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Author(s): D.S. MIKKELSEN
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Nitrogen budgets in flooded soils used for rice production

D.S. MIKKELSEN
Agronomy and Range Science, University of California, Davis, CA 95616, USA

Key words Ammonium fixation Ammonia volatilization Dentrification Immobilization Run off losses N use efficiency Rice

Summary The flooded soil-rice plant ecosystem is extremely complex and final N budgets are the products of many N transformations modified by physical, chemical and biological agents, to a large extent controlled by O_2 fluxes, but interacting with each other over time. Topics reviewed include mineralization-immobilization, nitrification-denitrification, NH_4^+ fixation, NH_3 volatilization, leaching and run-off lossess. Nitrogen budgets constructed for water sown rice using temperate climate data clearly show that the major mechanisms by which fertilizer N is removed is crop absorption, nitrification-dentrification and NH_3 volatilization. Proper fertilizer management can reduce losses and desirably increase fertilizer use efficiency. Nitrogen budgets have proven useful in describing gains and losses from the various N transformation processes, all of which are environment and management dependent.

Introduction

The development of practices to improve the efficiency of fertilizer nitrogen (N) for rice requires that agronomists have a knowledge of the fate of the applied N and its effect on crop production. Identification of the various transformation processes, quantification of the size and transport rate of the various N pools, the establishment of interrelationships between the various biological processes and ultimately the effects on crop growth and yield are all essential components of a N budget. Adequate N nutrition is the major nutritional constraint to rice production in the world and the plant nutrient most difficult to manage in the rice ecosystem. Flooded soils are particularly unique in their chemical, physiochemical and biological properties and difficult to characterize because of the complex transformations which are involved. Soil N budgets must consider such processes as nitrification-denitrification, ammonia (NH_3) volatilization, NH_4^+-fixation immobilization-mineralization (ammonification) processes, leaching, floodwater losses, and ultimately the growing crop. The use of ^{15}N-labeled fertilizers has greatly increased the sensitivity for tracing fertilizer N, but quantitative measurement of the various complex N pools and agreement on interpretation of the data is yet to be fully achieved.

The literature on N budgets in submerged soils is very extensive. Investigators have studied the effects on N rates, sources, methods and times of N application on all aspects of N gains and losses, plant absorption, plant growth, crop yields and quality. These studies have been conducted over a wide range of soils, climates and management systems and are too extensive for detailed review. This paper will deal primarily with an overview of the nature of the submerged soil, the N transformation processes and temperate zone N budgets. The budget process ultimately seeks to improve N use efficiency in rice production, the socio-economic conditions of both rural and urban people and to limit unnecessary contamination of the environment.

Effects of soil submergence on soil properties

Several excellent reviews deal with the chemistry of submerged soils[37,38,39,40,41,47]. A brief review of the salient points dealing with N transformations is presented below:

Effects on physical properties

The immediate effect of submergence is interruption of the normal processes of gaseous exchange between the soil and the atmosphere. The pore space becomes saturated with water and the structural aggregates tend to break down. Water covering the soil acts as a barrier and diffusion of dissolved oxygen (O_2) into the interstitial water is reduced by four orders of magnitude slower than through a porous medium. Thus in a submerged soil, the chemical and the microbial demand for O_2 greatly exceeds the supply. As a consequence, O_2 levels in the soil drop quickly and within 6 to 8 hours of submergence the soil is virtually O_2-free except for a thin layer of soil at the soil-water interface. This thin layer of surface soil contains O_2 and is a few millimeters to about a centimeter thick.

Effects on physicochemical properties

Oxygen dissolved in the flooded water, from the atmosphere or from the photosynthetic activity of various hydrophytes, diffuses below the water layer into the thin oxidized soil layer. This layer supports microorganisms carrying on aerobic biological processes and the various mineral species are typically in oxidized forms such as SO_4^{-2}, NO_3^-, Fe^{+3} and Mn^{+4} compounds. The soil color in this zone is similar to wet aerobic soils.

Effects on biochemical properties

Immediately below the thin oxidized layer the O_2 content drops sharply and approaches zero within a very short distance. The depth of O_2 penetration into the soil depends on the balance between diffusion and

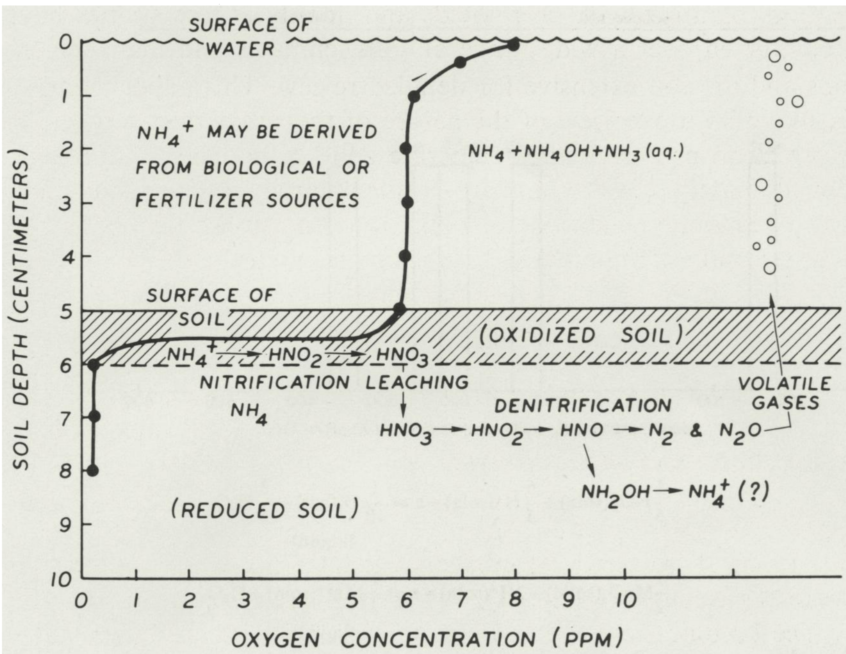
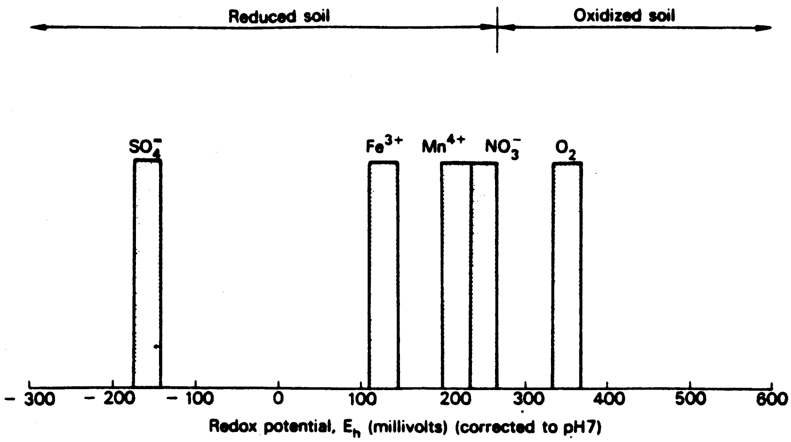


Fig. 1. Schematic representation of differentiated flooded soil profile.

consumption. In the absence of O_2, the aerobic microorganisms die or become quiescent and facultative or true anaerobes become active in the anaerobic zone. A schematic representation of the differentiated flooded soil profile is shown in Figure 1.

As a result of submergence, the redox potential of the reduced layer drops sharply as diagramatically represented by Patrick and Mahapatra[38] (Fig. 2). A well aerated soil is characterized by a redox potential of +400 millivolts (mV) or greater. If the reduction process is sufficiently intense, the soil may have a redox potential as low as −300 mV. The redox potential (Eh) of the oxidized zone of flooded soils may remain as high as +500 mV. The degree of oxidation and reduction of the redox systems — such as oxygen, nitrate, nitrite, manganese, iron and sulfur systems as well as various organic compounds determine the redox potential of soil. Free O_2 functions both physicochemically and biochemically to maintain these systems in an oxidized form.

In the reduced soil layer, anaerobic organisms utilize progressively weaker electron acceptors in place of O_2 for respiration. After O_2, the next strongest electron acceptor is NO_3^-. Nitrate is reduced to N_2 or N_2O gas at around +220 mV redox potential. This process, called denitrification, requires an energy source for the denitrifying bacteria. When O_2 and NO_3^- become exhausted redox potentials drop and Mn^{+3}, Mn^{+4} and



$$\frac{1}{5}NO_3^-(\text{soln}) + \frac{6}{5}H^+(\text{soln}) + e \rightleftharpoons \frac{1}{10}N_2(\text{gas}) + \frac{3}{5}H_2O \ (\text{liquid})$$

$$\frac{1}{2}MnO_2(\text{solid}) + 2H^+(\text{soln}) + e \rightleftharpoons \frac{1}{2}Mn^{2+}(\text{soln}) + H_2O \ (\text{liquid})$$

$$Fe(OH)_3(\text{solid}) + 3H^+(\text{soln}) + e \rightleftharpoons Fe^{2+}(\text{soln} + 3H_2O \ (\text{liquid})$$

$$\frac{1}{8}SO_4^-(\text{soln}) + \frac{5}{4}H^+(\text{soln}) + e \rightleftharpoons \frac{1}{8}H_2S(\text{gas}) + \frac{1}{2}H_2O \ (\text{liquid})$$

Fig. 2. Redox potential thresholds where oxidized mineral species become unstable[38].

Fe^{+3} hydroxides are reduced to Mn^{-2} (at +200 mV) and Fe^{+2} (at +120 mV), respectively. These reduced forms of Fe and Mn have higher solubilities than their oxidized forms. As a result, the availability of Fe and Mn increases under flooded condition. If the supply of electron acceptors is less than the rate at which electrons are made available, even stronger reducing conditions result and redox potential drops to around −150 mv and sulfate (SO_4^{-2}) is then reduced to S^{-2}. When SO_4^{-2} is exhausted, microorganisms use some of the energy stored in organic compounds by reducing H^+ and H_2 and by fermenting organic matter to CO_2, organic acids and alcohols. On further reduction CH_4 is produced from organic matter, usually at the values below −250 to −300 mV. Soils tend to maintain Eh values in a specific range until the oxidized soil components are exhausted. The Eh then drops further and reduction of still weaker electron acceptors take place. For example, a reduced soil will tend to maintain an Eh around −220 mV as long as NO_3^- is present. When NO_3^- is exhausted, Eh drops and reduction of the next strongest electron acceptor occurs.

On submergence the solubility of soil P also increases. There is an accumulation of NH_4-N and disappearance of preexisting NO_3-N. Ammonia, amines, mercaptans and sulfides are produced from protein decomposition in submerged soils. Ammonification is positively correlated with the organic C and N percent in soil but negatively correlated with C:N ratio. Ammonium accumulation is greatly accentuated in a flooded soil system.

The pH of most soils after submergence tends to approach neutrality. The pH adjustment has several favorable and adverse effects on plant growth. Due to pH adjustment, the adverse effects of extremely high or low pH are minimized which reduces Al, Fe and Mn toxicities and increases the availability of P and Si. On flooding, the partial pressure of carbon dioxide (pCO_2) in the soil increases sharply and is the dominant gaseous product of anaerobic decomposition. The increased pCO_2 has a profound effect on soil pH. The change in pH on flooding is also affected by several other factors such as valence change from Fe^{+3} to Fe^{+2}, accumulation of NH_4^+-N and transformation of sulfate (SO_4^{-2}) to sulfide (S^{-2}). Ponnamperuma[41] concluded that the decrease in pH on submergence of alkaline soils is regulated by the Na_2CO_3-CO_2-H_2O system for sodic soils, $CaCO_3$-CO_2-H_2O system in calcareous soils while increase in pH in acid ferruginous soils is regulated by the $Fe(OH)_3$-Fe^{+2} system.

As a result of submergence, the ionic strength of the soil solution increases, reaches a maximum value during the peak soil reduction period, then decreases. In acid or slightly acid soils, the reduction of relatively insoluble Fe^{+3} and possibly Mn^{+4} to more soluble forms accounts for much of the increase in the ionic strength. In neutral to alkaline soils, Ca^{+2} and Mg^{+2} also make a contribution to ionic strength. Organic matter enhances the solubilities of Fe, Ca and Mg. If the soil is initially high in NO_3-N, the ionic strength of the soil may decrease on submergence due to the loss of NO_3^- by denitrification.

Reduction of soil is purely a biochemical process and microorganisms are essential for the changes. Reduction of minerals does not occur in sterile soils. Rice plants also affect the degree of reduction of soil due to O_2 secretion from the roots. A narrow zone of soil around the actively growing roots, however, may be oxidized while the bulk of the soil is reduced. During the active vegetative growth of rice the redox potentials of cropped-flooded soils are usually higher than fallow-flooded soils. Biochemical transformations of nutrients in the oxidized rhizosphere have not been widely studied, but their behavior is probably similar to aerated systems.

Effects of submergence on rice plants

Unlike many plant species, rice has unique qualities that allow it to survive and reproduce under upland, lowland and deep water conditions.

Although an aquatic medium is favored for rice growth and yield, root growth requires a supply of O_2 and an escape mechanism for CO_2 liberated during respiration. Due to a unique air-carrying channel system (aerenchyma) from the leaf blades to the root cortex, roots can aerate without the need of O_2 from the soil.

Physical and physicochemical processes of nitrogen transformation

Nitrogen fertilization is one of the most important factors affecting rice production in the United States and the world. In the temperate zone N fertilization accounts for 40–50% of the annual rice production. Nitrogen is one of the most difficult plant nutrients to manage because of the large number of potential transformation pathways. Figure 3 illustrates the complex interactions that exist in submerged soils where N losses may occur in the oxidized and reduced soil layers, from the floodwater, by outflow and leaching, absorption of nitrogen by plants and its loss by several mechanisms. The individual processes described in Figure 4 are discussed below.

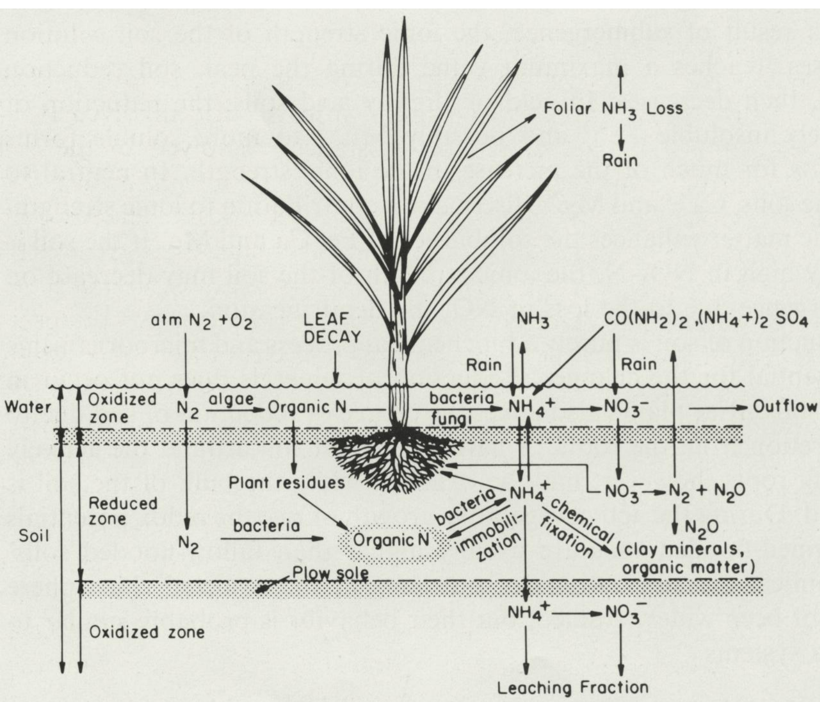


Fig. 3. Schematic representation of nitrogen transformations in a lowland rice ecosystem.

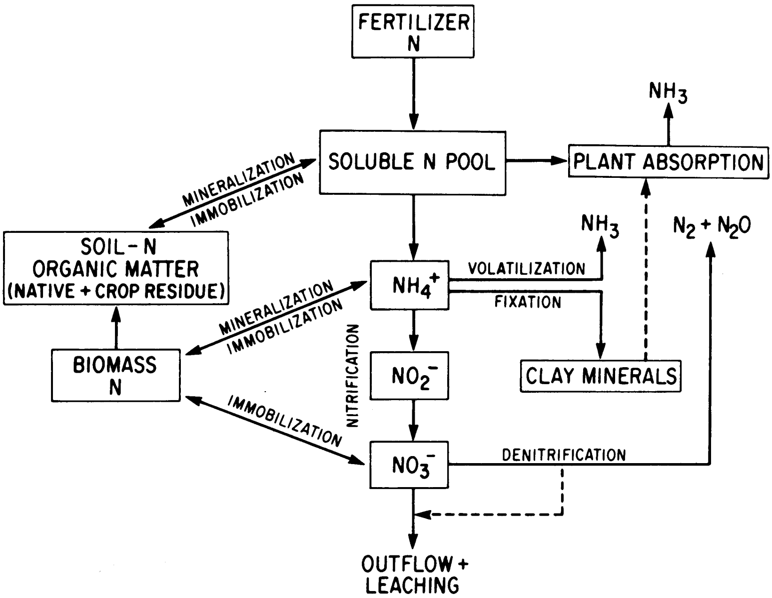


Fig. 4. Schematic representation of nitrogen transformation pathways in a flooded soil system.

Nitrogen transport in submerged soil

The movement of N in soils plays an important role in determining its availability for plant growth. Two main processes are involved in N transport, namely (i) convection of substances dissolved in the soil solution due to the mass-flow, and (ii) molecular or ionic diffusion due to concentration gradients[16]. Another possible mechanism includes ionic movement in an electrical field. Movement of N species, such as NH_3 (aq), NH_4^+, NO_3^- and urea occurs in soil by mass-flow, diffusion or both.

A factor which often determines N movement is the degree of interaction between the soil solution and the soil particle surface. A strongly adsorbed cation such as NH_4^+ will move less readily than an anion like NO_3^- or urea which are lightly adsorbed by most soils[16,36]. The quantity of NH_4^+-N transferred by diffusion per unit area per unit time is proportional to the diffusion coefficient and the concentration gradient. The apparent diffusion coefficient of NH_4^+-N is 0.216 cm^2/day as compared with 1.33 cm^2/day for NO_3^-, suggesting NO_3^- moves about 6 times faster than NH_4^+-N[42]. The transport of NH_4^+-N by ionic diffusion from the anaerobic to aerobic layer of the flooded soil is facilitated by large amounts of reduced Fe^{+2} and Mn^{+2}, lower CEC and high moisture content of the flooded soil. The general movement of NH_4^+-N is downward > lateral > upward[47]. Leaching and run-off processes also affect the movement and loss of N in these systems and are discussed below.

Leaching and run-off losses

Continuous submergence leads to losses of soluble soil and fertilizer N through leaching and run-off processes. Ammonium-N is much less subject to leaching than NO_3^- because of its adsorption on the cation exchange complex. Loss of NH_4^+ by leaching, however, is greater in waterlogged soil than in well drained soil. This is because NH_4^+ accumulates in waterlogged soil and reduced Fe and Mn displace NH_4^+ from the exchange complex and under a constant head of water NH_4^+ moves downward as percolation[38]. Losses of N by leaching may vary from 1 to 70% of applied N, while run-off and leaching losses from rice fields can range from 4 to 16 kg N/ha and 5 to 25 kg N/ha, respectively. Leaching may occur rapidly in coarse textured wetland soils or in soils with appreciable amounts of hydrous oxides of Fe and Al due to low CEC[47]. Leaching losses are less from slow-release fertilizers such as SCU and IBDU.

Chemical and biological transformations of nitrogen under submerged soil conditions

Nitrogen undergoes several chemical and biological transformation processes in the soil[4,5,37,38,39,47]. The chemical transformations include clay fixation of NH_4^+ and direct NH_3-volatilization. Biological transformation of nitrogen include mineralization-immobilization, biological N_2-fixation, nitrification-denitrification, and plant absorption.

The voluminous literature on nitrogen transformations in soil is reviewed in *Nitrogen and Rice*[5,27,32,37,38], *Nitrogen in Agricultural Soils*[3,21,48,56] and *Nitrogen Economy of Flooded Soils*[10]. Much of the research on N transformations has been done on upland crops. Biochemical transformations of N, especially in the oxidized rice rhizosphere, have not been widely studied. A recent study[45] extrapolating mass balance data suggests that nitrification-denitrification reactions do occur in the rice rhizosphere.

The systems of rice culture involving continuous and alternate flooding affects the behavior of both native and applied N. The special condition prevailing under the waterlogged soil environment accelerates the normal ammonification process and completely suppresses nitrification when O_2 is not present. On flooding, NH_4^+-N accumulates in the soil and NO_3^--N disappears. Large losses of NH_4^+-N, either applied as fertilizer at the soil-water interface or mineralized during the decomposition of organic matter, occurs as a result of waterlogging[46]. Nitrogen losses are usually more pronounced in the absence of crop residues[5,51]. The presence or absence of a growing crop also affects N transformation.

Nitrogen fertilizer sources for rice can be divided into two groups;

namely, organic crop residues and inorganic-N fertilizers. Organic crop residues must first undergo biological degradation before participating in other transformations as were described earlier. Inorganic N sources could be either soluble conventional type such as ammonium sulfate and urea or controlled (slow) release fertilizers such as SCU and IBDU. Urea and organic-N sources undergo enzymatic hydrolysis and are converted to NH_4^+-N. Addition of energy-rich organic material to the soil stimulates soil organic matter transformation (priming action) either positively or negatively[5,17,19]. The addition of N fertilizer has several actual and apparent effects on soil N transformations and plant uptake. Crop residue additions can affect the transformation and distribution of fertilizer N into different soil N fractions[8]. Biologically fixed-N is also subjected to these transformation processes[20].

Mineralization and immobilization

Tracer experiments have shown that there is a simultaneous synthesis (immobilization or tie-up) and degradation (mineralization or release) of organic compounds in the soil. These are due to microbial activity which leads to a continuous interchange between organic and inorganic N forms[5,14,21]. Thus, only the net mineralization or net immobilization of the mineral N is usually measured during the mineralization process[51]. It is the net balance of the two opposing processes that exerts a large influence over the availability of N to plants and the conversion of N in the soil as organic or fixed forms.

A dynamic equilibrium exists between the available (soluble plus exchangeable) and unavailable (organic and clay-fixed) forms of N in the soil. The individual changes are difficult to assess, since we can only measure the end result of these processes at a particular time. By using labeled-^{15}N materials, however, it is possible to measure and account for the dynamic changes of mineralization-immobilization processes.

Results of such studies indicate that added sources of inorganic N undergo rapid immobilization initially followed by a decrease in mineralization rate[4,5,7,8]. The magnitude and duration of inorganic-organic N equilibrium and transformation processes vary with conditions[4,9,47]. Net immobilization of N is less in flooded soil than aerobic, well-drained soils[7]. Yet, 20–80% of the added fertilizer N can be immobilized depending upon the conditions[6,9,13]. To achieve efficient use of N from the soil as biologically fixed-N, crop residues and fertilizer, it is necessary to consider the time-rate aspects of mineralization relative to the N requirement of rice. In the short-term, the supply of N to rice is governed by the rate of mineralization of organic-N to NH_4^+-N. Amino acid N is more susceptible to mineralization than other fractions of soil N.

Net mineralization does not occur until a wide C:N ratio of soil organic matter is narrowed to 20:1 or less[4,5]. Ammonification patterns can be rectilinear for air-dried soil brought under flooding, linear under continuous flooding or sigmoidal in very fine-textured soil under flooding[47]. Ammonification patterns of recently immobilized N show deviation from that of the native soil N in that the immobilized N slowly undergoes remineralization. Some N may progressively be stabilized and may remain for long periods, possibly decades, showing resistance to mineralization. Broadbent and Nakashima[7] and Hauck[18] have reported that mineralization of immobilized N can range from 2–10% during the growing season and about 1–3% per year thereafter. According to Ito and Watanabe[20], the mineralization rate can be about 5 times greater for biologically fixed-N (23.4% mineralized) as compared to native soil-N (4.6% mineralization). The amount of N mineralized in a soil during the growing season of a crop varies with soil and environmental conditions as well as the techniques used for measurement, and can range between 5–1166 ppm.

Non-exchangeable NH_4^+

The capacity of submerged soils to bind NH_4^+ and K^+ in a non-exchangeable form is determined largely by the amount and kinds of 2:1 type clay minerals present. Entrapment occurs between silica sheets through interlayer bonding accompanied by contraction of interlayer spacing[33]. Fixed-NH_4^+ is not removed by extraction with usual soil extractants which traditionally defines the fixed portion as being unavailable to plants and microorganisms. Lamm and Nadafy[24] suggest that like K^+, NH_4^+ may exist in several release forms characterized by a dynamic equilibrium such as:

$$\text{soluble } NH_4^+ \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{exchangeable } NH_4^+ \overset{\text{slow}}{\rightleftharpoons} \text{intermediate } NH_4^+ \overset{\text{very slow}}{\rightleftharpoons} \text{fixed } NH_4^+$$

In this characterization 'intermediate NH_4^+' may be considered to occupy interlayer sites on the clay lattice which is exchangeable with K^+ and H^+ and in which defixation increases when the clay lattice is expanded. A distinction between 'native' and 'culturally induced' NH_4^+ fixation is made by some investigators who note a difference in their plant availability. 'Culturally induced' fixed-NH_4^+ is more available to crops and may be influenced by such factors as soil K^+ and NH_4^+ status, degree of lattice weathering, soil moisture status, particle size, competing ions and confined root masses[33]. Bajwa[1] reported that soils dominant by vermiculite and montmorillonite fix the largest amounts of applied NH_4^+ (94% and 91%, respectively), followed by beidelite (72%) and amorphous clays (45–64%). Fixation is negligible (10%) in clays with hydrous micas, halloysite and chlorite.

The clay-fixed (non-exchangeable) NH_4^+ can be slowly replaced and released by Na^+, Ca^{+2} and Mg^{+2}. Clay fixation of NH_4^+ increases with NH_4^+ concentration, depth of soil, alternate drying, high pH and liming, freezing and thawing, addition of nitrification inhibitors, and depletion of K^+ from the soil. The release of fixed-NH_4^+ increases when the situations mentioned above are reversed. Ammonium ions are also released when the exchangeable NH_4^+ content decreases below the equilibrium value as a result of plant uptake and leaching. Keerthisinghe *et al.*[22] showed that non-exchangeable NH_4^+ was released for plant uptake in submerged soil. As much as 2.2% of the total plant N was derived from the labeled fixed NH_4-N. The amount of ^{15}N-label taken up by rice was inversely related to the N application rate.

Soluble plus exchangeable nitrogen

The soluble plus exchangeable (available) N is the most important fraction in crop nutrition. The main sources of available N are added fertilizer and mineralized-N. When the N fertilizer sources are added to flooded soils, a rapid decline in the available N occurs with time, usually 30 to 45 days. Crop uptake of fertilizer N virtually stops early in the growing season. The exchangeable NH_4^+-N content in flooded rice soils may increase, however, due to mineralization of soil organic matter and the release of clay-fixed NH_4^+-N after a few days of flooding. Soil incorporation of straw decreases available N levels in the early season because of immobilization and increases in the late season due to its release. The available N is subjected to crop uptake, biological and non-biological fixation, nitrification-denitrification and volatilization[56].

Biological N_2-fixation

Nitrogen balance studies with rice often show an excess of N recovery over soil supply. This is assumed to be due to biological N fixation and these contributions vary from 15 to 50 kg N/ha per crop[23]. More N is biologically fixed in the presence of the rice plant, especially in the wet tropical seasons. Submerged soils with bluegreen algae and N-fixing bacteria fix N but a part of this may not be available for the current crop[44]. Reddy[42] has estimated the extent of biological N_2-fixation to be 0.41–0.74 mg N per kg dry soil per day.

Ammonia volatilization

Ammonia volatilization is an important pathway of N loss, especially in fertilized cropping systems. During recent years a number of studies

Table 1. Ammonia volatilization losses from wetland rice soils determined by different techniques

Kind of soil	Kind of study	Fertilizer	N fertilizer rate (kg/ha)	N loss (%)	Remarks	Reference
Flooded soils, pH 8.4	Laboratory	Ammonium sulfate Urea Surface applied	66	22	Laboratory incubation	17
Flooded soils, pH 8.4	Laboratory	Ammonium sulfate Urea Incorporated-broadcast	200	1.7–16.7	Laboratory incubation	25
Crowley silt, pH (8.0) flooded	Laboratory	Ammonium sulfate	112,224, and 448	0.04–0.10	Boric acid used as trap with air train	11
Flooded soils	Laboratory	Ammonium sulfate	50 and 200	0.50–7.0	Sulfuric acid used as trap for NH_3 without air train	26
Maahas clay	Greenhouse	Ammonium sulfate Incorporated broadcast	100	1–19.0	–do–	51
(Flooded)	Field	Ammonium sulfate Urea broadcast	100	3.3–4.0	–do–	51
Maahas clay (pH 7.0–8.4)	Field	Ammonium sulfate Broadcast	60	17–40	Open-dish system	2
Maahas clay (Flooded)	Field	Ammonium sulfate Broadcast	40–60	30–60	Open-closed systems	2
Maahas and Luisiana clays (pH 7–9.5)	Greenhouse	Ammonium sulfate Placed-broadcast	30–90	0.01–5.8	Sulfuric acid used as trap for NH_3 with air train	34
	Field	Ammonium sulfate Urea Placed-broadcast	90 30–90	0.25–6.8 0.25–5.8 1.0–20	–do–	27

Flooded soil (pH 7.0–7.5) Thailand	Field	Ammonium sulfate Incorporated-broadcast	50–100	0.8–12.4	–do–	28
Mahaas Clay	Field	Ammonium sulfate	80	5	Micro-meteorological	15
		Broadcast-incorporated		11	Micro-meteorological	15
		Top-Dresser-PI	40			
Sacramento clay	Field	Ammonium sulfate				
		Broadcast-incorporated	80	5.6	Air train and ammonia Trapping	[a]
		Banded	80	1.6		
Mahaas clay	Field	Urea-incorporated	60	13	Micro-meteorological	13
Clay loam (7.6)		Urea-surface	100	21	Air Train-Acid Trap	49
Mahaas clay						
Maligaya si cl.	Field	Urea-broadcast	80	27–47	Micro-meteorological	12
Maligaya si cl.	Field	Urea-broadcast	58	36%	Micro-meteorological	12
		Ammonium sulfate-broadcast		38%		

[a] Mikkelsen *et al*, unpublished

have been concerned with NH_3 volatilization losses from flooded soils[27,53]. Under conditions where NH_4-N fertilizers are broadcast directly onto soil or water without adequate incorporation NH_3 volatilization losses can be appreciable (10–50%). Where appropriate technology is used to manage fertilizer application by placement either by banding, mud-ball or supergranule placement, NH_3 losses are very minimal (< 5.0%). Poor fertilizer management practices contribute to large N losses from flooded rice systems and may be a factor in reduced rice yields.

A wide range of NH_3 volatilization losses are reported from flooded soil systems[27]. Inconsistencies in reported losses exist because of imperfect systems of measurement and the complex range of cultural practices, floodwater, soil and atmospheric variables that make measurements very site specific. Forced-air exchange methods using enclosures and acid-traps are frequently used, although they have many limitations. Micrometeorological methods using energy balance and aerodynamic techniques measure NH_3 in the air but losses vary with wind speed, air and water temperature, heat fluxes and net radiation at a specific site. This methodology is perhaps most precise but is extremely labor intensive and require extensive instrumentation and analytical accuracy. The method lacks capability of comparing various ecosystems in close proximity.

A number of water, soil, air and fertilizer management factors affect the kinetics of NH_3 volatilization. The water parameters include NH_4^+-N concentration, diurnal pH, pCO_2, total alkalinity, water buffering capacity, depth, temperature, turbulence, transport fluxes and biotic activity. Dominant soil factors affecting volatilization are soil pH and pe, pCO_2 and carbonate chemistry, cation exchange characteristics and microbial activity. Atmospheric conditions of wind velocity, PNH_3, air temperature and radiation directly influence NH_3 loss. Crop and fertilizer management directly affect the loss patterns depending on N source, timing and method of application, cultural practices, transplanting, direct seeding, or seed drill, water management factors, field layout and plant canopy status.

Ammonia volatilization losses from flooded rice are highly dependent on the particular ecosystem involved. The range of losses measured by various researchers is found in Table 1. From these data it is evident that rate, source and method of N fertilizer application influence the concentration of NH_4^+ in the floodwater. Where urea is applied, urease activity as well as immobilization of N in the aquatic biota exchange reactions and water transport affect the quantity of NH_4^+ available for NH_3 volatilization. In addition to floodwater NH_4^+ concentration, volatilization depends to a large extent on floodwater pH, water depth, temperature and wind velocity. Aqueous NH_3 increases by a factor of 10 in the pH range of 7.5–9.5 in floodwater and increases in a linear fashion with increasing wind speed and volatilization temperature. Diurnal pH fluctuations occur with maximum values about 2 pm and decreasing during the evening, a pattern synchronized with cyclic photosynthesis and respiration of the aquatic biota. Water alkalinity derived chiefly from HCO_3-sources or from urea hydrolysis acts as a pH buffer which is essential if NH_3 volatilization is to be sustained over a prolonged period. The movement of NH_4^+ and urea-N in flooded soils has not received attention as a factor influencing NH_3 volatilization. Nitrogen movement in the soil can readily take place by liquid phase diffusion, solid phase diffusion and mass flow. Ammonium and urea-N spacial distribution, leaching and percolation losses are closely linked and may influence volatilization, denitrification, clay fixation, outflow and leaching losses.

Nitrification and denitrification losses

The biological oxidation of NH_4^+-N to NO_3^--N (nitrification) results in the conversion of the relatively immobile cation NH_4^+ into a more mobile anionic (NO_3^-) form, which in turn is susceptible to denitrification. The submerged soil is an ideal environment for denitrification since it possesses a thin oxidized surface underlain by a thick reduced layer. The oxidized layer supports nitrification and the reduced zone, deficient in oxygen and providing decomposable organic matter to energize the reduction of oxidized forms of nitrogen, supports denitrification. The existence of aerobic and anaerobic zones in close proximity in submerged soil, aided in part by the rice plant which transports oxygen to the rhizosphere, facilitates nitrification-denitrification. These reactions likely occur simultaneously. The anaerobic nature of the submerged soil causes the instability of NO_3^-, NO_2 and N_2O, which are used as terminal electron acceptors in the anaerobic respiration of various heterotrophic microorganisms lead to N_2 and N_2O loss[14].

The loss of N by denitrification may vary from 0 to 70% of the applied N fertilizer. The estimated average fertilizer N deficits range between 25 and 35% but field data are lacking to accurately characterize these losses. Diffusion of NH_4^+ from anaerobic to aerobic soil layers may account for half of the total loss. Where alternate soil submergence and drainage occur, conditions are highly favorable to nitrification and subsequent denitrification[43,46]. Denitrification rates depend on available soil C, temperature, pH, O_2 supply, redox potential, NO_3^--N concentrations and the activity of denitrifiers.

Denitrification is widely recognized as a major cause of N loss in lowland rice culture, but documentation of the absolute quantities involved are lacking. The low recovery of fertilizer N in rice is largely attributed to nitrification and subsequent denitrification. Such losses unaccounted for in plant absorption and soil retention are attributed to 'apparent denitrification loss.' Tracer studies, using ^{15}N enriched fertilizers in a N-budget approach, are needed in the field over long periods of time to statistically characterize denitrification losses. To date limitations due to costs, equipment and analytical sensitivity have precluded rapid advances in quantifying denitrification losses.

Some control of denitrification losses are possible which can improve N use efficiency. Proper placement of N in the soil reducing layer and timing of applications to meet the needs of growing crops are probably the most cost-effective means of reducing denitrification losses. The use of nitrification and urease inhibitors and controlled release N fertilizers have some promise to reduce N loss by retarding the soil nitrification process.

Nitrogen losses from plants

Recognition that significant N losses can occur from plant tops of annual and perennial crop species has been reviewed by Wetselaar and Farquhar[54]. Evidence that the absolute amounts of N in the aboveground parts decrease before harvest has been demonstrated for a number of crops, including rice. These losses, heretofore overlooked, represent real losses from the soil-water-plant system and need assessing in developing accurate N budget information. Typical N loss from plant tops observed in Australia and California are shown in Figure 5.

Tanaka and Navasero[50] reported N losses from rice crops grown under high levels of N application. The losses appear greatest about 3 weeks prior to flowering and maturity under high N inputs and somewhat later with lower N inputs. Other data support the observation that the N content of plant tops decline from the onset of flowering to maturity and may reflect significant plant losses both as direct NH_3 and amine loss from foliar parts but also possible excretions from roots. Foster and Stutte[14] provide data that N volatilization does occur from many plant species, including rice. Glutamine synthetase appears to be a main pathway of ammonia assimilation and catalyzing the refixation of NH_3 released during photorespiration. Preliminary data indicates that N released during photorespiration may escape as NH_3 and amines *via* plant foliage. Losses vary with increasing temperature in the range of 28 to 35°C. Various mechanisms of N loss from plants including gaseous losses, require further evaluation and need to be considered in developing N-budgets for rice and other crops.

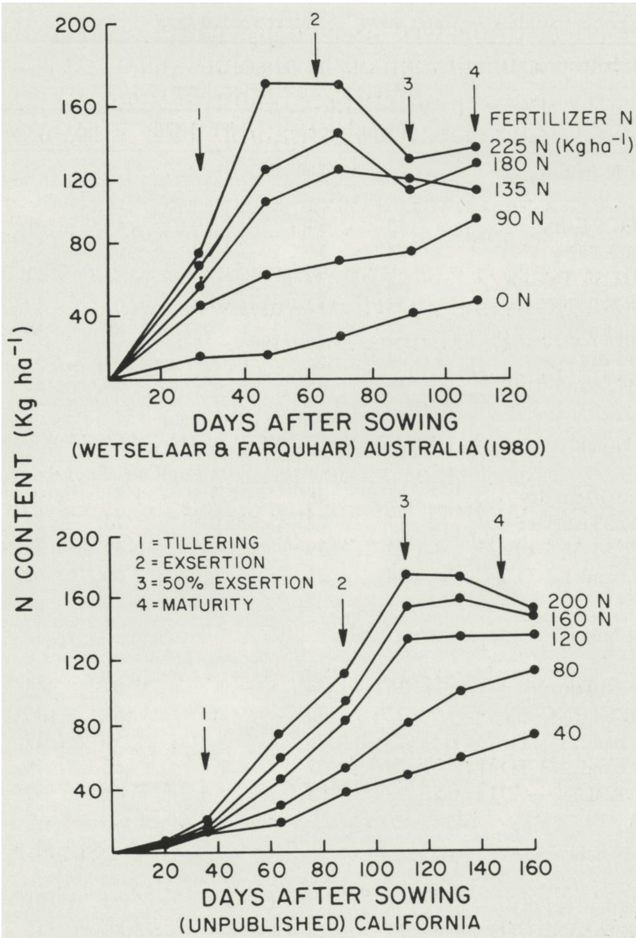


Fig. 5. Losses of N from plant tops during the reproductive period of rice in Australia and California.

Nitrogen budgets in rice

Nitrogen budgets have been used widely in recent years to expand knowledge of the N cycle for various ecosystems. Their major use has been to estimate the net N losses, or unaccountable N losses from specific cropping systems. Until labeled-^{15}N fertilizer materials became available, accurate accountability was difficult and the interrelated biological processes of mineralization, immobilization, NH_3 volatilization, clay fixation, nitrification-denitrification, outflow losses and plant absorption difficult to characterize. The methodology of ^{15}N uses in soils research, the advantages and limitations have been described by several authors[3,18,25]. These investigators emphasize that N-budget studies are

Table 2. Fertilizer ^{15}N management studies — water sown — direct seeded rice

Soil	Fertilizer treatment	Recovery of ^{15}N-fertilizer (%)				
		Plant	Soil	NH_3-VOL	Total	Loss
Montmorillonitic mollisol California	100 kg N-field					
	AS-BDCST-dry	15	34	–	49	51
	U-BDCST-dry	34	31	–	65	35
	AS-BDCST/INC-dry	22	39	–	56	44
	U-BDCST/INC-dry	29	32	–	61	39
	AS-band-dry	23	41	–	64	36
	U-band-dry	24	32	–	56	47
	Aq NH_3-band-dry	36	33	–	68	32
Montmorillonitic mollisol California	90 kg N-field					
	U-band-10 cm-dry	31	48	1.3	81	19
	U-BDCST surface-dry	17	22	35.0	73	27
	U-BDCST/INC-dry	22	39	1.6	62	38
	U 1/2 band 1/2 TD	34	25	–	60	40
Kaolinitic typic haploxeralfs California	100 kg N-field					
	U-band-10 cm-dry	26	34	–	60	40
	U-BDCST/INC-dry	22	32	–	54	46
	U 2/3 band, 1/3 TD (MT)	23	28	–	51	49
	U 2/3 band, 1/3 TD (PI)	25	27	–	52	48
	U 1/3 BDCST + 2/3 band	18	25	–	43	57
Montmorillonitic vertisol California	90 kg N-field					
	AS-band-10 cm-dry	48	27	4	79	21
	AS-2/3 band, 1/3 TD	57	23	8	88	12
	AS-TD 1/3 × 3	23	26	15	64	36
	120 kg N-field					
	AS-band-10 cm-dry	63	25	1	89	11
	AS-TD 1/3 × 3	24	29	18	71	29
Montmorillonitic mollisol California	124/248 ppm N pot					
	AS-BDCST surface-dry	29/34	57/48	–	86/82	14/18
	AS-banded-10 cm-dry	40/44	52/50	–	92/94	8/6
	AS-BDCST/INC-dry	29/33	54/49	–	83/82	37/28
	AS-TD — 1/2 × 2	36/40	49/48	–	85/88	15/12
	AS-split band + TD	39/47	50/40	–	89/87	11/13
	124/269 ppm N pot					
	U-BDCST surface-day	26/27	56/52	–	82/79	18/21
	U-banded-10 cm-dry	37/37	56/46	–	93/83	7/17
	U-BDCST/INC-dry	28/28		–	76/66	24/34
	U-TD — 1/2 × 2	32/33	48/42	–	80/75	31/34
	U-split band + TD	33/38	42/27	–	75/65	25/35

Table 2 cont.

Montmorillonitic mollisol	100 ppm N-pot		Broadbent and Mikkelsen (1968)			
California	AS-cropped	9.7	76		86	14
	AS-uncropped	–	57		57	43
Montmorillonitic mollisol	90 kg N		Manguiat and Broadbent (1977)			
California	AS-band 10 cm dry	59	25	2	86	14
	AS-BDCST/INC dry	29	33	10	72	28
	AS-2/3 band 1/3 TD	55	22	2	79	21
	AS-1/3 band, 2/3 TD	28	32	6	66	34

empirical, usually estimate events occurring over a single season, and that soil characteristics, environmental factors and crop management affect results. The 'priming effect' whereby fertilizer additions frequently increases soil N mineralization and crop recovery is not always considered.

Nitrogen transformation patterns and budgets with rice have been described by Vlek and Craswell[53] (53) for transplanted rice. They have shown that 40 to 60% of ^{15}N-labeled ammoniacal fertilizer N was lost when broadcast to floodwater when applied 2–4 weeks after transplanting and that broadcast and incorporation before transplanting resulted in a general reduction in fertilizer losses. Crop recovery of fertilizer N at harvest varied from 17.4 to 54.2%.

Nitrogen budget studies of mechanized rice production in the United States, where ammoniacal-N sources are usually applied to dry soil prior to direct sowing into water, have not been reported and represent a fertilizer use pattern of increasing importance in the world.

A summary of fertilizer budgets obtained from dry soil pre-flood fertilizer-^{15}N applications recorded from different soils in California appears in Table 2.

Rice ^{15}N budgets have been conducted with agronomic evaluations made with conventional fertilizer materials in randomized macro-plots. Application of ammoniacal N fertilizer by deep placement has been shown to be superior to surface application in several early studies[6,29,30]. Using ^{15}N-enriched ammonium sulfate and urea in a greenhouse experiment measuring the effects of N-source, timing placement and rate (30 *vs* 60 mg N/kg soil), data were presented showing that overall N losses were greater with urea than ammonium sulfate, especially at the higher N rate. Urea lost about 14% of the fertilizer N at the 30N rate and 23% at a higher rate. Actual uptake of ^{15}N-fertilizer ranged from 26 to

47%. Plants recovered 44 and 37% of banded ammonium sulfate, respectively, from band applications, and 29 and 26% of broadcast ^{15}N, respectively. Split N application recovery by the crop was intermediate. Fertilizer applications influenced the release of soil N and produced a dividend of crop N equivalent to 20–25% of the amount of fertilizer applied[6]. Reddy and Patrick[43] showed that when ammonium sulfate was deep placed, 49% of the fertilizer N was recovered by the crop, 26% was recovered in the soil and 25% was lost from the system. The same authors[43] report crop recovery of ^{15}N-labeled ammonium sulfate of 49 and 64% with multiple surface applications showing superior crop recovery. Residual ^{15}N measurements show that 24–26% remained in the soil organic fraction, from which about 6% was utilized by a succeeding rice crop.

In California field studies, ^{15}N-labeled fertilizers have been widely used to develop N budgets for the various pathways by which N is either utilized or lost and to develop strategies for fertilizer use which are consistent with the best crop yields (Table 2 and Figure 6). Labeled fertilizer N recovery by rice at harvest has varied from 10 to 59%. The magnitude of plant recovery from applied fertilizer has been poorly

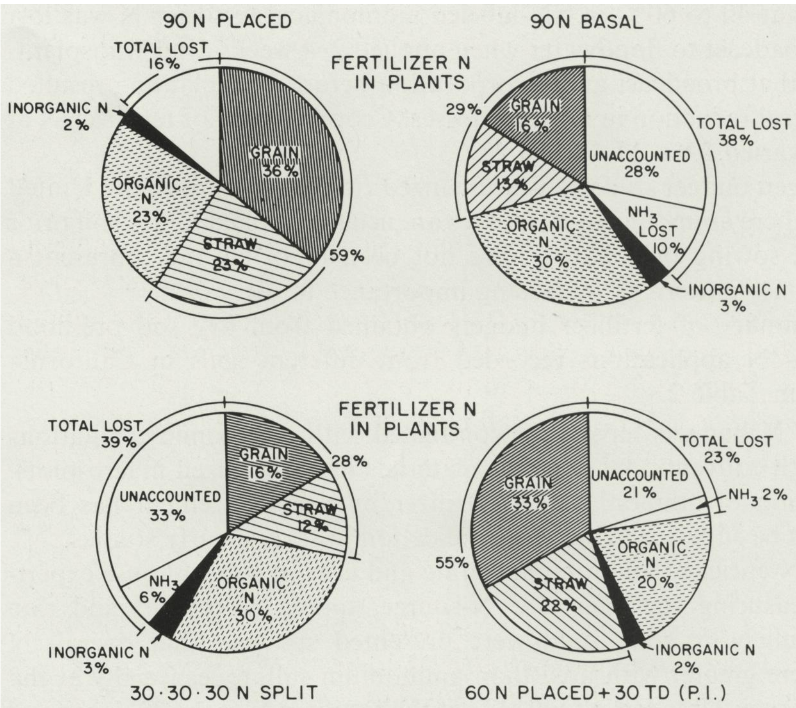


Fig. 6. Fate of fertilizer nitrogen in a direct-seeded rice ecosystem (California).

correlated with yield, although excellent correlations are observed with total N in the harvested crop and plant analysis. In general, however, high plant recovery of fertilizer N is correlated with low losses. It is evident that the application of fertilizer N has enhanced total uptake of N by the crop. In most cases where fertilizer has been applied, uptake of soil N has increased from 20–30%, in part due to the 'priming effect,' biological interchange, more vigorous plants and enhanced root development.

Soil retention of applied ^{15}N fertilizer has ranged from 22 to 57% with no consistent relationship to method or timing of N application. Banded fertilizer N usually provides the highest rate of fertilizer retention followed by broadcast-incorporated N and the least retention in surface or water broadcast applications. Labeled fertilizer N is found ultimately in the soil organic matter fraction representing from 19 to 34% of the total N applied. In typical clay soils used for rice production, possessing impervious clay layers, 90–96% of the residual nitrogen is retained in the 0–30 cm depth with the major portion in the 0–15 cm depth. These data indicate that relatively little movement of fertilizer N occurs in these typical soils with 25 to 40% clay. Clay fixation of NH_4^+-N accounts for 3 to 9% of fertilizer N retained in the soil. With cropping histories of 30–50 years continous rice, receiving an average of 100 kg N/ha annually and soils rich in K minerals, non-exchangeable NH_4^+ does not constitute a large portion of retained fertilizer N.

Total recovery of fertilizer N from crop and soil ranges between 51 and 93%, the highest values being recorded from large container experiments. Recovery of N from a urea source is usually slightly less than from ammonium sulfate, each applied in the same manner. With equal amounts of total N applied, ammonium sulfate gives an increased grain yield of about 5–10% more than urea. Losses of urea-N from the flooded soil system is usually significantly greater than for applied ammonium sulfate. Field experiments record that method of irrigation, flow rates and factors determining direction of water flow greatly influences the distribution of urea-N in the soil flow layer. Banded ammonium sulfate of aqua-NH_3 distribution are much less affected by the water transport system.

Ammonia volatilization measurements indicate that deep placement of ammoniacal-N, 10 cm deep in submerged soils, will reduce NH_3 volatilization to very low levels. One to 2% NH_3 volatilization losses are typically observed from deep placed applications, measured by micrometeorological and forced-air trapping methods. In contrast, fertilizer N applied broadcast on soil or into floodwater have shown volatilization losses as high as 35% of the total N applied. Urea-N consistently

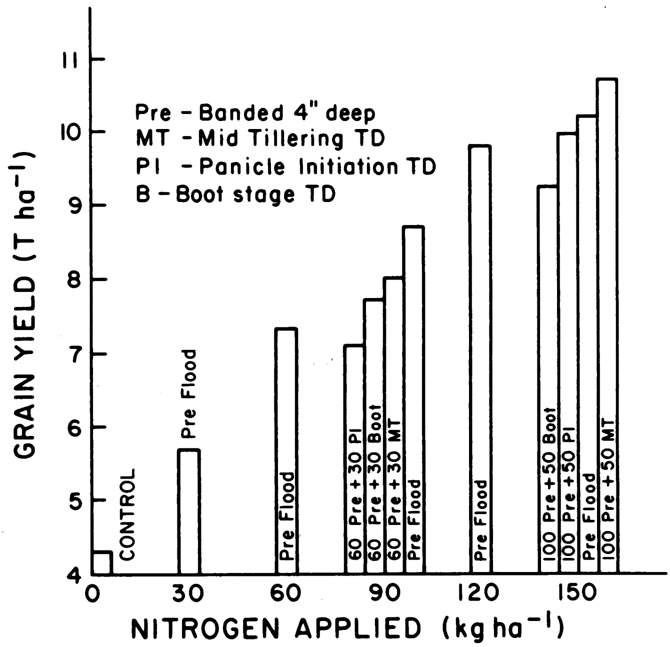


Fig. 7. Response of direct-seeded rice to rates and methods of nitrogen fertilization.

maintains higher volatilization losses applied broadcast than does ammonium sulfate.

Crop yields as affected by method of N application in 17 fertilizer experiments conducted under a wide range of soil conditions with water-sown rice show a highly significant difference with method of N application (Fig. 7). Deep placement of N gives statistically significant increases in grain yield over split applications, 2/3 N applied banded by pre-flood placement and 1/3 N applied at mid-tillering, at panicle initiation or in the boot stage of development. Split N applications applied at mid-tillering have been superior or equal to applications top-dressed at the panicle initiation stage.

Losses of plant N have been observed progressively from the time of panicle exsertion in rice until harvest. The seasonal loss from plant tops is sometimes of the order of 5% of the total plant N uptake. Further investigations are needed to more adequately quantify the magnitude of this loss and to characterize the conditions under which they occur (Fig. 5).

Nitrogen use efficiency

Efficient fertilizer use is one benefit desired from the development of N budgets in rice. It is apparent that ^{15}N-crop recovery values reveal only part of the effect of fertilizer N on crop yields. Valuable comparisons are provided on the benefits and losses likely to occur with specific N transformation processes, but they are very site specific, have value only within the context of specific soil-water-cropping systems, and do not provide useful indices of fertilizer benefits to increase grain production.

The effectiveness of fertilizer N treatments can be assayed by measuring the ratio of grain yield to N application rate. This is called the 'agronomic efficiency (AE)' of the fertilizer and is best measured as the increase in grain yield due to a given treatment. AE is defined as:

$$\mathrm{AE} = \frac{\text{kg grain}}{\text{kg N applied}} = \left(\frac{\text{kg grain}}{\text{kg N absorbed}}\right)\left(\frac{\text{kg N absorbed}}{\text{kg N applied}}\right)$$

The ratio of grain yield to N absorbed is termed its 'physiological efficiency,' while the ratio of N absorbed to N applied is called the 'recovery fraction (RF).' This 'recovery fraction' is defined as:

$$\mathrm{RF} = \left(\frac{\text{kg N absorbed}}{\text{kg N supply}}\right)\left(\frac{\text{kg N supply}}{\text{kg N applied}}\right)$$

It can be seen that RF is a measure of the effectiveness of a given treatment in increasing plant N uptake. The ratio of N absorbed to the N supply is termed 'uptake efficiency' and is a function of the properties of the root-surface area, distribution, and uptake per unit area. These factors are dependent upon soil physical and chemical status, and health and growth characteristics of the plant.

Moore *et al.*[31] applied this concept in describing the efficiency of fertilizer use in flooded rice. Available (soluble and exchangeable) N was measured with time in fertilized and unfertilized plots with concommitant measurements of N uptake by plants. They found that if 'the difference in plant N between fertilized plants and controls was plotted as a function of the parallel differences in soil N' for the first four weeks after application, a high correlation ($r^2 = 0.96$) resulted, with a slope of -0.55. This can be interpreted as a rate constant for the uptake of effective fertilizer N per unit change (decrease) of supply, or uptake efficiency. Calculation by the standard difference method gave a value of 63 percent for fertilizer N effectiveness. The difference between these two methods is the (kg N supply/kg N applied) term in the above equation for RF (actually fertilizer effectiveness). Values for AE will vary widely with soil fertility, rates of N applied, crop variety, and a wide range of management factors affecting yield. Values calculated from reported data fall in the range of 32.3–108 for field trials with much higher values calculated from pot trials[6]. Factors affecting AE generally parallel those affecting N uptake, yield, and fertilizer uptake efficiency. The shortcoming of this value is that it includes the grain yield due to soil N uptake which is undefined at a zero rate of application. For this reason it would perhaps be more useful to use the yield increase due to a given application rate as the numerator in the equation. This point is underscored by the findings of Reddy and Patrick[44] that show the uptake of fertilizer N to be more highly correlated with relative yield increase than with absolute yield.

The physiological efficiency (kg grain/kg N absorbed) portion of the AE equation is a function of the distribution of N in the plant at harvest and the percent of N in the grain. Murayama[32] reports that rice crops take up from 19–21 kg of N to produce a ton of brown rice and that this value is 'nearly constant.' This implies a physiological efficiency of about 50. Koyama *et al.*[23] call this value the productive efficiency and measured it for different times of top-dressing, finding that it varied with time of top-dressing and variety. Yoshida[57] suggests that a combination of parameters be used in determining efficiency of fertilizer use namely,

$$\begin{array}{l} \text{Efficiency of fertilizer N} \\ \text{(kg rice/kg applied N)} \end{array} = \begin{array}{l} \text{Percentage N recovered} \\ \text{(kg absorbed N/kg applied N)} \end{array} \times$$

$$\begin{array}{l} \text{Efficiency of utilization} \\ \text{(kg rice} \times \text{kg absorbed N)} \end{array}$$

using values for recovery percentage and utilization efficiency for tropical transplanted rice. Yoshida[57] reports values of fertilizer use efficiency of 15 to 25 kg rice/kg applied N[57]. Nitrogen budgets have provided a large amount of research information about the N transformation processes in submerged soils. There remain many unanswered questions, however, that must be studied to fully integrate fertilizer management to the highest level of efficiency in the complete environment of wetland rice. Increased understanding of N budgets will lead to better fertilizer management practices, increased N use efficiency and improved socio-economic status of farmers.

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