Eh or pE) of the system. The floodwater and a few mm to one cm thickness of the surface soil in contact with the water is partially aerated, usually has a relatively high redox potential and supports aerobic microbial reactions (Table 1). The pH of the overlying water phase rapidly fluctuates diurnally in response to algae growth. Removal of CO_2 during photosynthesis results in marked increase in pH of the floodwater, and volatilization of NH_3, if NH_4^+ is present, can result in significant N losses [51, 52, 108]. The plow layer of a flooded lowland usually is several cm thick and has a low Eh or pE ($pE = -\log e = Eh/0.059$) conductive for NH_4^+ accumulation. The presence of the oxidized zone in close proximity to the reduced soil zone is also conductive for the loss of N through nitrification (oxidized layer) followed by denitrification (reduced zone) [72, 73].

Ponnamperuma [67] described the NO_3^-–N_2 system by the following equation, which indicates that in the flooded soil, where pE may range from − 1 to 3, NO_3^- is extremely unstable:

$$pE = 21.06 - 1/5\ pNO_3^- + 1/10\ pN_2 - 6/5\ pH$$

The instability of NO_3^- in flooded soils has been long recognized [64] and its loss via denitrification when applied to wetland rice soils has also indirectly been recognized by the poor performance of NO_3^- fertilizers as a N source for lowland rice [19, 41].

The rhizosphere of a lowland rice plant is partially oxidized due to entry of O_2 to rice roots through the rice aerial parts. Savant and DeDatta [92] reported that the apparent pE of the rhizosphere of 5 to 6 week old IR36 rice plants growing in a reduced clay soil ($pE = 0$ to -3) ranged from + 2 to + 5. Thus, rhizosphere of a submerged lowland rice field may support aerobic N reactions such as nitrification, mineralization of organic N via oxidative deamination and biological N_2 fixation by aerobes and facultative anaerobes.

Physical and chemical processes

Nitrogen movement and distribution

Ammonium can be leached more readily in a reduced than in an arable soil. The rate of movement increases as the pE of the soils declines and is the result of the release of cations such as Fe^{2+} and Mn^{2+} that compete with NH_4^+ on the exchange sites [68].

Nitrate leaching may be prevalent in light-textured (sandy) soils that are hard to maintain in the flooded state. Examples of these soils are found in Punjab (India) where high percolation rates result in large losses of deep point-placed N. A greenhouse study by Vlek et al. [107] provided evidence of high N loss due to leaching in soils with low CEC and high percolation rates. Savant and DeDatta [92] have summarized the recent information on movement and leaching of N in lowland rice soils. The puddling of a soil and its compaction should reduce greatly the rate of water movement and thus N leaching. However, there is very little data on N leaching of flooded soils under field conditions. In a recent field study in Louisiana using ^{15}N fertilizers, negligible amounts of N moved beyond the 20-cm depth in a flooded Crowley silt loam [71]. Similarly, Savant and DeDatta [91] reported that NH_4^+ formed from surface applied urea had moved 12 to 14 cm in a submerged undisturbed clay soil by 4 weeks after application of urea in the absence of rice plants. The movement of NH_4^+ in a lowland field was: downward $>$ lateral $>$ upward from the deep placement (10 cm) of urea. The NH_4^+ concentration gradient disappeared earlier in the dry than in the wet season, probably due to faster movement of NH_4^+ and/or greater root sink effect in the dry season [91, 92].

Ammonium fixation and release

Less emphasis seems to have been given to the dynamics of NH_4^+ fixation and release in flooded soils than in arable soils. This is mainly due to the generally accepted belief that NH_4^+ fixation is not of any significance in lowland rice soils. For example, it is generally stated that the 2:1 type clay minerals that are known to entrap NH_4^+ in arable soils do not fix NH_4^+ in flooded soils because fixation is usually associated with drying to moisture contents usually not relevant to flooded soils. However, it is known [7] that soils containing significant amounts of vermiculite and illite are capable of fixing NH_4^+ under moist conditions [76]. Moreover, recent studies have indicated that NH_4^+ fixation is important even in lowland rice soils [44, 77]. Also, flooded soils are often drained and used for rice-based cropping systems where the second crop is grown under upland conditions. It was further shown in a study with 12 diverse tropical rice soils that these soils fixed NH_4^+ when treated with $(NH_4)_2SO_4$ solution under flooded conditions. The NH_4^+-fixing capacity of the soils ranged from 3.8 to 7.7 meq/100 g of soil. Ammonium fixation in these soils was not related to pH, organic matter, or clay content but was significantly correlated ($r = 0.61^*$) with the amount of active iron [77]. It was suggested that because of the reversible oxidation and reduction of iron oxides in rice soils, this mechanism of NH_4^+ fixation may be of special importance in sorption and desorption of NH_4^+ and its availability to rice. It was also found that the oxidation of organic matter by hydrogen peroxide in Maahas clay (the major soil series at the IRRI farm) doubled NH_4^+ fixation probably due to exposure of fresh NH_4^+ fixing sites. Similarly, a recent study with the clay fractions separated from 14 lowland Philippine rice soils showed that beidellitic and vermiculite clays fixed more than 90% of the applied NH_4^+ under hydromorphic conditions, while a montmorillonite clay fixed 50% of the applied NH_4^+. Clays of all other mineralogical compositions containing chlorite, hydrous mica, halloysite, kaolinite and amorphous materials did not fix significant amounts of ammonium [5].

Tilo et al. [104] studied the distribution of native fixed NH_4^+ in the profiles of 16 Philippine soils including some used for lowland rice. Fixed NH_4^+-N ranged from 7 to 428 mg/kg of soil and constituted 1 to 56% of the total N. The surface sample collected from a lowland rice field contained the highest concentration of fixed NH_4^+-N (428 mg/kg) and this comprised 17.9% of the total soil N. These and other studies [44] clearly indicated the potential importance of fixed NH_4^+ in the N cycle in flooded rice soils. Better understanding of the dynamics of fixation and release of NH_4^+ is highly desirable for its relevance to N management of lowland rice. Results of a recent greenhouse pot study indicated that the release of fixed NH_4^+ under submerged conditions of rice culture may be faster and more significant than commonly reported for arable soils [48]. Using ^{15}N-labeled ammonium sulfate fertilizer, it was found that the residual fixed NH_4^+ decreased from 45 to 23% during cropping with rice under flooded conditions. The dynamics of NH_4^+ and its fixation in flooded rice soils is further discussed by Mengal et al. (this volume).

Nommik and Vahtras [57] have comprehensively discussed the retention and fixation of NH_4^+ in soils, covering mainly the arable soils. It was suggested that the question of availability of interlayer fixed NH_4^+ in soils cannot be fully resolved by the nitrification test or by chemical laboratory tests used for determining NH_4^+ fixing capacity of soil in relation to its availability to field crops. Fixation of NH_4^+ may be a desirable factor in preventing loss of N, thus ensuring sustained supply of N to plants in a growing season [7]. This hypothesis has been confirmed by field studies by Keerthisinghe et al. [44].

Ammonia volatilization

Loss of nitrogen through NH_3 volatilization from soils including flooded soils has been a subject of several recent comprehensive reviews [51, 55, 102, 108]. Additionally, this issue has been dealt in reviews on N transformations by several authors [7, 22, 34, 52, 59, 75, 92]. Fillery and Vlek (this volume) have reported the significance of NH_3 volatilization as a N loss mechanism in flooded rice soils. We briefly cover the salient principles relevant to NH_3 volatilization from flooded rice fields. It is clearly evident from literature that estimates of the magnitude of NH_3 volatilization loss may vary widely with the technique used for its measurement [22, 92].

Of the several factors that affect NH_3 volatilization, the pH of the floodwater has been recently recognized as the single most important determinant [52]. However, its importance in aquatic systems and its sensitivity to CO_2

concentration as a result of photosynthetic activity has long been recognized [58]. The pH of the floodwater of a flooded soil follows diurnal fluctuations and may increase or decrease by two units during the 24-hour period in response to photosynthetic activity of biota and temperature [51, 52]. Ponnamperuma [68] suggested that the pH of floodwater was related to CO_2 concentration and HCO_3^- activity:

$$pH = 7.85 + \log(HCO_3^-) - PCO_2$$

Thus high bicarbonates in a system with constant removal of CO_2 may greatly increase the pH which can increase NH_3 volatilization of surface applied fertilizer or of NH_4^+ which diffuses into the water layer. The fluctuation in the floodwater pH is further governed by the buffering capacity of the flooded soil-water system.

Floodwater pH is the result of interactions of several floodwater properties including concentration of dissolved CO_2 and NH_3, pH buffering capacity, alkalinity, temperature and biotic activity. Several other factors involving the soil (pH, CEC, PCO_2, buffering capacity, and alkalinity) and the environment (temperature and wind velocity, etc.) as well as the nature and amount of fertilizer N applied and size of plant canopy affect NH_3 volatilization loss from a flooded soil [92].

In general, losses of NH_3 are higher in alkaline and calcareous soils and increase with an increase in soil pH, temperature and solar radiation but decrease with an increase in CEC of the soil and other cultural and management practices including the presence of rice canopy activities which decrease the amount of NH_3 in solution. Also, higher losses of volatile NH_3 are reported from urea fertilizer compared to other NH_4^+ sources because hydrolysis of urea provides alkalinity which can maintain or initiate volatile loss of NH_3.

Volatilization of NH_3 generates protons [4] which tend to acidify the system and will eventually retard loss unless there is constant supply of alkalinity (e.g., by urea hydrolysis). Application of N fertilizer in the reduced layer or to the crop when its root system is well established apparently curtails these losses because both practices decrease the amounts of ammonium that is available for volatilization [18].

Biological processes

Nitrogen fixation

Flooded soils are an ideal habitat for N fixation by nonsymbiotic, anaerobic and aerobic microbes. This can contribute significantly to the N nutrition of lowland rice [12, 20, 67, 110]. Nitrogen fixation is greater in flooded than in upland soils [114, 115]. This topic is covered in detail by Roger and Watanabe (this volume).

Table 2. Range and mean values of ammonification rates in 39 Philippine lowland rice soils at two temperatures as determined by anaerobic incubation tests[a]

Incubation temperature (°C)	Period of incubation (days)	Rate of NH_4^+-N production ($mg\ NH_4^+$-N kg dry $soil^{-1}$ day^{-1})	
		Range	Mean
30	14	1.2–30.6	5.6
40	7	1.9–74.6	14.0

[a]Calculated from Sahrawat [82]; soils had a wide range in pH (4.3 to 7.9), organic C (0.63 to 5.46%) and total N (0.06 to 0.60%) contents.

Mineralization-immobilization

Mineralization and immobilization processes occur simultaneously in flooded soils with their rates and magnitude influenced by soil and environmental factors [7, 59, 92]. Both oxidative and reductive deamination processes contribute to ammonification in flooded soils. Lack of oxygen supply generally inhibits nitrification and greatly influences the rate of ammonification.

Mineralization of organic N to NH_4^+ is the key process in the N nutrition of lowland rice [7, 8, 40, 59, 85, 86, 92]. Important environmental factors that affect mineralization-immobilization are temperature, soil moisture regime, and soil drying; soil characteristics include pH, organic matter content, C/N ratio, and amount and quality of organic residues.

Net mineralization of soil organic N in four Philippine soils under anaerobic incubation increased with an increase in temperature from 15 to 45°C; the Q_{10} for ammonification ranged from 1.0 to 1.8 [36]. Numerous other studies also emphasize the importance of temperature on the rate of net N mineralization in flooded soils [7, 28, 85, 92]. In a recent study of 39 diverse Philippine lowland rice soils, Sahrawat [82] found that the mean rate of NH_4^+ production increased from 5.6 to 14.0 mg NH_4^+-N kg dry $soil^{-1}$ day^{-1} when the incubation temperature was increased from 30 to 40°C (Table 2). These findings indicate that the temperature prevalent during the growing season should be considered when assessing the N supplying capacity of lowland rice soils.

Immobilization is also a temperature-dependent microbial process and under conditions favorable for N immobilization (application of high C/N ratio residues), immobilization also increases with an increase in temperature.

Drying of soils enhances the N mineralization rate [94–96]. For example, a marked effect of soil drying was observed in four permanently waterlogged histosols in the Philippines [81]. Nitrogen availability to wet season rice was affected by the dry season soil conditions [106].

Among the soil characteristics, organic matter content as measured by organic C and total N account for the most variation in NH_4^+ production under anaerobic incubation. In a recent study, Sahrawat [85] reported that NH_4^+ production in Philippine lowland soils under anaerobic incubation was

Table 3. Distribution of mineralizable N in 39 lowland rice soils in relation to total N and organic C content[a]

Mineralizable N[b] (mg kg^{-1} dry soil)	No. of samples	Associated soil properties	
		Total N (%)	Organic C (%)
50	24	0.06–0.16	0.63–1.15
50–100	7	0.16–0.21	1.48–2.14
100–200	4	0.16–0.26	1.97–2.50
200	4	0.31–0.60	2.44–5.46

[a] From Sahrawat [85].
[b] NH_4^+-N released under anaerobic incubation of soils at 30°C for two weeks.

highly correlated with total N (r = 0.94**), organic C (r = 0.91**) and C/N ratio (– 0.46**), but was not significantly correlated with CEC, clay or pH. Multiple regression analysis of CEC, pH and clay on mineralizable N accounted only for 36% of the variability. While soil properties such as pH, clay and CEC may be related to N mineralization, their individual contribution to this process could not be clearly quantified because of the numerous interactive effects and cross-correlations of these properties. The association of organic C and total N with mineralizable N in 39 soils studied is evident from data in Table 3.

Liming has been reported to increase the availability of N in flooded soils and its availability to lowland rice [2, 6, 65]. The effect of pH per se cannot be evaluated from such studies. However, a recent investigation showed that net N mineralization occurred in the two acid sulfate soils from the Philippines having a pH of 3.4 and 3.7, respectively [78] (Table 4). It would appear from this study and other evidence that ammonification seems to operate under a wide pH range in flooded soils [85], although the tendency of pH to approach neutrality might also be a factor.

In addition to soil and environmental factors, the quantity and quality (C/N ratio) of organic residues added also affect the release of NH_4^+ in submerged soils. Earlier researchers realized that the 'N factor' commonly used for characterizing the N immobilizing capacity of the decomposing residues is lower for flooded soils than for the aerobic incubation [3]. Thus it follows that organic residues with similar C/N ratio will immobilize less N, and the net release of N from these will occur at a relatively higher C/N ratio under flooded than under nonflooded, aerobic conditions. This is supported by results from field studies [111].

Ammonification is also affected by tillage and other operations used for preparation of lowland rice fields [28], but it is difficult to quantify the positive effects of these practices because puddling of soil affects N utilization by lowland rice [23] in ways other than by enhancing mineralization (for example, lessening the movement of N) [90].

Mineralization of soil N is also affected by the presence of the rice plant. For example, Broadbent and Tusneem [9], in a greenhouse study using ^{15}N

Table 4. Mineralization of soil organic nitrogen under anaerobic incubation at 30°C for two weeks in two acid sulfate soils from the Philippines[a]

Soil	pH (1:1 H_2O)	Organic C (%)	Total N (%)	NH_4^+-formed (mg kg dry soil^{-1})
Calalahan sandy loam	3.4	1.57	0.110	83
Malinao loamy sand	3.7	1.22	0.090	72

[a] From Sahrawat [78].

fertilizer calculated the apparent net mineralization of soil N from soil N uptake in a flooded Maahas clay (Andaqueptic Haplaquolls). They found that soil N mineralization was higher in the presence of the rice plant than in the unplanted soil because the presence of active rice roots decreased N loss due to nitrification-denitrification. They felt the observed pattern of N mineralization was more closely related to the actual field situations than in incubation tests where the NH_4^+-N accumulation peak tends to level off or decrease with time.

Studies on N immobilization by rice straw under flooded conditions indicate that the fertilizer N was mainly immobilized into the α-amino N fraction and a good part of the immobilized N was remineralized under subsequent anaerobic incubation [105].

Nitrogen release in relation to plant needs

Mineralization of soil organic N in flooded soils is the key process for N nutrition of lowland rice. Even in well-fertilized lowland rice fields, rice utilizes 50–75% of soil N through mineralization [7, 35, 46, 86].

Studies indicate that much of the mineralizable N in a flooded soil is released as NH_4^+ within two weeks of flooding provided temperature is favorable and the soil is neither strongly acid nor greatly deficient in available P [67]. The release of NH_4^+ in laboratory incubated flooded soils follows approximately an asymptotic curve [66]. This NH_4^+ release pattern may not be ideally suited to the N needs of lowland rice because N uptake by rice follows a sigmoidal curve [37].

As pointed out by Broadbent [7], incubation tests may at times give misleading N release patterns because during these test NH_4^+ production, after reaching a peak, tends to level off as early as 2 to 4 weeks of incubation. Nitrogen uptake data under field conditions using ^{15}N fertilizer, however, indicate constant supply of soil N throughout the growing season. If incubation tests are to be useful in predicting the N supplying capacity of lowland rice soils, the pattern of NH_4^+ release should be, in theory, similar to the N release pattern in the field in the presence of rice plants. It is possible that if the NH_4^+ released during anaerobic incubation of soil were periodically removed to simulate N uptake by the rice plant a better characterization of the N supplying capacity of lowland rice soils would result. This is technically very difficult. Comparison of N release in laboratory incubation and N mineralization under field conditions during a growing season should give useful leads in devising and standardizing incubation tests for realistic estimate of the N supplying capacity of a soil. Such studies should also provide information regarding factors that should be considered for modeling of the N cycle. No such studies have been attempted for flooded rice soil but reports comparable to those used for arable soils have been published [39, 101].

Prediction methods

The inefficient use of fertilizer N and heavy dependence by rice on the soil mineralizable N pool emphasizes the need for methods to assess the N supplying capacity of lowland rice soils. Recently, Sahrawat [86] has reviewed the available information about the methods currently used for predicting N availability to lowland rice. Among the biological indices used, anaerobic incubation methods involving incubation of soils under waterlogged conditions at 30°C for two weeks or at 40°C for 1 week are regarded as most useful in predicting the soil N availability to lowland rice. Most of these evaluations have involved greenhouse trials, but there were also a few field tests. These indices would likely be more useful if the temperature prevalent in the region during the growing season were used.

Among the chemical indices, organic C content has been widely evaluated for predicting N availability to submerged rice especially in India [see ref. 86 for review]. This method has been more successful in predicting N availability to rice in greenhouse than in the field situations. However, recent work suggests that this simple test could be made more useful if some component pertaining to the quality of organic matter is also incorporated. The characterization of quality of organic matter might help in explaining the difference in the amounts of N released in soils with the same content of organic matter. Chemical characterization of the soil organic N pool in some Philippine lowland rice soils using alkaline permanganate, acid permanganate, acid dichromate, H_2O_2 and acid hydrolysis suggests that it may be possible to quantify the fraction of soil organic matter which is the source of mineralizable N [82]. This work led to the development of a simple method based on modification of the Walkley–Black (acid dichromate oxidation) method of organic C determination, which can be used for simultaneous determination of organic C and potentially mineralizable N in soils [83]. This method offers an opportunity to test a combination of total organic matter and mineralzable N for predicting N availability to lowland rice.

Among the chemical methods, the one based on the measurement of NH_4^+ released during the digestion of soil samples with alkaline permanganate for a brief period has been widely tested in India for predicting soil N availability. Results, however, have been mixed [86]. Recent research on this method has improved our knowledge about its chemistry [88, 89]. A study by Sahrawat and Burford [88] suggests that this method is a relatively poor predictor of N availability to crops grown in arable soils because of its inability to include NO_3^--N in the available N pool. It is much better for submerged rice, where NH_4^+ is the dominant mineral N form and NO_3^- contributed little to N nutrition.

Greenhouse studies with submerged rice using diverse soils suggest that the chemical methods based on the release of NH_4^+-N from soils by the oxidative action of acid permanganate, acid dichromate and hydrogen peroxide are relatively good predictors of N availability [86].

Recent studies employed the electroultrafiltration (EUF) technique [56] for fractionation of soil N into N fractions which are in soil solution (intensity) or in soil reserve (capacity) by using varying voltage and temperature. This research suggests that EUF-NH_4^+, which comes in soil solution (fraction I) at low voltage (intensity factor), is a good measure of readily available N to lowland rice [50].

The A-value concept [33] has been evaluated in several field studies. Different workers have found that the A-value of a soil varies not only with interactions of fertilizer N with rice but also with the method, rate, and time of fertilizer N application [7, 34, 46]. However, under well-characterized conditions, this method could be of utility in assessing the N supplying capacity of lowland rice soils. With the availability of ^{15}N depleted N fertilizers, this method may prove less expensive and in need of further evaluation. Results obtained with A-values for lowland rice are summarized by Sahrawat [86].

Importance of temporary immobilization

Immobilization is a key process in the N turnover in lowland rice soils, especially in situations where organic residues or manures are used as N sources. Organic N and mineral N pools in a soil are in dynamic equilibrium and the net effects of factors which affect mineralization-immobilization reaction govern the availability of N to plants. As Kai and Wada [40] state, our knowledge regarding the immobilization process in lowland rice is limited compared to what is known in arable soils. They posed three questions: (1) What is the mineralization pattern of native soil organic N and of the recently immobilized N? (2) How long is the immobilized N tied up before it is remineralized? (3) How effectively and efficiently are soil organic N and immobilized N recovered by the rice crop?

These questions cannot be satisfactorily answered because the behavior of immobilized N in lowland rice culture is not fully understood. However, recent laboratory and greenhouse studies using ^{15}N fertilizer suggest that remineralization of immobilized N is slower under flooded soils [40, 48, 105]. Immobilized N acts as a slowly available N source and at times may be helpful in locking up mineral N from physical and biochemical reactions in soils which lead to N loss. We have to learn more about biological N immobilization to appreciate its effects on N economy in lowland rice soils.

Nitrification

General

Nitrification, a strictly aerobic microbial process, occurs in the oxidized surface layer of a flooded soil. However, it is difficult to study nitrification *in situ* in a flooded soil system because as soon as NO_3^- is formed it diffuses down to the reduced layer and is lost from the system by denitrification or reduced to NH_4^+ by dissimilatory NO_3^- reduction [7, 10, 30, 92, 105]. Thus, it is not surprising that the occurrence of nitrification in the oxidized soil layer has been difficult to document. However, occurrence of nitrification is recognized as a mechanism of N loss via nitrification-denitrification in flooded soils and has led to the conclusion that NO_3^- is an inefficient source of N for submerged rice culture [1, 19, 21, 41, 53, 61].

In a laboratory experiment using ^{15}N labeled $(NH_4)_2SO_4$, Yoshida and Padre [116] found that the oxidized layer of a clay soil had high nitrifying activity. After 30 days, nearly one-third of the NH_4^+-N applied (400 mg kg^{-1} NH_4^+-N) was converted into NO_3^- (123 mg kg^{-1} NO_3^--N) at 20°C and was detected in the soil solution. A pure strain of *Nitrosomonas europaea* added to an autoclaved soil resulted in oxidation of NH_4^+ to NO_2^--N. This indicated that nitrifiers are active in submerged soils. Nearly one-fourth of the NH_4^+-N applied was converted into NO_3^--N under flooded conditions at 30°C.

Reddy et al. [74] reported that the net nitrification rate in the oxidized surface layer of a flooded soil was 2.07 mg NO_3^--N kg^{-1} soil day^{-1}. Its occurrence and extent was controlled by oxygen diffusion rates, NH_4^+ concentration, thickness of the oxidized layer, and the levels of inorganic C [71].

Occurrence of nitrification in the rhizosphere of a rice plant, which Savant and DeDatta [91] referred to as site II, growing under flooded conditions is a subject of speculation as much as the oxidized or reduced state of the rhizosphere itself. No data are available on the occurrence of in situ nitrification in the rhizosphere of a flooded rice soil.

Problem soils

Sahrawat [84] studied the nitrification of soil N in several problem rice soils having a wide range of pH (3.4 to 8.6) and organic C (1.22 to 22.70%) by incubating them under aerobic conditions for 4 weeks at 30°C. It was found that the two acid sulfate soils (pH 3.4 and 3.7) and an acid soil (pH 4.4) did not nitrify during this period. Mineral and organic soils having pH $>$ 6.0 nitrified at rapid rates and accumulated NO_3^--N ranging from 98 to 123 mg kg^{-1} of dry soil. Alkalizing a near-neutral clay soil by adding 13 g kg^{-1} Na_2CO_3 increased the soil pH from 6.5 to 8.6 but the amount of NO_3^--N produced increased from only 106 mg to 118 mg NO_3^--N kg^{-1} of soil.

Nitrification in these soils, as measured by NO_3^- accumulation, was highly significantly correlated with the soil pH ($r = 0.86^{**}$, $n = 10$), but was not significantly correlated with their organic C or total N contents. However, no

Table 5. Depletion of carbon, total N and different soil N fractions in nine organic soils during six months of incubation at 30°C under aerobic or waterlogged conditions[a]

				Hydrolyzable N			
Incubation	C	Total N	Nonhydrolyzable N	Ammonium	Hexosamine	Amino acid	Unidentified[b]
			% loss on incubation[c]				
Aerobic	18.7	20.1	– 171.5	13.4	44.6	19.1	49.3
Waterlogged	18.2	16.2	– 188.4	9.8	47.8	18.0	40.2

[a] Adapted from Isirimah and Keeney [38]. Results reported are average for nine soil samples.

[b] Unidentified N = total hydrolyzable N – (ammonium + hexosamine + amino acid N).

[c] $\frac{\mu g\ N\ g^{-1}\text{ soil in original sample fraction} - \mu g\ N\ g^{-1}\text{ soil in incubated sample}}{\mu g\ N\ g^{-1}\text{ soil in original sample fraction}} \times 100.$

significant correlation existed between nitrification and soil pH when six soils having pH > 6.0 were considered, indicating that increase in soil pH beyond 6.0 did not significantly affect nitrification. It is known that NH_4^+ oxidation is slow in soils having pH lower than 5.0 but increases with increase in pH up to 8.0, although the rate of NO_2^- oxidation is greatly retarded at high pH because of toxicity of free NH_3 to *Nitrobacter* [30].

Isirimah and Keeney [38] studied N transformations in nine organic soils from Wisconsin by incubation under aerobic or waterlogged conditions at 30 °C for six months. Mineralization was faster in the more decomposed histic materials. The rate of decline in total organic C and N of the samples was similar under the two moisture regimes. On the average, 20 and 16% of the N was lost from the soil organic pool under aerobic and anaerobic conditions, respectively. Much of the mineralizable N released in these soils during incubation was derived from the acid-hydrolyzable organic N, largely the hexosamine-N, amino acid-N, and unidentified-N fractions. Microbial turnover of hydrolyzable N to refractory (nonhydrolyzable) N fractions was evident (Table 5). These results suggest that the unidentified soil N fraction and the hexosamine fraction contributed most to the mineralizable N pool under aerobic and anaerobic incubation.

Control of nitrification

Nitrification is at low ebb in soils having pH lower than 5, and an acid soil ecosystem is a deterrent to nitrification and its subsequent loss. But since the pH in reduced flooded soils tends to converge to near neutral, nitrification is likely to occur in acid soils which are kept flooded for prolonged periods and have enough organic matter to effect reduction.

Placement of fertilizer N in the reduced zone of a flooded soil reduces nitrification. While the NH_4^+ formed may diffuse to the oxidized layer, the amount susceptible to nitrification will be much less than if N fertilizer is applied to the surface. Also, application of fertilizer N when the rice root system is established and N is being rapidly taken up greatly reduces the availability of NH_4^+ for nitrification [7, 92].

Use of nitrification inhibitors, such as nitrapyrin or dicyandiamide, should be helpful in retarding nitrification, particularly in lowland rice fields where the moisture regime is fluctuating. Application of a nitrification retarding chemical at the site where nitrification occurs should be the most effective way of controlling nitrification [80]. Recent literature on the use of nitrification inhibitors and slow release N fertilizers for lowland rice soils is summarized by Prasad and DeDatta [69]. Sahrawat [80] and Mulvaney and Bremner [54] have discussed the potential of regulating the nitrification process in soil with the use of chemicals, and most of the recent literature on nitrification inhibitors can be found in these reviews.

Denitrification

General

Flooded soils adequately supplied with organic matter under warm climate provide a conducive environment for denitrification loss if the substrate NO_3^--N is available. Until recently [17], most of the denitrification loss estimates were made indirectly by the N balance approach. Thus the measured loss due to denitrification ranges widely. The denitrification process in soil ecosystems has been the subject of several excellent recent reviews [26, 29, 31, 62]. Focht [30], Patrick [59], and Savant and DeDatta [92] have covered the aspects of denitrification relevant to the mechanism of N loss in lowland rice soils. We will briefly discuss the recent work on the direct measurement of denitrification in flooded soils.

Several factors including soil pH, organic matter content, temperature, O_2 diffusion, and nitrification rate affect the denitrification rate in a flooded soil. Broadbent and Tusneem [9], using ^{15}N labeled $(NH_4)_2SO_4$, demonstrated that $^{15}NH_4^+$-N underwent nitrification and denitrification in flooded soil. They further found that when O_2 was absent in the system, no loss of $^{15}NH_4^+$-N occurred. This study provided direct evidence of the occurrence of concurrent nitrification-denitrification in a flooded soil. The loss of $^{15}NH_4^+$-N by denitrification as N_2 was 9.3% in an O_2 atmosphere but only 0.2% in an anaerobic (100% Kr) environment (Table 6). No labeled N_2O was detected. Growing rice plants markedly lessened the extent of N loss. However, inhibition of nitrification with nitrapyrin did not lessen loss of the surface applied $^{15}NH_4^+$-N.

Denmead et al. [27] reported that the loss of N as N_2O from a flooded field containing 40 kg NO_3^--N ha^{-1} in the surface soil (pH 5.8) was only 1.4% of the apparent loss. Similarly, Smith et al. [97] found that the loss of urea N (90 and 180 kg N ha^{-1}) applied to lowland rice as N_2O represented only 0.01 to 0.05% of the urea-N applied. Freney et al. [32] studied the loss of N as N_2O following applications of $(NH_4)_2SO_4$ to flooded rice in the Philippines

Table 6. Distribution of ^{15}N in various fractions in a Sacramento clay after 24 days of incubation under flooded conditions as affected by composition of atmosphere[a]

Composition of incubation atmosphere	NH_4^+-N	NO_3^--N	Organic + clay-fixed N	N_2	Total
		($\mu g\,g^{-1}$ of soil)			
100% O_2	4.9	8.1	68.4	9.3	90.7
30% O_2-70% Kr	13.7	0.4	8.6	1.2	96.9
100% Kr	13.3	0.2	83.9	0.2	97.6

[a]From Broadbent and Tusneem [9].

and reported that N_2O losses were only 0.1% of the 120 kg N applied. Similar low values of N_2O losses were reported by Craswell and DeDatta [17].

These studies suggest that N_2O is not a significatnt gaseous product of denitrification loss in lowland rice soils. Dinitrogen would appear to be the major gaseous product of denitrification in anaerobic soils because the capacity for reduction of N_2O to N_2 is much greater and also there are more limitations of terminal electron acceptors in anaerobic soils than in the well-aerated or upland soils, and thus N_2O is reduced more rapidly in anoxic soils [30].

The most accepted pathway of denitrification is

$$\underset{(+5)}{NO_3^-} \rightarrow \underset{(+3)}{NO_2^-} \rightarrow \underset{(+2)}{NO} \rightarrow \underset{(+1)}{N_2O} \rightarrow \underset{(0)}{N_2}$$

According to Delwiche [25] considering only the free energy change for the dissimilatory reduction of NO_3^- ion, the most efficient reaction with limited supply of organic substrate is that which results in the production of N_2. He hypothesizes that production of N_2O indicates some reaction barrier involving activation energy of some intermediate products which prevent the full utilization of the energy:

	$-\Delta G'298$ at pH 7	
	(per H_2)	(per NO_3^-)
$NO_3^- + 2H_2 + H^+ \rightarrow 1/2N_2O + 2\ 1/2H_2O$	46.67	93.35
$NO_3^- + 1\ 1/2H_2 + H^+ \rightarrow 1/2N_2 + 3H_2O$	53.62	134.07

where $\Delta G'298$ is the free energy change at the pH indicated.

Recently, Qi and Hua-Kuei [68] reported the isolation of a NO_2^- bacteria from lowland rice soil which oxidizes NH_4^+ to NO_2^- under anaerobic cultural conditions. The organism is a facultative anaerobic ecotype of NO_2^- bacteria and is reported to be closely associated with the denitrifying bacteria. This interesting association of the nitrifying and denitrifying bacteria suggests a unique route of loss of NH_4^+-N to N_2 through NO_2^- at the same location in a flooded soil.

The effect of the presence of plants on denitrification in a flooded soil has not been satisfactorily resolved and reports have indicated both positive and negative results [29, 92].

Dissimilatory nitrate reduction

Thermodynamically, under conditions of abundant organic substrate and limited availability of electron acceptors, the reduction of NO_3^- to NH_4^+ would be more efficient than the formation of N_2 [25].

$$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O$$

with $-\Delta G'298$ at pH 7 being 37.25 per H_2 or 149.00 per NO_3^-.

This has been verified by studies that have shown that significant amounts of NO_3^--N may be reduced to NH_4^+-N in anaerobic soils or sediments [10, 11, 14, 43, 45, 48, 98, 100, 103]. The process is termed dissimilatory because it is not inhibited by NH_4^+ or glutamine. These reports indicated that up to 50% of the NO_3^--N could be reduced to NH_4^+-N in some situations, particularly in highly reduced sediments. However, the significance of this process in the N economy of lowland rice soils under field conditions is yet to be ascertained. There is little doubt that if it does occur it could be an important process for conserving N from loss.

Urea hydrolysis

General

Comparatively less emphasis has been placed on urea hydrolysis and urease activity meansurements in flooded soils compared to upland soils. We do know that urease is common in flooded soils. DeLaune and Patrick [24] reported that urease activity was affected by pH but not by water content. Urea hydrolysis occurred in the soil and was negligible in the floodwater overlying the soils. Sahrawat [79] studied urease activity in some Philippine lowland rice soils and found that the urease activity was the lowest in two acid sulfate soils but was higher in mineral soils with near-natural pH and an organic soil. The urease activity in a near-neutral clay was not affected by adding 0.5% NaCl but was markedly increased by 1.3% Na_2CO_3 addition. The floodwater of 11 diverse Philippine lowland rice soils collected from field or greenhouse experiments indicated that the urease activity varied markedly among soils. Except for the floodwater from an acid sulfate soil, all other water samples exhibited significant amounts of urease activity. The highest urease activity was detected in the floodwater of a submerged Histosol. Mineral soils with high pH showed higher urease activity in their

Table 7. Urease activity in floodwater of some Philippine lowland rice soils[a]

	Floodwater		Urease activity[b]	
Soil	Source	pH	Range[c]	Mean
Calalahan sandy loam	Greenhouse	3.9	0–0	0
Quingua silty loam	Greenhouse	6.8	4–6	5
Luisiana clay	Field	6.0	5–7	6
Buenavista clay loam	Greenhouse	7.6	5–7	6
Maahas clay salinized	Field	8.8	6–10	8
Maahas clay	Field	8.0	8–11	9
Pila clay	Greenhouse	7.6	8–11	10
Paete clay loam	Greenhouse	7.5	10–14	12
Lipa loam	Field	8.5	13–19	16
Maahas clay, alkalized	Field	9.4	27–31	29
Lam Aw peat	Field	6.0	33–40	36

[a] From Sahrawat [79].
[b] Urease activity expressed as μg NH_4^+-N formed 25 ml floodwater^{-1} h^{-1} at 30 °C.
[c] Four analyses.

floodwaters than those with lower pH (Table 7). This study suggested that the urease activity in floodwater of some soils would hydrolyze significant quantities of surface-applied urea. Studies are needed to evaluate the various factors that affect the urease activity in surface waters because this may be important in relation to NH_3 volatilization loss.

Sahrawat [87] found that the urease activity to ten Philippine lowland rice soils was highly significantly correlated with total N ($r = 0.91^{**}$) and organic C ($r = 0.89^{**}$), but was not significantly correlated with other soil properties. Multiple regression analyses showed that organic matter content of these soils as measured by organic C and total N accounted for most of the variation in urease activity.

Vlek et al. [109] studied urea hydrolysis in three flooded soils and reported that the hydrolysis of urea occurred at the floodwater-soil interface. They showed that the urease activity in the flooded soils was dynamic and was affected by the length of the presubmergence period.

Savant and DeDatta [92] have summarized the recent results obtained on the transformations of different kinds of urea fertilizers in lowland rice soils.

Control of urea hydrolysis

Control of urea hydrolysis in lowland rice soils has received little research attention compared to arable soils [54, 80]. It would be advantageous to control urea hydrolysis in flooded soils since this would decrease N loss due to NH_3 volatilization. However, any advantage may be offset by leaching of urea [54, 80].

Use of controlled release urea-based fertilizers or formulations of urea with urease inhibitors are the two approaches most often suggested for slowing urea hydrolysis. In a recent study, Vlek et al. [109] evaluated the effect of three urease inhibitors with and without an algicide on urea hydrolysis in three flooded soils. Application of potassium ethyl-xanthate and 3-amino-l-H-1,2,4-triazole at 2% (w/w) of urea had no effect on urea hydrolysis or on the dynamics of NH_4^+ concentration in the flood water of soils. Phenylphosphorodiamidate (PPD) [49] applied at 1% (w/w) of urea was very effective in retarding urea hydrolysis for three days. Use of an algicide (simazine herbicide) application to the floodwater of the soils depressed the concentration of NH_3 in floodwater but had little effect in the presence of PPD. A subsequent study by Byrnes et al. [13] showed that PPD was effective in retarding urea hydrolysis in a flooded soil and that its use decreased the loss from 23% to 9% of the ^{15}N applied in a greenhouse experiment. However, application of PPD lowerd dry matter production of rice.

Summary and perspectives

Critical pathways for control

The review of literature on N transformations in flooded soil indicates that NH_3 volatilization could be an important mechanism of loss, especially with urea fertilizers. Control of NH_3 volatilization losses from flooded soils could be achieved by: (i) Placement of the fertilizer in the reduced layer and by proper timing of its application. (ii) Use of algicides may help stabilize pH changes in flood waters and thereby reduce losses of volatile NH_3 [109]. However, use of an algicide may retard biological N_2 fixation in the floodwater and this aspect needs to be carefully evaluated before recommending their use. (iii) Some recent studies have suggested that PPD is an effective blocker of urease activity in flooded soils, and in improving the recovery of fertilizer N by rice under greenhouse conditions. Field studies are needed to further evaluate the efficacy of this and other urease inhibitors for their role in minimizing losses from fertilizer urea. As mentioned earlier, the advantage of retarding urea hydrolysis in some situations may be offset by leaching of urea and should be considered while recommending their use. (iv) Control release of urea can be achieved by use of sulfur-coated ureas and larger granules of urea (called urea supergranules). Their slow-release characteristic combined with the ease in their point application in a flooded soil further increases their efficacy to retard urea hydrolysis and subsequent loss as volative NH_3 [92].

Control of nitrification to control denitrification

Since denitrification occurs only when NO_3^- is present, the best way to control this mechanism of N loss is to minimize nitrification. Also, to date there are no chemicals available that can retard denitrification directly. There is an obvious need to develop chemicals that are cheap and effective inhibitors of nitrification in a flooded soil water system with a wide range in oxidation status. Placement and timing of the fertilizer is probably the most cost-effective means of reducing losses of N due to nitrification-denitrification. Use of urea supergranules or coated fertilizer with controlled release of N which allows plants to compete with microorganisms for fertilizer N should help in reducing N loss by any mechanism, including nitrification-denitrification.

Leaching

In flooded soils with sandy texture, the losses of N due to leaching could be significant. Under these situations, nitrification inhibitors should be more effective than urease inhibitors in minimizing loss of NO_3^-. Urease inhibitors and urea supergranules under these specific high percolation soil conditions may not have any advantage. Perhaps the best answer to minimize leaching loss of N still lies in cultural practices such as split application of fertilizer N and puddling of the rice fields before planting. Slow-release sulfur-coated urea also minimizes N losses by leaching and maximizes N use efficiency.

Need for management

It becomes clear from the foregoing discussion that the most economic and at times even the most effective way of minimizing N losses by controlling critical pathways of N transformations, lies in the best crop and soil management practices. These practices allow the plants to compete effectively with microorganisms involved in the loss of N and thus help in minimizing such losses. Any mechanism or management practice which minimizes NH_4^+ availability for nitrification or volatilization, including plant uptake, should minimize losses of N. We need also a clearer picture of N mineralization patterns so that crop N needs and N release patterns from the soil organic matter can be harmonized.

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