Nitrogen Transformations in Submerged Soils

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Soils with continuous or intermittent submergence by water are widely distributed worldwide. They occur in a range of ecosystems including rice (*Oryza sativa* L.) fields, wetlands, estuaries, and floodplains. Such ecosystems often occur at low elevation in the landscape and are poorly drained with high retention of water. In addition, some upland areas with poor drainage can undergo periodic submergence and soil saturation. Moreover, the sediments in ocean, lake, and stream bottoms have similar biogeochemical and physical characteristics and N transformations as submerged agricultural soils.

Rice fields surrounded by earthen levees to retain rain and irrigation water and ensure soil submergence are one of the world's major agricultural ecosystems. Rice is a staple food for nearly half the world's population, and about 95% of the global rice production occurs on fields with soil submerged during at least part of the rice-cropping period. The sustained productivity of this rice ecosystem, which ensures production of sufficient food for a growing world population, relies heavily on the input and management of N.

Nitrogen transformations in submerged soils are markedly different from those in drained, aerated soils. These differences affect the prevalent soil microorganisms and microbial activities and the turnover, availabilility, and losses of N. To deal with the differences in N transformations between submerged and drained soils it is necessary to understand the biogeochemical conditions existing in submerged soils. This chapter is an update of an earlier review by Patrick (1982).

Properties of Submerged Soils

A unique feature of submerged soils, affecting N transformations, is the depletion of oxygen (O_2) throughout most of the root zone (Ponnamperuma, 1972).

When a soil is submerged with water, the supply of O_2 into the soil is greatly reduced because the diffusivity of O_2 in water is about 10,000 times less than its diffusivity in air. As a result of this tremendous decrease in gas exchange between air and soil after submergence, the supply of O_2 cannot meet the demand of aerobic organisms. Within hours of soil submergence, facultative microorganisms predominate. After a few hours to days, anaerobic microorganisms accumulate in soil layers. Facultative and anaerobic organisms use oxidized soil substrates as electron acceptors in their respiration, thus reducing the soil components in a sequence predicted by thermodynamics.

The water column overlying a submerged soil contains dissolved O_2, which typically moves a small distance into the soil before it is depleted. A submerged soil is consequently differentiated, based on O_2 penetration, into an aerobic (oxidized) surface layer and an underlying anaerobic (reduced) layer. The thickness of this oxidized surface layer of soil is determined by the net effect of O_2 supply from the overlying water and the consumption rate of O_2 in soil. A high O_2 consumption rate in soil results in a thin oxidized soil layer of about 1 mm in thickness. A low O_2 consumption rate results in a thicker oxidized layer.

The consumption of O_2 in soil is directly related to the concentration of an energy source, including electron donors. Soils with an appreciable supply of readily decomposable organic matter, a typical electron donor, usually have a thin oxidized soil layer because of the high O_2 consumption. When decomposable organic matter is high in the overlying water or at the soil surface, the dissolved O_2 in water can be consumed before it reaches the soil surface. In such case, there is no surface aerobic soil layer (DeLaune et al., 1979). This condition is typically transient with the continuous supply of O_2 from the atmosphere into the overlying water eventually satisfying the O_2 demand in the water column and O_2 then diffusing into soil.

Plants adapted to submerged soils have developed gas exchange processes enabling O_2 and other gases to pass through the plant's emergent parts into the root zone. In many of these plants, including rice, O_2 is transported through porous internal aerenchyma tissue to roots, where most of the O_2 is consumed in root respiration. Some of the O_2 reaching the roots escapes into the surrounding soil and oxidizes reduced components. This creates a thin aerobic zone surrounded by a much more extensive anaerobic soil zone.

The aerobic zone surrounding plant roots and on the surface of submerged soils can often be distinguished by a thin yellowish layer associated with oxidized iron (Fe^{3+}). The aerobic layer is characterized by the presence of high redox potential, whereas the adjacent anaerobic soil zone is associated with low or more negative redox potential. The adjoining aerobic and anaerobic soil zones support a diversity of microbial populations and associated metabolic activities. Aerobic microorganisms are distributed in submerged soil based on the presence of O_2, and facultative and obligate anaerobic microorganisms are distributed based on the presence of electron acceptors for their respiration. In the absence of O_2, aerobic microorganisms die or remain inactive, while anaerobic microorganisms proliferate. Anaerobic microorganisms use oxidized soil components, such as mineral constituents containing Fe^{3+} and Mn^{4+} and dissimilation products of soil organic matter (SOM) as electron acceptors in their respiration.

Lowland rice fields in Asia are globally the main agricultural ecosystem with submerged soils. These rice fields are typically flooded before plowing and harrowing for rice production. This process of tillage at soil saturation, referred to as
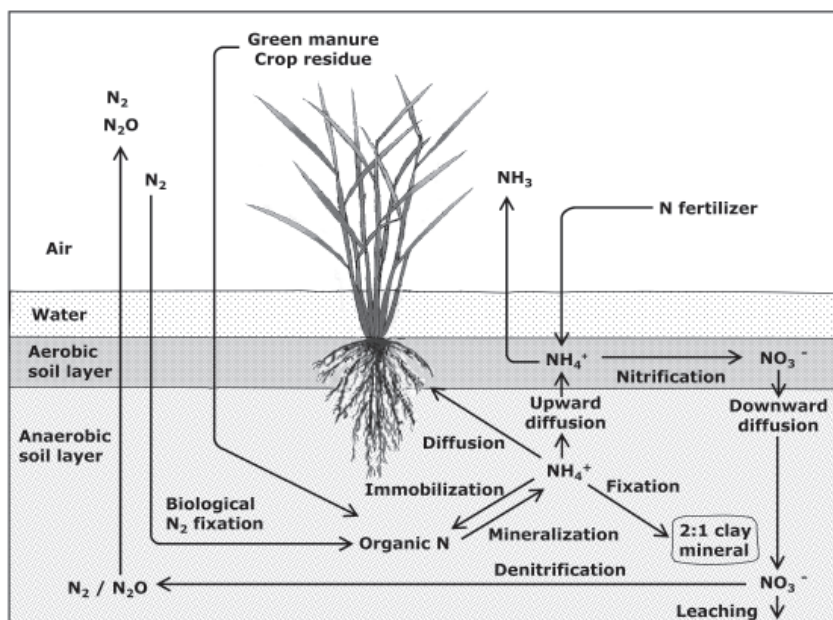
Fig. 11–1. A schematic diagram of N transformations in a submerged soil.

puddling, destroys soil aggregates. Puddling eliminates water transmission pores, reduces the percolation rate, and reduces gas exchange between the soil and outer atmosphere (Sharma and De Datta, 1986). As a result of the reduced gas exchange, O_2 entering the soil is rapidly depleted near the soil surface leading to a relatively thin aerobic soil layer. Puddling also results in the formation of a hardpan that restricts downward water flow, thereby helping to maintain soil saturation and reduce loss of nutrients by leaching. The rice crop is established either by transplanting or by broadcasting of germinated seeds on flooded or saturated soil, and the soil is maintained flooded or saturated throughout most or all the period of rice growth.

Some lowland rice is also grown on nonpuddled soils, but in these production systems the soil is typically submerged at least part of the time. One method of rice crop establishment, including in the USA, is to sow germinated seeds onto nonpuddled, saturated, or flooded soil. In such case, the rice field is irrigated and left flooded for much of the growing period. Another method, practiced in some temperate irrigated rice production systems and some tropical rainfed lowland ecosystems in Asia, is to establish rice by seeding on nonpuddled, nonsaturated soil. The soil becomes submerged after crop establishment by either irrigation or water accumulating from monsoon rains.

On an annual basis, most lowland rice fields undergo alternate submergence and drying. The soils are submerged for at least part of the period during production of rice, but they typically dry and become aerated during the period between rice crops. At this time the soil is normally either left fallow or grown with upland crops. In California, rice fields are often reflooded during the winter months between rice crops to increase residue decomposition and provide a habitat for migratory waterfowl. In rainfed ecosystems and irrigated environments with insuf-

ficient or irregular water supply, the soils can also undergo alternate drying and rewetting during rice growth. In some irrigated rice ecosystems with good water control in China, farmers drain rice fields during the vegetative growth phase. This midseason drainage and short-term drying of the submerged soil can control excessive tillering of rice, help regulate leaf area of rice at desired levels, and improve root activity. The midseason drainage can, however, also influence N transformations and N loss processes.

Nitrogen Transformations

The forms of N present in submerged soils are generally similar to those in aerated soils; but the relative magnitude of the N forms, particularly nitrate (NO_3^-) and ammonium (NH_4^+), and N transformation are markedly affected by the oxidation status of soil (Fig. 11–1). Nitrate is the dominant form of inorganic N in drained, aerated soils; whereas NH_4^+ is the dominant and stable form of inorganic N that accumulates in submerged soils. When O_2 is present, such as in aerated soils and in the localized aerobic zone of submerged soils, NH_4^+ is converted to NO_3^-. This NO_3^- is not readily denitrified (reduced) in the aerated soil, and it can consequently accumulate. In the anaerobic zone of submerged soils, which constitutes the vast proportion of a submerged soil, NH_4^+ is not converted to NO_3^-. Nitrate moving into the anaerobic zone or residing in the soil before submergence and depletion of O_2 can be readily denitrified.

Nitrogen is typically the main limiting nutrient in the production of lowland rice, and use of N fertilizer is vital for the sustained production of sufficient rice to meet demand. About 20% of the global production of fertilizer N is used in rice production systems that experience soil submergence (Dat Tran, personal communication, 2001). Yet the use efficiency of this fertilizer N by the crop is typically low, due at least in part to losses of the applied fertilizer N arising from unique features of submerged soils as compared with aerated soils.

The main N transformation processes in submerged soils—as in aerated soils—are mineralization, immobilization, nitrification, denitrification, ammonia (NH_3) volatilization, and biological N_2 fixation. Soil submergence modifies these processes, and a unique feature of submerged soils is the simultaneous formation and loss of NO_3^-, occurring within the adjoining aerobic and anaerobic soil zones. Submerged soils as compared with aerated soils are favorable environments for loss of N by nitrification–denitrification, NH_3 volatilization, and for addition of N via biological N_2 fixation (BNF).

Mineralization and Immobilization

Mineralization, or more specifically ammonification—the conversion of soil organic N to ammonium—supplies plant-available N in submerged agricultural soils. Even with high-yielding rice crops receiving high rates of fertilizer N, >50% of the total N assimilated by the crop typically originates from the breakdown of soil organic N compounds (Mikkelsen, 1987; Cassman et al., 1998). This breakdown of organic N in submerged soils is characterized by anaerobic decomposition, which involves different microorganisms and endproducts than aerobic decomposition. Ammonium accumulates in anaerobic decomposition due to the absence of O_2, which is required for conversion of NH_4^+ to NO_3^-.

Microbial decomposition of organic matter in aerated soil is accomplished by a wide range of microorganisms including fungi, heterotrophic bacteria, and actinomycetes. Respiration by these organisms is associated with high energy release, and the decomposition of substrates progresses rapidly with evolution of CO_2. As cell synthesis proceeds, there is a heavy demand for mineral nutrients, particularly N. Decomposition in the bulk volume of a submerged soil, on the other hand, depends on a relatively restricted bacterial microflora. These anaerobes operate at a lower energy level and are less efficient than aerobes as a consequence of incomplete decomposition of carbohydrates and synthesis of fewer microbial cells per unit of organic C degraded (Waksman, 1929; Payne, 1970). The processes of both decomposition and cell synthesis are consequently slower under anaerobic than aerobic conditions. In aerobic soil the main endproducts of decomposition are CO_2, NO_3^-, SO_4^{2-}, water, and resistant residues. The main endproducts of anaerobic decomposition are CO_2, CH_4, organic acids, NH_4^+, H_2S, and resistant residues (Acharya, 1935a, 1935b; Tusneem and Patrick, 1971).

The breakdown of SOM and plant residues is typically slower in submerged than aerobic soil (Acharya, 1935c; Villegas-Pangga et al., 2000). Hence, a lower gross N mineralization rate would be expected in submerged soils as compared with aerobic soils. Gross N immobilization is characteristically lower in submerged soils because of the low metabolic requirement of anaerobic microorganisms for N (Acharya, 1935a). The net effect of the lower gross mineralization and lower gross immobilization is often a higher net N mineralization in submerged than aerobic soils, leading to higher rates of inorganic N release in submerged soil (Tusneem and Patrick, 1971). Because of the low N requirement of anaerobic metabolism, the net release of inorganic N from decomposing plant residue would expectedly occur at a higher C/N in submerged rather than aerobic soil. Incubations with 20 soils without residue confirmed lower gross N immobilization in submerged rather than aerobic conditions (Wang et al., 2001b). Net N mineralization was not always higher under submerged rather than aerobic conditions in this study, but it is possible the observed instances of lower net N mineralization with submerged soil resulted from higher N loss in submerged soil (Wang et al., 2001b). The net buildup of inorganic N in submerged soils is reportedly higher in the presence than the absence of rice plants. The influence of the rice plant depends on rice genotype (Ghosh and Kashyap, 2003) and supposedly involves more processes than merely a reduction in N loss (Kundu and Ladha, 1997).

Microbes in rice soils are an important temporary sink for N applied as fertilizers and residues (Bird et al., 2001, 2003). In a series of experiments using ^{15}N-labeled residues and fertilizers in a temperate rice system in California, mobile humic acid and microbial biomass became the primary active sink for sequestered ^{15}N following the incorporation or burning of rice residues for 4 yr. About 30% of the fertilizer ^{15}N recovered in the soil was in the mobile humic acid fraction and about 20% was in microbial biomass (Bird et al., 2002). The half-life of immobilized ^{15}N was significantly lower for microbial biomass (0.65 yr) than for mobile humic acid (8.9 yr) and fulvic acid (6.9 yr), and microbial biomass ^{15}N was the main source of ^{15}N recovered by the following rice crop (Eagle et al., 2001; Bird et al., 2002).

The total amount of microbial biomass N in a temperate rice system in California ranged from 45 kg N ha^{−1} during the winter months to 120 kg N ha^{−1} during the growing season, and the incorporation of residues significantly increased microbial

biomass N (Bird et al., 2001). Microbial biomass N by contrast in a continuous double-cropped rice system in the Tropics was lower and remained relatively stable at about 20 to 35 kg N ha^{-1} throughout the growing season (Witt et al., 1998). In this study, microbial biomass N was not strongly affected by residue incorporation or fertilizer N application. Even though microbial activity influenced residue decomposition and the net release and availability of N, microbial biomass N was a poor indicator of N dynamics and availability of N to the rice crop (Witt et al., 1998, 2000a).

Many studies have examined relationships between measurements of net N mineralization and the N accumulation or yield of rice grown on submerged soil. In a number of instances, direct relationships were reported between laboratory measurements of "plant-available N" and the N content or yield of rice (Dolmat et al., 1980; Kai et al., 1984; Manguiat et al., 1994). The total accumulation of N by rice in the absence of fertilizer N has increasingly been used as a field-based measurement of soil N supply, referred to as soil N-supplying capacity (SNSC) or indigenous N supply (INS) (Olk et al., 1999b; Dobermann et al., 2003). Studies in the 1990s, highlighted the high spatial and temporal variability associated with field-measured INS, based on total accumulation of N by rice in zero-N plots (Cassman et al., 1996b). Field-measured INS is often not correlated with SOM, laboratory measurements of soil N availability, or field measurements of inorganic soil N (Cassman et al., 1996b; Adhikari et al., 1999), and even when relationships exist, the measured soil parameters explain only a small portion of the variation in rice yield in zero-N plots (Yadav, 2003). These findings highlight the importance of site-specific management of fertilizer N, in which the times and rates of N fertilization are dynamically adjusted for variations in INS (Cassman et al., 1996c; Dobermann et al., 2002).

Whereas lowland rice soils are submerged for all or part of the rice-growing season, they typically are dry and become aerobic between rice crops when fields are fallow or upland crops are grown. In some parts of Asia, access to irrigation has enabled intensification of rice cropping with production of two and three rice crops per year. Under such conditions the period of soil submergence is prolonged and soil aeration between crops decreases or disappears. Prolonged soil submergence promotes C and N sequestration, leading to maintenance or buildup of SOM (Cassman et al., 1995; Bronson et al., 1997a; Witt et al., 2000b; Pampolino et al., 2008).

Prolonged soil submergence and anaerobic soil conditions can, however, also promote a buildup of less-decomposed substances, which become incorporated into young SOM fractions. Prolonged duration of soil submergence increased phenolic content of SOM and increased mobile humic acid and calcium humate content, which represented about 20 to 25% of the total SOM in intensively cultivated tropical rice soil (Olk et al., 1996, 1998, 1999a; Bao Ve et al., 2004a, 2004b). Concern was raised that a buildup of phenolic compounds originating from less humification could immobilize N abiotically, thereby reducing the rate of net N mineralization (Olk et al., 2000, 2007). An analysis of soils from intensively cropped long-term experiments in the Philippines did not indicate formation of heterocyclic N or other aromatic forms of N arising from long-term continuous cropping of rice on submerged soils (Mahieu et al., 2000). Long-term yield trends in these experiments reveal no yield decline in the past 10 to 20 yr in zero–N plots receiving other nutrients, thereby suggesting no decline in INS (Padilla, 2001). Soil drying immediately after rice harvest has been proposed as a practice to prevent a net decline in N-supplying capacity arising from abiotic immobilization of N (Olk et al., 2007);

but recent field research consistently found no net increase in soil NH_4^+ or INS following soil drying rather than continuous soil submergence between rice crops with and without the retention of rice residues (Thuy, 2004; Buresh et al., unpublished data, 2007). Greater inputs of N during continuous soil submergence via BNF, biological N mineralization, and irrigation water matched or exceeded any decline in N-supplying capacity arising from abiotic immobilization of N.

Soil submergence during the fallow winter months in a temperate rice system in California has been promoted to provide a habitat for migratory waterfowl. The inclusion of an anaerobic period by flooding the fields had no significant effect on young SOM fractions as determined by the mobile humic and fulvic acid contents. Two relative short periods of soil aeration at the start and finish of the winter flooding, which presumably enable aerobic microbial communities to flourish, were sufficient for the degradation of any accumulation of abiotically immobilized N during the periods of soil submergence (Bird et al., 2002).

Ammonia Volatilization

Ammonia volatilization is now recognized as a major process by which fertilizer N is lost from rice fields with submerged or saturated soils. A substantial portion of the fertilizer N broadcast into the floodwater of rice fields or incorporated into puddled soils before rice establishment can accumulate in the floodwater as ammoniacal N ($NH_4^+ + NH_3$) within the week after N application. Urea, a common fertilizer for rice in Asia, is rapidly hydrolyzed within the week after application to submerged soils (Fillery et al., 1984). Ammoniacal N originating from the hydrolyzed urea accumulates in floodwater, and the peak concentration of ammoniacal N in the floodwater of tropical rice fields typically occurs within 1 to 5 d after urea application. High concentrations of ammoniacal N together with high floodwater pH and temperature favor loss of added fertilizer N by NH_3 volatilization (Vlek and Stumpe, 1978; Cai, 1997).

The magnitude of NH_3 loss from submerged soils is directly related to the content of aqueous NH_3 or partial pressure of ammonia (ρNH_3) in water at the interface with the atmosphere. Aqueous NH_3 as a fraction of total ammoniacal N is directly influenced by water pH and temperature. Aqueous NH_3 is negligible below pH 7.5, but it increases rapidly from pH 7.5 to 10. At pH 9.2 about 50% of the ammoniacal N in water is present as NH_3 (Vlek and Craswell, 1981). Aqueous NH_3, at a constant ammoniacal N concentration and pH, increases linearly with temperature, resulting in nearly a fourfold increase with a change in temperature from 10 to 40°C (Vlek and Craswell, 1981). Water pH is, however, a more important factor influencing NH_3 loss than temperature (Jayaweera and Mikkelsen, 1990).

Photosynthetic activity by aquatic biomass in floodwater and on the surface of saturated soil results in depletion of CO_2 during the daytime and an accompanying elevation in water pH. Floodwater pH typically displays a diurnal pattern synchronized with the cycle of photosynthesis and net respiration or the depletion and addition of CO_2 to floodwater (Mikkelsen et al., 1978). Elevations in the midday pH of floodwater to above 9 in the week following N fertilization have commonly been reported for puddled rice soils in the Tropics (Fillery et al., 1986a). Photosynthetic activity by aquatic biomass in the floodwater and the associated elevation in midday pH of floodwater are typically most pronounced in the 3 wk

after rice establishment when algal growth can be favored by basal applications of fertilizer, particularly P, and minimal shading from rice plants.

Ammonia loss from fertilizer N applied to young rice increases linearly with wind speed and ρNH_3 (Fillery et al., 1984). Increasing wind speed enhances NH_3 loss by accelerating the transfer of NH_3 away from the water–atmosphere interface, thus maintaining a gradient in ρNH_3 between the water and adjoining atmosphere. Ammonia loss can be reduced with rice establishment practices that reduce wind speed near the floodwater surface. Young broadcast-seeded rice has been reported to have lower wind speed at 3 to 10 cm above floodwater and lower associated NH_3 loss from applied fertilizer N than young transplanted rice (De Datta et al., 1991). The denser plant population and greater surface cover with broadcast seeded rice, which restricted gas exchange at the floodwater–atmosphere interface, presumably accounted for the lower ammonia loss.

The magnitude of NH_3 loss at a given wind speed follows diurnal patterns that parallel the diurnal fluctuations in floodwater pH, which are directly related to ρNH_3. Ammonia loss, floodwater pH, and ρNH_3 typically peak at about 1200 to 1400 h and are lowest overnight. The ρNH_3 can be calculated from measured ammoniacal N, temperature, and pH in floodwater (Denmead et al., 1982). Use of calculated ρNH_3 together with measured wind speed at one height in a rice field provides a simple technique for approximating the relative NH_3 loss among fertilizer N sources and management practices (Freney et al., 1985).

Ammonia volatilization was generally not considered an important N loss process in submerged agricultural soils before the mid-1970s. Research in the mid-1970s, however, created awareness that NH_3 volatilization might be a mechanism for appreciable rapid loss of fertilizer N and highlighted the need for quantification of the importance of NH_3 volatilization in rice fields (Bouldin and Alimagno, 1976; Mikkelsen et al., 1978; Vlek and Craswell, 1979). Micrometeorological techniques enabled the direct field measurement of NH_3 loss without disrupting natural environmental conditions. These techniques overcame the uncertainties regarding the reliability of NH_3 loss measurements conducted with static or forced-air-exchange enclosures that disrupted processes influencing the exchange of gases at the floodwater–air interface. The first use of the micrometeorological technique to directly quantify NH_3 loss from an irrigated rice field was at a site in the Philippines, which was fertilized with ammonium sulfate (Freney et al., 1981). The measured losses of NH_3 were relatively small (5–11% of applied N). A series of subsequent studies focused on urea, the main N fertilizer for rice in Asia and a source generally prone to higher NH_3 loss than ammonium sulfate.

Numerous micrometeorological measurements were conducted at diverse sites in the 1980s to quantify the effect of various methods, times, and rates of urea application on loss of applied urea N (De Datta and Buresh, 1989). The directly measured losses started within a few hours after N application and ranged up to >50% of applied urea N within 7 to 10 d after N application. Ammonia loss was generally greater when broadcast to young rice within 3 wk after transplanting than to older rice near the panicle initiation stage. In a series of experiments in the Philippines, directly measured NH_3 loss accounted for 27 to 56% of the urea N broadcast into floodwater at 10 to 21 d after transplanting (Fillery et al., 1984; Fillery and De Datta, 1986; De Datta et al., 1989). Ammonia loss at panicle initiation in contrast represented only 10 to 15% of the applied urea N (Fillery et al., 1984). The lower NH_3 loss from urea applied to older rice arises from greater shading of

the floodwater by the rice canopy, which reduces photosynthetic activity of the aquatic biomass thereby reducing CO_2 depletion and the associated elevation in pH and pNH_3. The larger canopy of the rice plant might also reduce NH_3 loss by restricting gas exchange at the floodwater–atmosphere interface (Humphreys et al., 1988).

Incorporating urea before transplanting rather than broadcasting into floodwater at 10 to 21 d after transplanting often reduces NH_3 loss (De Datta et al., 1989). The loss of NH_3 from basal incorporated urea is reportedly less when floodwater is first removed and urea is broadcast and incorporated into saturated soil with no floodwater rather than broadcast and incorporated with standing floodwater (De Datta et al., 1987b, 1989). Tillage to incorporate fertilizer is, however, typically more energy demanding in the absence of floodwater. Implements available to Asian rice farmers are moreover only partially effective in reducing the buildup of ammoniacal N and pNH_3 in floodwater (Padilla et al., 1990), and N losses from incorporated urea can still remain substantial under farmers' practices. The crop requirement for fertilizer N is small in the 2 to 3 wk following transplanting or sowing rice, and Asian rice farmers were reluctant to adopt the incorporation of fertilizer N before transplanting or sowing rice (Fujisaka, 1994).

Ammonia volatilization is now well recognized as a major pathway for loss of fertilizer N applied to lowland rice fields (Zhu, 1997; Cai et al., 2002). The key to curbing this NH_3 loss is to reduce pNH_3 in water at the water–atmosphere interface of saturated or submerged soils. This can be achieved by preventing an elevation in water pH, restricting gas exchange at the water–atmosphere interface, or preventing the buildup of ammoniacal N (Simpson et al., 1988). The use of algicide can restrict the elevation in floodwater pH and reduce buildup of pNH_3 following N fertilization because floodwater pH is largely associated with the photosynthetic activity of algae (Chaiwanakupt et al., 1996). The use of algicide, however, can result in increased ammoniacal N in floodwater (Muirhead et al., 1989) because algae when present assimilate some ammoniacal N (Meyer et al., 1989). Films of organic compounds (Cai et al., 1987), algal scum (Zhu et al., 1989), and azolla (Vlek et al., 1995; Mandal et al., 1999; de Macale and Vlek, 2004) on the surface of floodwater have been shown to reduce NH_3 loss by restricting the transfer of ammonia from floodwater to the overlying atmosphere. Azolla can also assimilate excess fertilizer N during early crop growth stages when the supply of N from fertilizer exceeds crop demand, and then subsequently cycle this fertilizer N to the rice through mineralization of azolla N when the crop demand for N is higher (Cisse and Vlek, 2003a, 2003b).

The buildup of ammoniacal N in floodwater can be reduced by more effective incorporation and placement of fertilizer N into puddled soils (De Datta et al., 1987b, 1989; Schnier et al., 1990, 1993; Devasenapathy and Palaniappan, 1996), application of fertilizer N immediately before rather than after permanent flooding in nonpuddled soils (Bacon et al., 1988; Humphreys et al., 1992), controlled release fertilizers (Oertli, 1980), and urease inhibitors (Buresh et al., 1988a, 1988b; Byrnes and Amberger, 1989; Freney, 1997). The application of fertilizer N immediately before rather than 14 d before permanent flooding reduces NH_3 loss during production of dry-seeded rice on nonpuddled soils (Griggs et al., 2007). Deep placement of N fertilizer to minimize N loss was first reported in Japan (Mitsui, 1955), and it has since received considerable research attention (Cao et al., 1983; De Datta et al., 1987a; Savant et al., 1992). Urease inhibitors offer the attractive option of adding

a small quantity of chemical additive to urea that slows urea hydrolysis and prevents a buildup of ammoniacal N in floodwater.

Nitrification–Denitrification

Nitrification—the biological conversion of NH_4^+ to NO_3^-—requires free O_2. As a result it is restricted in submerged soils to oxidized zones, which include the water column, a small layer of surface soil, and soil in the root zone of aquatic plants. The magnitude of nitrification is regulated by the availability of O_2, which determines the fraction of the total soil volume occupied by aerobic zones, and NH_4^+ concentration in these aerobic zones. Ammonium in aerobic zones originates from formation by ammonification within the aerobic zone, inputs of external N including fertilizer, and diffusion of NH_4^+ from adjacent anaerobic soil zones. Nitrate formed by nitrification is stable within an aerobic zone, but it can be readily reduced in adjacent anaerobic soil zones. Oxygen availability is typically the factor most limiting nitrification in submerged agricultural soils.

Nitrate does not accumulate in the anaerobic zone because of the high demand for NO_3^- to serve as an electron acceptor in the absence of O_2. Denitrification is the dissimilatory reduction of NO_3^-, whereby NO_3^- serves as a terminal electron acceptor and is reduced to gaseous endproducts of nitrous oxide (N_2O) and nitrogen gas (N_2). Denitrification is mediated by heterotrophic microorganisms; and its rate is regulated by NO_3^- concentration and available C, which serves as an energy source or electron donor. The supply of NO_3^- originating from the aerobic zones is typically the factor limiting denitrification in submerged soils (Aulakh et al., 2000a).

In submerged soils, the demand for NO_3^- to serve as an electron acceptor is typically much greater than the demand for NO_3^- as an N source for microbes and plants. Assimilatory reduction of NO_3^- where NO_3^- is used as a nutrient source and incorporated into cell biomass is consequently not a significant process. Anaerobic soil conditions promote the accumulation of NH_4^+, which serves as the primary inorganic N source for microbes and plants. Assimilatory reduction of NO_3^- would only be expected when NH_4^+ levels are low and NO_3^- levels are high.

Dissimilatory reduction of NO_3^- to NH_4^+ can occur in highly reduced soil (Stanford et al., 1975). This pathway involves transfer of eight electrons for a change in oxidation state of N from +5 (NO_3^-) to –3 (NH_4^+), whereas denitrification involves transfer of four or five electrons for a change in oxidation state of N to +1 (N_2O) or zero (N_2). Dissimilatory reduction of NO_3^- to NH_4^+ is mediated by strict anaerobic microorganisms (Caskey and Tiedje, 1979) and consequently requires the presence of NO_3^- in a strongly anaerobic soil zone (Buresh and Patrick, 1981). However, it typically represents only a small fraction of the total dissimilatory reduction of NO_3^- in submerged soils. Nitrate reduction to NH_4^+ for example represented <5% of the total reduction of NO_3^- following the flooding of a rice soil (Buresh et al., 1989). Denitrification is the dominant pathway of dissimilatory NO_3^- reduction in submerged soils (Patrick, 1982; Aulakh et al., 1992).

A characteristic of submerged soils with important implications for N cycling is the adjoining presence of aerobic zones where nitrification occurs and anaerobic zones where denitrification occurs. The environments suitable for the growth of nitrifiers and denitrifiers are mutually exclusive, but the transport of substrates and products between the aerobic and anaerobic zones couples nitrification and denitrification. Nitrogen loss by coupled processes of simultaneous nitrification

and denitrification is consequently a unique feature of submerged soils (Reddy and Patrick, 1986). Nitrate derived through nitrification in an aerobic zone can rapidly diffuse into anaerobic soil layers where it serves as an electron acceptor and is reduced typically to N_2O and N_2. A NO_3^- concentration gradient across the aerobic–anaerobic interface resulting from the high demand for electron acceptors and sufficient supply of electron donors (available organic C) in anaerobic zones favors the rapid flux of NO_3^- from aerobic to anaerobic zones (Reddy et al., 1978). Because NO_3^- is rapidly lost by denitrification, low levels of NO_3^- in submerged soils do not necessarily reflect low N loss by nitrification–denitrification.

The addition of fertilizer N, transport of NH_4^+ from anaerobic to aerobic zones, and ammonification in aerobic zones typically supply adequate NH_4^+ for nitrifiers (Patrick and Reddy, 1976). High NH_4^+ levels in aerobic zones suggest the supply of NH_4^+ exceeds the rate at which NH_4^+ is converted to NO_3^-. The loss of N by coupled nitrification–denitrification is usually limited by the formation of NO_3^- (Reddy et al., 1976), and the supply of NO_3^- can consequently control the size and activity of denitrifiers. The rhizosphere of rice, in addition to the aerobic surface soil layer, is a potentially important site for coupled nitrification–denitrification (Arth et al., 1998; Arth and Frenzel, 2000). The loss of ammonium N through coupled nitrification–denitrification cannot occur in the absence of an aerobic zone.

Before the mid-1980s denitrification was generally considered the main process for N loss in submerged agricultural soils. The high losses of fertilizer N obtained from ^{15}N balance studies in submerged rice soils were often attributed to simultaneous nitrification–denitrification at aerobic–anaerobic interfaces near the soil surface, and in the rhizosphere of rice. It is, however, not possible to directly distinguish and quantify the processes responsible for the large portion of added N typically not accounted for in ^{15}N balances. The increasing awareness in the 1980s of the importance of NH_3 loss from fertilizer N in tropical rice soils heightened the need to directly quantify nitrification–denitrification and determine its importance relative to NH_3 volatilization as an N loss process (Fillery et al., 1986b).

A number of ^{15}N tracer studies were consequently conducted from the mid-1980s in diverse rice fields to directly quantify the evolution of N_2O and N_2 from fertilizer N applied with a range of methods, times, and rates. These studies typically used urea because of its global importance as an N source for rice. Directly measured evolution of N_2 and N_2O to the atmosphere represented ≤2% of the urea N applied to continuously saturated or submerged soils in a series of studies in the Philippines, Indonesia, and Thailand (Buresh and Austin, 1988; John et al., 1989; Buresh et al., 1991; De Datta et al., 1991). Total N loss as determined from unaccounted for N in ^{15}N balances in these studies represented 10 to 56% of the applied urea N. Metal borders surrounding the plots for ^{15}N balances prevented N loss by runoff, and leaching was negligible on these puddled soils. The quantity of N_2O and N_2 formed by denitrification but entrapped or dissolved in the soil–floodwater system rather than evolved and included in the measured flux of ^{15}N-labeled N_2O and N_2 was relatively small (Samson et al., 1990). Rice plants can act as a conduit for the transport of N gases from soil to the overlying atmosphere (Reddy et al., 1989; Ni and Zhu, 2004), and the evolution of N_2O and N_2 originating from added urea N is typically greater when gas collection chambers are placed over rather than between rice plants (Mosier et al., 1990; Buresh et al., 1993c; Chen et al., 1998a). However, even when accounting for entrapment of formed N_2O and N_2 and preferential transport of formed N_2O and N_2 through the rice canopy, the con-

version of applied urea N to N_2O and N_2 was small in puddled soils that remained saturated or submerged. Therefore, it was concluded that NH_3 volatilization and not emission of N_2O and N_2 was the dominant mechanism for loss of applied urea N, representing >90% of the lost urea N in the investigated rice soils (Buresh and De Datta, 1990).

Additional direct measurements of denitrification from submerged rice soils with ^{15}N tracer techniques confirm relatively small losses of fertilizer N by nitrification–denitrification as compared with NH_3 volatilization. Measured evolution of N_2O and N_2 accounted for ≤10% of the total loss of applied urea N in a study in India (Mosier et al., 1990), and much less than estimated NH_3 loss from applied NH_4^+–N in Australia (Chen et al., 1998a). The findings of Chen et al. (1998a) support the widespread observation that N loss by denitrification in continuously submerged or saturated rice soil is limited by the rate of nitrification. Directly measured evolution of N_2O and N_2 accounted for 10% of the applied urea N in a study in Thailand when crop residue was removed, but no loss of N as N_2O and N_2 was detected when crop residue was retained, presumably because of immobilization of added N (Phongpan and Mosier, 2003).

Some studies, particularly in the 1980s, indirectly estimated denitrification as the difference between unaccounted for N in ^{15}N balances and measured or estimated loss by NH_3 volatilization. These estimates of denitrification ranged up to about 50% of the applied urea N, leading to speculation that NH_3 volatilization and denitrification were concurrent, complementary loss mechanisms (De Datta and Buresh, 1989; Freney et al., 1990). In such case the management of urea to reduce NH_3 volatilization would lead to concurrent increases in denitrification, resulting in little or no reduction in total loss of fertilizer N. A high variance and uncertainty is, however, associated with indirect estimates of denitrification by difference, and indirectly estimated denitrification rates ranging up to 50% of the applied urea N would require much higher nitrification rates than the maximum reported for submerged rice soils (Buresh and De Datta, 1990). An underestimation of NH_3 loss, particularly with the simplified bulk aerodynamic method, might have contributed to overestimation of denitrification loss, and high indirect estimates of denitrification have never been substantiated by direct measurements using the ^{15}N tracer technique.

The reported ineffectiveness of nitrification inhibitors (Simpson et al., 1985) and low reported losses of N_2O in continuously submerged or saturated rice soils (Bronson et al., 1997b) support the findings of small N losses by nitrification–denitrification while a soil with relatively low percolation remains submerged. Drainage and reflooding of a soil during rice growth can, however, increase the emission of N_2O (Bronson et al., 1997b; Chen et al., 1997; Hua et al., 1997) and presumably N losses by nitrification–denitrification. Some of the emission of N_2O following soil drainage could, however, arise from the release of dissolved and entrapped N_2O, which was formed before drainage.

Drainage and drying of submerged soils increases the penetration of O_2 and the volume of soil pore space filled by air. This can lead to increased nitrification following a lag period for buildup of nitrifiers. The NO_3^- arising from the increased nitrification can be assimilated by plants and soil microorganisms. Nitrate remaining in soil at the time of reflooding can be rapidly used as an electron acceptor following the depletion of O_2 and thereby denitrified to N_2O and N_2. A number of studies have reported enhanced loss of N with alternate soil drying and

flooding (Patrick and Wyatt, 1964; Sah and Mikkelsen, 1983; Sharif Zia and Waring, 1987). As a general principle the magnitude of the N loss depends on the amount of accumulated soil NO_3^-, which reflects the net effect of supply via nitrification and assimilation by plants.

Buresh et al. (1993a) estimated the nitrification–denitrification loss from urea N during soil drying and wetting as the increase in unaccounted for N in ^{15}N balances for alternate soil drying and wetting as compared with continuous soil submergence. Soil drying for 20 d from 15 to 35 d after transplanting during the vegetative growth phase of rice increased unaccounted-for N— which presumably represented nitrification–denitrification—by 12 to 16% of the applied urea N. Soil drying for 22 d from 41 to 63 d after transplanting during the reproductive phase had no significant effect on unaccounted-for N indicating the older rice plants effectively assimilated NO_3^- thereby preventing accumulation of NO_3^- and subsequent denitrification.

Nitrogen losses by nitrification–denitrification could, however, be relatively higher on porous soils with high rates of water percolation leading to alternate flooding and drainage during cultivation of irrigated rice. Nitrification–denitrification loss on a porous soil in northwestern India was up to 33% of the applied fertilizer N as estimated by an acetylene inhibition–intact soil core technique (Aulakh et al., 2001).

Most environments where rice is grown do not have year-round soil submergence and cropping with rice. These soils typically dry between rice crops and become aerobic, which favors nitrification and build up of NO_3^- (George et al., 1993, 1995; Ladha et al., 1996). The NO_3^- is denitrified when the soil becomes saturated by rain or irrigation (Buresh and De Datta, 1991). Rain in the fallow period between rice crops stimulates the emission of N_2O (Bronson et al., 1997c; Abao et al., 2000), which is associated with nitrification–denitrification. Appreciable NO_3^- can accumulate during the fallow period particularly when periodic rains help maintain a favorable soil water content for nitrification (Buresh et al., 1989). Flooding the aerobic soil in preparation for puddling and land preparation in the Tropics or through flood irrigations before permanent flooding for direct-seeded rice as practiced in Australia and the USA can lead to substantial losses of NO_3^- by denitrification and a flush in emission of N_2O (Bacon et al., 1986; Keerthisinghe et al., 1993).

The loss of fertilizer N by nitrification–denitrification can be reduced by controlling nitrification, which is typically the rate-limiting step in the process leading to N loss. The buildup of NO_3^- can be reduced by more effective placement of fertilizer N into the anaerobic zone of soil (Reddy and Patrick, 1977), amendment of fertilizer with a nitrification inhibitor (Keerthisinghe et al., 1996), and use of controlled release fertilizer (Shoji and Kanno, 1994). The reduction in NO_3^- accumulation with nitrification inhibitors, while effective in controlling N loss by nitrification–denitrification and leaching, can enhance NH_3 volatilization as a result of enhanced buildup of ammoniacal N in floodwater and surface soil (Mohanty and Mosier, 1990; Chen et al., 1998b).

Anaerobic Ammonium Oxidation

The majority of the soil profile in wetlands is anaerobic, resulting in accumulation of high levels of NH_4^+. In the absence of oxygen, it is thermodynamically possible that several other alternate electron acceptors can potentially oxidize NH_4^+–N

to N_2. However, this pathway assumes that some anaerobic bacteria are capable of using NH_4^+–N as an electron donor and derive energy through oxidation. The significance of these processes has been documented for wastewater lagoons and marine sediments (Mulder et al., 1995; Thamdrup and Dalsgaard, 2002; Schmidt et al., 2003). Ammonium oxidation to N_2 using nitrite (NO_2^-) as an electron acceptor is commonly now known as the "anammox" process (Mulder et al., 1995). The proposed reactions for this process are shown below:

$$5NH_4^+ + 3NO_3^- = 4N_2 + 9H_2O + 2H^+$$

$$NH_4^+ + NO_2^- = N_2 + 2H_2O$$
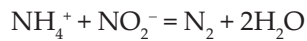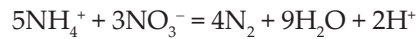
At present, this reaction is not reported in submerged agricultural soils, and the significance of the reaction to overall N loss remains a subject of speculation. The reaction is controlled by availability of NO_2^- and competition by heterotrophs, which are dominant in submerged soils. Under conditions of limiting available C, it is likely that some autotrophs might use NH_4^+ as an energy source and potentially oxidize it to N_2 gas. Submerged soils, however, are typically not limited by C; and when NO_3^- and NO_2^- are present in these systems, they will be used by heterotrophic denitrifiers.

Biological Nitrogen Fixation

Submerged soils are favorable environments for BNF because of their depletion of O_2 and ready supply of C substrate. Nitrogen inputs by BNF help sustain SNSC and maintain SOM, and the input of N by BNF has helped sustain rice yields at low levels without fertilizer N for hundreds of years on submerged soils. Long-term N balances for rice grown on submerged soils without fertilizer N typically indicate the maintenance of total soil N content, as a result of BNF by associative and free-living microorganisms (App et al., 1984).

Nitrogen fixers—diazotrophs—in submerged agricultural soils can be broadly grouped into indigenous and exogenous systems. The indigenous (autochthonous) BNF system comprises cyanobacteria and phototrophic bacteria inhabiting the floodwater and soil surface, and it comprises heterotrophic bacteria in the root zone and free-living in the soil. These diazotrophs are typically widespread and native in lowland rice ecosystems. The exogenous (allochthonous) BNF system comprises diazotrophs such as N_2–fixing cyanobacteria living in symbiosis with *Azolla* spp. and heterotrophic and phototrophic rhizobia harbored on aquatic legumes. The exogenous system is not ubiquitous in lowland rice ecosystems, and it must be applied or inoculated (Kundu and Ladha, 1995; Ladha and Reddy, 2003).

The diverse autotrophs and heterotrophs comprising the indigenous BNF system occur in soil and floodwater during rice growth and between rice crops when the water regime is favorable. Estimates of indigenous BNF based on N balances are typically in the range of 15 to 50 kg N ha^{-1} crop^{-1} for lowland rice ecosystems with soil submergence. A summary of 211 N balances compiled from 14 reports of field and pot experiments with rice revealed positive N balances ranging up to 90 kg N ha^{-1} crop^{-1} (Roger and Ladha, 1992). The average positive balance was 24 kg N ha^{-1} crop^{-1}, and the median was 27 kg N ha^{-1} crop^{-1}. The mean positive balance was higher in the absence of applied N (30 kg N ha^{-1} crop^{-1}) than when N was applied (4 kg N ha^{-1} crop^{-1}). The N balances in the absence of applied N,

when N losses are small or negligible, presumably approximate N inputs by the indigenous BNF system (App et al., 1980).

Estimated BNF based on an N balance during 27 seasons of growing two irrigated rice crops per year without fertilizer N in the Philippines was 46 kg N ha^{-1} crop^{-1} (Ladha et al., 2000). This is comparable with the approximate 50 kg N ha^{-1} crop^{-1} based on N balance for 2 yr of double rice cropping (Witt et al., 2000b), but higher than the 32 to 41 kg N ha^{-1} crop^{-1} estimated in an experiment in the Philippines with three continuous crops of rice per year (Cassman et al., 1995). In a more recent examination of four long-term experiments in the Philippines with two or three irrigated rice crops per year, indigenous BNF as determined by N balance in plots without fertilizer N, ranged from 19 to 44 kg N ha^{-1} crop^{-1} during a 15-yr period (Pampolino et al., 2008).

A summary of extensive measurements suggests a mean contribution of about 20 kg N ha^{-1} crop^{-1} from free-living cyanobacteria in the absence of fertilizer N (Roger and Ladha, 1992). The growth of free-living cyanobacteria and phototrophic bacteria inhabiting floodwater and the soil surface is limited by low pH, low P, grazer population (Grant et al., 1985), and high ammoniacal N concentration in floodwater (Roger, 1996). Deep placement of early fertilizer N can reduce the inhibitive effect of ammoniacal N in floodwater on cyanobacteria (Roger et al., 1981).

Associative BNF in the rice rhizosphere occurs mostly during the heading stage when soil inorganic N is low (Ladha et al., 1988). It depends on rice cultivar and environment (App et al., 1986; Shrestha and Ladha, 1996); and it is often estimated at <10 kg N ha^{-1} crop^{-1} although it could theoretically achieve a maximum of 40 kg N ha^{-1} crop^{-1} (Roger and Ladha, 1992). Estimates of BNF by free-living heterotrophic bacteria are typically <20 kg N ha^{-1} crop^{-1} (Roger and Ladha, 1992). The application of straw enhances heterotrophic and photodependent BNF by an estimated 2 to 4 kg N ha^{-1} Mg^{-1} of applied straw (Santiago-Ventura et al., 1986). The straw serves as a C substrate for heterotrophs, and it can create a more favorable environment for BNF by reducing inorganic N through temporary immobilization.

A widely studied exogenous BNF system in submerged rice soils is the symbiotic association of the *Anabaena azollae* Strasburger with the freshwater fern *Azolla* spp. (Watanabe, 1982; Roger, 1996). The cyanobacterium inhabits the leaf cavity of azolla, which can grow rapidly in submerged soils before the rice crop and during the early growth of rice. Estimates of BNF under field rather than experimental conditions suggest symbiotic BNF from the azolla–cyanobacterium association can contribute 10 to 50 kg N ha^{-1} crop^{-1} (Roger and Ladha, 1992).

Ammonium Fixation

The accumulation of NH_4^+ and the anaerobic conditions following soil submergence are favorable for the temporary fixation of NH_4^+ in soils with high amounts of expandable 2:1 clay minerals (Wen and Cheng, 1997; Schneiders and Scherer, 1998; Zhang and Scherer, 1999, 2000). A buildup of exchangeable NH_4^+ from mineralization following soil submergence could lead to a concentration gradient favoring NH_4^+ diffusion into the interlayers of clay minerals. Soil submergence can increase NH_4^+ fixation through the reduction and dissolution of Fe^{3+} oxide coatings on the surface of clay minerals thereby reducing obstacles for NH_4^+ movement in and out of interlayers of the clay minerals (Scherer and Zhang, 1999). Soil submergence can also increase NH_4^+ fixation through the reduction of octa-

hedral Fe^{3+}, which increases the negative charge of interlayers of the clay minerals (Scherer and Zhang, 2002). The temporary fixation of NH_4^+ could protect N from losses, while still enabling a timely release of the NH_4^+ to plants (Keerthisinghe et al., 1984; Schnier et al., 1987a). Nonexchangeable NH_4^+ can be an important source of N to rice on submerged soils rich in vermiculite (Keerthisinghe et al., 1985).

Leaching

Leaching is normally not an important process on puddled rice soils with low water infiltration, which represent the majority of rice-growing areas worldwide. The leaching loss of fertilizer N is often lower during rice cropping on puddled, submerged soils than during the aerobic soil phase in rice–upland crop rotations, such as rice–wheat (*Triticum aestivum* L.) (Zhu et al., 2000). Even in rice-growing areas without soil puddling, leaching is typically not considered a problem when the management of fertilizer N is effective (Humphreys et al., 1987a, 1987b). Nitrate that accumulates during the period of soil drying before a rice crop can in some cases be partially lost by leaching after soil is saturated by either rain or irrigation (Becker et al., 2007).

Some rice is grown on porous soils with high infiltration and poor retention of nutrients. One such example is northwestern India where relatively high solar radiation, together with irrigation and nutrient inputs, enables the porous soils to be very productive (Aulakh and Bijay-Singh, 1997). Irrigation and rain can transport urea N and ammoniacal N following fertilization into soil where it is more prone to nitrification–denitrification than NH_3 volatilization. Low available C in subsoil can limit denitrification (Aulakh et al., 2000b), leading to accumulation of NO_3^- below the crop rooting zone. Inefficient management of irrigation water and overuse of fertilizer N are increasingly recognized as contributing to localized NO_3^- pollution of groundwater (Bijay-Singh et al., 1995; Bijay-Singh and Yadvinder Singh, 2003). Management of fertilizer N to better match crop needs and rotation of rice with a deeper rooted crop offer opportunities to reduce NO_3^- leaching (Aulakh et al., 2000c). Point-placement of urea below the soil surface is particularly prone to N loss by leaching on porous soils (Vlek et al., 1980), and deep point-placement of fertilizer N is consequently not recommended on porous soils (Katyal et al., 1985).

Nitrogen Management in Submerged Soils

Nitrogen Fertilizer Management for Rice

A distinguishing feature of submerged agricultural soils is the low efficiency of fertilizer N use, arising from the high losses of fertilizer N. Observations from 179 irrigated rice farm sites in six Asian countries in the mid- to late 1990s revealed an average recovery of only 30% of the applied fertilizer N. The average fertilizer N use efficiency was an incremental increase of only 11 kg grain yield kg^{-1} of applied N (Dobermann et al., 2004). Despite this typically low efficiency of fertilizer N use in Asian rice fields, rice has considerable capacity to take up fertilizer N when its application is synchronized with crop demand. Nitrate-containing fertilizers have long been recognized as inappropriate for lowland rice because of the rapid loss of NO_3^- by denitrification in submerged soils. Urea, because of its high N analysis, is the main N fertilizer source for rice worldwide, and much research attention has been devoted to improving its use efficiency for rice.

Research from the 1970s to early 1990s was instrumental in quantifying the processes and magnitudes of the high fertilizer N loss. Reducing N losses understandably received much attention during this period. These efforts particularly focused on the improved placement of urea (Schnier, 1995) and the development of modified N fertilizer sources less prone to N loss (Singh and Buresh, 1994). Broadcast application of urea or ammonium-based fertilizer into floodwater of young rice, as often practiced by Asian rice farmers, was discouraged by researchers because of the high N losses. For puddled soils, researchers advocated the incorporation without standing floodwater of commercially available N fertilizers before crop establishment (De Datta et al., 1989). For nonpuddled soils, the application of fertilizer N before permanent flooding was advocated (Bacon et al., 1988).

The point placement of urea or ammonium-based fertilizer has long been recognized as effective in reducing N loss (Mitsui, 1955; Broadbent and Mikkelsen, 1968). Much effort has been devoted to developing techniques to facilitate deep placement. These techniques included use of a "mud ball" containing urea with soil (De Datta et al., 1968), large granules of urea (Pasandaran et al., 1999), injection of granular urea (Scholten, 1992), and injection of liquid urea (Schnier et al., 1993). The increased labor and cost associated with placement of fertilizer N into soil has been a constraint to its adoption in the Tropics (Mohanty et al., 1999), although localized adoption of the production and deep placement of urea briquettes for rice is taking place in Bangladesh (Bowen et al., 2005).

Amendment of urea with chemical additives to inhibit biological processes of urea hydrolysis and nitrification and the coating of urea granules to control the rate of N release have received considerable attention as approaches to reduce fertilizer N losses. A number of urease inhibitors and controlled release fertilizers have shown an ability to reduce NH_3 loss and achieve higher yields with less fertilizer N. The modification of conventional N fertilizer sources with chemical additives or coatings, however, adds cost to the fertilizer. This added cost must be small relative to the benefit associated with using lower rates of fertilizer N in order for the modified N fertilizer sources to be financially attractive (Buresh and Baanante, 1993).

The recognition arising from research in the 1990s of high spatial and temporal variability in SNSC and crop demand for fertilizer N in farmers' fields (Cassman et al., 1996b) created awareness of the need for site-specific N management enabling dynamic adjustments in N fertilization to accommodate field-to-field and year-to-year variation in crop requirements for fertilizer N (Doberman and White, 1999). A site-specific nutrient management (SSNM) approach for rice was formulated in which the need for fertilizer N was determined from the gap between the supply of N from indigenous sources—as measured with an N omission plot—and the demand of the rice crop for N as estimated from the total N required by the crop to achieve a yield target for average climatic conditions (Witt et al., 1999; Dobermann and Witt, 2004).

The chlorophyll meter provided a quick and nondestructive method for estimating leaf N content, which is closely related to photosynthetic rate and biomass production and a sensitive indicator of changes in crop N demand within a growing season (Peng et al., 1993, 1996; Balasubramanian et al., 1999, 2000; Hussain et al., 2000). The relatively high price of the chlorophyll meter, however, limits its use by individual farmers. A simple, nondestructive alternative is to monitor leaf N status with a leaf color chart (LCC) (Furuya, 1987; Balasubramanian et al., 1999, 2003; Bijay-Singh et al., 2002; Shukla et al., 2004). The LCC is typically

a durable plastic strip about 7 cm or more wide and about 13 cm or more long, containing four or more panels that range in color from yellowish green to dark green. Whereas the chlorophyll meter measures light absorption, the LCC is used to monitor leaf greenness and associated leaf N by visually comparing light reflection from the surface of leaves with the gamut of green-colored panels on the LCC. Several types of LCCs have been developed including ones by Zhejiang Agricultural University (People's Republic of China), the University of California (USA), and the International Rice Research Institute (IRRI) based on a Japanese prototype. Even though the gamut of green colors is visually different among these three LCCs, Yang et al. (2003) reported strong correlations among the scores for the three types of LCCs and direct relationships between chlorophyll meter and LCC readings. In 2003, IRRI in collaboration with the University of California Cooperative Extension (UCCE) developed a new LCC with four colored panels (ranging from yellowish green to dark green) that better matched the reflectance spectra of rice leaves (Witt et al., 2005). The LCC is now widely recommended across Asia for managing the within season applications of fertilizer N for rice (Buresh, 2007; IRRI, 2007; Witt et al., 2007).

Use of the chlorophyll meter or LCC enables a "real-time" option to N management in which fertilizer N is applied in congruence with crop need, as determined by leaf color appearance, rather than applied at a prepackaged, uniform rate for large geographical areas (Alam et al., 2005). Measurements with the chlorophyll meter and LCC are typically taken at 7- to 10-d intervals on the most recent fully expanded leaves, beginning at midtillering and continuing to preflowering—when the N demand by the rice crop is high (Schnier et al., 1987b; Peng and Cassman, 1998). About 20 to 45 kg N ha^{-1} is then applied whenever the chlorophyll meter or LCC reading falls below a critical threshold. With such real-time N management, the timing of N application is not preset and depends on crop N demand (Peng et al., 1996). The relatively frequent and moderate rates of N application ensure plant assimilation of a relatively high proportion of the fertilizer N before it can be lost. The critical threshold values for the chlorophyll meter and LCC can vary among genotypes of rice.

The real-time option for N management requires periodic observations of the rice crop, which can become less feasible as rice farmers increasingly engage in off-farm employment. Another option referred to as "fixed time–adjustable dose" management of N involves less frequent crop observations. This option initially used a decision support system (Witt and Dobermann, 2004) to provide—before planting—a pattern for splitting an estimated total fertilizer N requirement among preset critical growth stages. The predetermined N doses in the splitting pattern are then dynamically adjusted upward or downward based on either chlorophyll meter of LCC readings at the predetermined times of N application. Such a fixed time–adjustable-dose option has effectively increased yield and profitability of fertilizer use as compared with existing farmers' practices in intensive irrigated rice ecosystems in Asia (Dobermann et al., 2002, 2004). It has subsequently been refined into a set of guidelines based on rice response to fertilizer N and a targeted efficiency of fertilizer N use (IRRI, 2007; Witt et al., 2007).

The management of conventional N fertilizer sources to better match the field- and time-specific need of the rice crop offers considerable potential for increasing the efficiency of fertilizer N use for lowland rice in Asia. Approaches for better matching N fertilization with plant demand for added N are increasingly high-

lighting the low N demand for fertilizer N before midtillering and the opportunity for Asian rice farmers to increase fertilizer N use efficiency by reducing early use of fertilizer N and better matching N fertilization with crop demand during the period of rapid rice growth (Wang et al., 2001a, 2004, 2007; Hu et al., 2007). The real-time and fixed-time adjustable dose options to N management were equally effective in increased fertilizer N use efficiency and yield in multilocation evaluation in China (Buresh et al., 2004), and they are now promoted as two options for improved fertilizer N management for rice through use of the LCC (Buresh et al., 2005; IRRI, 2007; Witt et al., 2007).

Some fertilizer N applied in excess of crop demand can be lost as inorganic N from rice fields and accumulate in groundwater and water bodies (Xing and Zhu, 2000). The concentration of dissolved inorganic N in river water in China, for example, has been shown to correlate with annual application of fertilizer N in its catchment (Duan et al., 2000). The concentration of nitrate in percolating water has also been related to rates of fertilizer N application (Ma, 1997), and there are increasing reports of nitrate accumulation in groundwater in rice-growing areas with relatively high fertilizer N rates (Bijay-Singh and Yadvinder Singh, 2003). The management of fertilizer N to better match the field- and time-specific need of the rice crop offers considerable potential for preventing the buildup and subsequent transport of fertilizer-derived N into groundwater and water bodies. Nitrogen fertilizer management should ensure that inorganic N does not accumulate in the soil profile at harvest of rice (Zhu and Chen, 2002).

During the 20 yr from about 1987 to 2007 the focal message for increasing the efficiency of fertilizer N use for rice has evolved from "reducing N losses" per se to "feeding crop needs for N" (Buresh, 2007). Varying basal and midseason applications of fertilizer N to optimally match the field-specific needs of a crop for supplemental N enhances opportunities for increasing yield per unit of applied fertilizer N and increasing profit for rice farmers, while also reducing losses of reactive N (Pampolino et al., 2007).

Crop Residue and Green Manure Management

The retention and incorporation of crop residues in lowland rice fields often has little or no short-term benefits on rice yield (Bijay-Singh et al., 2001; Samra et al., 2003; Thuy et al., 2008), and crop residues are frequently burnt or removed from lowland rice fields. Rice residue with a high C/N ratio is a poor-quality source of N for the subsequent crop. The incorporation of rice residue can have short-term detrimental consequences arising from microbial immobilization of N, leading to temporary decreases in plant-available soil N (Norman et al., 1990).

The plant recovery of rice residue N is typically low (Table 11–1), although low reported recoveries of ^{15}N from labeled residues by rice in studies limited to 1 yr might underestimate the role of residue in providing N to the crop. After four consecutive seasons of incorporating rice straw in California, ^{15}N-labeled residue was incorporated and followed during the subsequent growing season. The recovery by rice of ^{15}N from labeled residue did not exceed 4% of the total N applied, which represented <2 kg N ha^{-1} (Eagle et al., 2001). Moreover, most of the ^{15}N was derived from belowground plant sources rather than from the aboveground residue. The total N accumulation by rice in adjacent microplots not receiving fertilizer N, however, increased by 19 kg N ha^{-1} after 5 yr of straw incorporation (Eagle

Table 11–1. Recovery of ^{15}N by field-grown rice following the incorporation of ^{15}N-labeled rice residue or green manure.

Residue	Experimental conditions	Residue characteristics			^{15}N Recovery[†]		Reference
		^{15}N applied	N content	C/N	% applied	Amount	
		kg ha^{-1}	g kg^{-1}			kg ha^{-1}	
Rice	Above- + belowground	51	5.5	71	3.5	1.8	Eagle et al., 2001
Rice	belowground only	ND‡	5.5	ND‡	3.0§	1.5	Eagle et al., 2001
Rice	incorporated, winter flooded	151	18.6	26	11.1	16.8	Bird et al., 2003
Rice	incorporated, not winter flooded	151	18.6	26	5.8	8.8	Bird et al., 2003
Rice	burned, winter flooded	43	13.5	15	11.1	4.8	Bird et al., 2003
Rice	burned, not winter flooded	43	13.5	15	10.6	4.6	Bird et al., 2003
Rice	straw + roots	104	6.8	59	3	3	Norman et al., 1990
Sesbania rostrata Bremek &Oberm.	dry season	90	44	10	44.1	49	Diekmann et al., 1993
Aeschynomene afraspera J. Leonard	dry season	90	49	9	42.3	47	Diekmann et al., 1993
Sesbania rostrata Bremek &Oberm.	dry season	60	NR¶	NR¶	28.2#	16.9	Becker et al., 1994a
Sesbania emerus (Aubl.) Urb.	dry season	60			32.6	19.6	Becker et al., 1994a
Sesbania rostrata Bremek &Oberm.	dry season, + rice straw	60			23.9	14.3	Becker et al., 1994a
Sesbania rostrata Bremek &Oberm.	wet season	60			15.2	9.1	Becker et al., 1994a
Sesbania emerus Bremek &Oberm.	wet season	60			13.0	7.8	Becker et al., 1994a
Sesbania rostrata Bremek &Oberm.	wet season, + rice straw	60			14.1	8.5	Becker et al., 1994a
Azolla pinnata var. *imbricata* R. Brown	labeled *Azolla* applied at transplanting	20.4	17.2	26††	20.2	4.1	Rosenani and Azizah Chulan, 1992

Table cont.

Table 11–1. Cont.

Residue	Experimental conditions	Residue characteristics			^{15}N Recovery[†]		Reference
		^{15}N applied	N content	C/N	% applied	Amount	
		kg ha^{-1}	g kg^{-1}			kg ha^{-1}	
Azolla pinnata var. *imbricata* R. Brown	labeled *Azolla* applied 30 d after transplanting	29.7	30.5	15[††]	30.2	9.0	Rosenani and Azizah Chulan, 1992
Azolla microphylla Kaulf.	labeled *Azolla* applied before transplanting	35.7	47.5	9[††]	39.3	14.0	Watanabe et al., 1989
Azolla microphylla Kaulf.	labeled *Azolla* applied 42 d after transplanting	38.0	46.6	10[††]	62.9	23.9	Watanabe et al., 1989

[†] Includes recovery of N in grain and straw.

[‡] ND = not determined.

[§] Includes recovery of ^{15}N-fertilizer applied in the previous year plus belowground rice residue.

[¶] NR = not reported.

[#] Calculated from data presented in Fig. 2 of Becker et al. (1994a).

[††] Calculated from data presented, assuming a C content of 45%.

et al., 2000). This suggests that the total recovery of residue N by rice should not be based only on the 1st year following the application of the residues; but it should consider the cumulative effect over several years.

Several years of straw incorporation are often required before net increases in SNSC and benefits to rice become apparent in the absence of fertilizer N (Verma and Bhagat, 1992; Eagle et al., 2000). Long-term studies indicate increased supply of plant-available soil N after 5 to 10 yr of rice straw incorporation in Tropics (Cassman et al., 1996a) and temperate areas (Eagle et al., 2000; Bird et al., 2001). Long-term straw incorporation in temperate areas can increase the reservoirs of readily mineralized organic N, suggesting potential after several years for reducing fertilizer N rates for optimal rice yield (Bird et al., 2001; Eagle et al., 2001; Linquist et al., 2006). Long-term applications of straw, however, do not improve the trends in rice yield in tropical rice systems with two rice crops per year and high inputs of fertilizer N (Dawe et al., 2003). The retention of crop residue is not essential for maintaining soil C and INS in continuous rice cultivaton with soil submergence. Soil C was maintained or slightly increased during 15 yr of continuous cultivation with three irrigated rice crops per year and removal of all aboveground crop residues in the Philippines (Pampolino et al., 2008).

In California, the winter flooding of rice fields for 8 to 12 wk provides a wetland habitat for a large number of migratory, foraging waterfowl (Bird et al., 2000). Foraging waterfowl promote soil disturbance leading to a significant increase in residue decomposition (Van Groenigen et al., 2003). The presence of waterfowl, as compared with sites without waterfowl, reduced the residue remaining in the spring by 36%. Grassy weed seed, like rice seed, served as a food source for the foraging waterfowl, and the presence of foraging waterfowl significantly reduced grassy weed (*Scirpus mucronatus* L.) biomass even when a regular weed control program was followed (Van Groenigen et al., 2003).

Green manures in rice ecosystems are typically legumes or azolla, which have a high growth rate and a high potential to obtain their N from BNF (Kundu and Ladha, 1999; Ladha and Reddy, 2003). Green manures are excellent providers of N to a subsequent rice crop, reducing the need for fertilizer N (Yadvinder-Singh et al., 1991; Becker et al., 1995). Losses of N from applied green manure are often lower than from urea. Whereas the average loss from urea was 35% of the applied N, the average loss for green manure was 14% of the applied N for 18 ^{15}N balance studies (Becker et al., 1995). Losses of N from green manures can be reduced by better synchronizing the release of N from the green manure residues with N assimilation by rice. This can potentially be achieved by mixing green manure residue with other residues, such as rice straw, with high C/N ratio (Becker et al., 1994b).

The application of green manure with urea can reduce NH_3 loss from urea. The incorporation of green manure can lead to increased ρCO_2 concentration in floodwater leading to lower pH of floodwater, thereby reducing ρNH_3 and NH_3 loss. Application of green manure can, however, increase CH_4 production (De Datta, 1995).

The recovery of N by rice is typically higher from green manure residues (i.e., *Azolla* and *Sesbania*) than from rice residue, which reflects the higher N concentration of green manures (Table 11–1). There is, however, an apparent discrepancy in the amount of N accumulated by rice from green manures as determined by the ^{15}N recovery from labeled green manure and by the N difference approach using unfertilized rice as the control. Whereas the recovery from ^{15}N-labeled green manure did not exceed 20 kg N ha^{-1} (Table 11–1), recoveries by the N difference ap-

proach in the same studies were considerably higher (Diekmann et al., 1993; Becker et al., 1994a). This discrepancy in N recoveries is largely caused by an added N interaction whereby ^{15}N-labeled residue N is immobilized by soil microorganisms, which release unlabeled N that is subsequently accumulated by the crop. The ^{15}N-tracer technique is less appropriate than the N difference method for determining the total, long-term contribution of N from green manure and residue to the following crop. On the other hand, ^{15}N-labeled organic N sources remain an excellent tool to trace the temporal dynamics of N mineralization and to construct N recovery budgets for the various plant- and soil-N fractions.

Nitrogen in Lowland Rice–Upland Crop Rotations

Rice-growing areas in Asia are generally characterized by a wet season in which rice is a well-adapted crop, and a dry season suitable for growth of rice with irrigation or for growth of upland crops on aerated soil. In rotations of lowland rice with an upland crop, the soil is submerged or saturated for most or all of the rice-growing season, but then the soil dries and becomes aerobic when the upland crop is grown. During the period of soil submergence, NH_4^+ is the stable form of inorganic N, which accumulates in the soil. Soil NO_3^- is normally negligible at the end of the rice-growing season. During the subsequent period of soil aeration, NO_3^- forms via nitrification of indigenous soil N and fertilizer N applied to the upland crop. Accumulated soil NO_3^- can be rapidly lost by denitrification when soil is flooded and puddled for the next rice crop (Buresh and De Datta, 1991; George et al., 1992; Singh et al., 1999) or when nonpuddled soil is saturated by heavy rains before dry-sown rice takes up accumulated soil NO_3^- (Sharma et al., 2005). Denitrification losses following soil submergence can match the magnitude of N losses from fertilizer N applied to rice, particularly when NO_3^- formation is much greater than plant demand for NO_3^- during the aerobic soil phase (Sharma et al., 1985; Buresh et al., 1989).

Green manures and grain legumes, which grow during the phase of aerobic soil conditions, can assimilate soil NO_3^- and reduce the level of NO_3^- at the time soil is flooded for rice production (Buresh et al., 1993b; George et al., 1994). The N accumulated in the green manure and grain legume residues that are incorporated during land preparation can supply N to rice and reduce the need of fertilizer N (Ladha et al., 1996; Clement et al., 1998; George et al., 1998). Weeds growing during the fallow period between rice crops can also assimilate soil NO_3^- and recycle the N through the incorporation of biomass, thereby reducing N losses and effectively retaining N within the plant–soil system (Buresh et al., 1989; George et al., 1994).

Excessive application of N fertilizer to high-valued upland crops can result in large accumulations of soil NO_3^- before soil submergence for rice (Tripathi et al., 1997). The accumulated NO_3^- is typically denitrified on flooding and puddling of soils with low infiltration rate and sufficient electron donors for heterotrophic denitrifiers. On porous soils or cracking clay soils, however, the accumulated NO_3^- can move quickly with irrigation or rainwater into soil zones where insufficient electron donors or insufficient demand for NO_3^- as an electron acceptor can limit denitrification. Under such cases a sizable portion of the NO_3^- can leach and eventually accumulate in groundwater (Shrestha and Ladha, 1998). The growth of a crop or green manure without fertilizer N immediately before the rice crop can capture some

Table 11–2. Examples of potential denitrification rates in several natural and constructed wetlands.

Wetland	Rate	Units	Reference
Wet meadow, Sweden			Davidsson and
Sandy soil	6–43	g N m^{-2} yr^{-1}	Leonardson, 1998
Peat soil	22	g N m^{-2} yr^{-1}	
Lake edge wetland, New Zealand	8–9	mg N m^{-2} d^{-1}	Lusby et al., 1998
Forest soil swamp, Louisiana (USA)	82, 232	mg N m^{-2} d^{-1}	DeLaune et al., 1998
Mangrove wetland, Thailand	13–46	µmoles N m^{-2} d^{-1}	Kristensen et al., 1998
Treatment wetland marsh, Arcata, California (USA)	950–1020	mg N m^{-2} d^{-1}	Frankenbach and Meyer, 1999
Forested treatment wetland, Louisiana (USA)	100	mg N m^{-2} d^{-1}	Blahnik and Day, 2000
Forest peat soil, Sweden	11	mmoles N m^{-2} d^{-1}	Davidsson and Stahl,
Sandy loam soil, Sweden	2	mmoles N m^{-2} d^{-1}	2000
Undisturbed wetlands, New Jersey (USA)	<20–260	µmoles N m^{-2} h^{-1}	Seitzinger, 1994
Disturbed wetlands, New Jersey (USA)	180–260	µmoles N m^{-2} h^{-1}	
Swamp forest, Minnesota (USA)	2–8	mg N m^{-2} d^{-1}	Zak and Grigal, 1991
Riparian fen, Denmark	2–22	mg N m^{-2} yr^{-1}	Ambus and Christensen, 1993
Red maple swamps, Rhode Island (USA)			Hanson et al., 1994
Unenriched sites	0.5–1.6	g N m^{-2} yr^{-1}	
Enriched sites	0.7–3.9	g N m^{-2} yr^{-1}	
Mesohaline marsh, Virginia (USA)	1.8–17.6	mmoles N m^{-2} h^{-1}	Tobias et al., 2001

of the accumulated soil NO_3^- (Agustin et al., 1999), but management to effectively match fertilizer N use with crop N demand remains the most effective strategy for preventing NO_3^- contamination of groundwater (Shrestha and Ladha, 2000).

Nitrogen Loss into Adjacent Wetlands and Streams

Wetlands and streams are commonly associated with agricultural ecosystems in many landscapes. Wetlands within a watershed function as effective sinks for NO_3^- discharged from agricultural operations. Along the continuum from uplands to wetlands and adjacent streams, NO_3^- is rapidly processed through denitrification (Galloway et al., 2003). The efficiency with which riparian wetlands adjacent to streams remove NO_3^- from subsurface and surface flow can vary with landscape setting. Devito et al. (2000) showed that the width of vegetated strips might be less important than the depth of permeable riparian sediments, groundwater flow path, and the location of organic-rich subsurface deposits in influencing the ability of riparian zones to remove NO_3^-. Channelization of rivers destroys riparian wetlands and decreases the water residence time, thus decreasing overall NO_3^- removal via denitrification (Galloway et al., 2003).

Nitrogen transformation processes in riparian zones and adjacent wetlands are comparable with those in submerged soils, and the efficiency of riparian zones and wetlands to remove NO_3^- depends on nitrification and denitrification rates. When rates are expressed on a dry soil weight basis, values are typically higher for organic soils with low bulk density as compared with mineral wetland soils with higher bulk density. However, van Hoewyk et al. (2000) noted no significant difference between these two soil types when values were expressed on a soil volume basis. Wetland soils can have a large capacity to process inorganic N entering from

agriculture runoff (DeLaune et al., 1998). Selected examples of N removal through denitrification in wetlands are shown in Table 11–2.

Nitrate removal in a bottomland hardwood swamp increased linearly with loading rates, with rates ranged up to 100 mg N m^{-2} d^{-1}, and nitrification was the primary source of NO_3^- in this system (Blahnik and Day, 2000). Using isotopic dilution method in a Louisiana swamp forest soil, DeLaune et al. (1998) estimated nitrification rate at 24 mg N m^{-2} d^{-1}, while denitrification rate was 232 mg N m^{-2} d^{-1}. In a lake-edge wetland in New Zealand, Lusby et al. (1998) reported N loss due to coupled nitrification–denitrification as 9 mg N m^{-2} d^{-1}.

Nitrate is usually reduced to N_2, and emissions of N_2O are typically small compared with emissions of N_2 (DeLaune et al., 1998). The potential for high N_2O flux is greater in wetlands with high levels of NO_3^- and NO_2^-. Nitrous oxide emissions increased linearly with decrease in water table height of peat wetland (Dowrick et al., 1999). Similarly, raising the water table in forested peatlands caused cessation of N_2O production (Regina et al., 1999).

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