

NITROGEN TRANSFORMATIONS AND LOSS IN FLOODED SOILS AND SEDIMENTS*

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I. INTRODUCTION

The biological, chemical, and physical processes involved in the loss of N from flooded soils and sediments include (1) mineralization of organic N; (2) nitrification of $\text{NH}_4\text{-N}$; (3) NH_3 volatilization; and (4) denitrification (Figure 1). The agronomic and ecologic significance of the simultaneous occurrence of these processes in the removal of N from flooded soil and sediment systems to the atmosphere have been examined only recently.

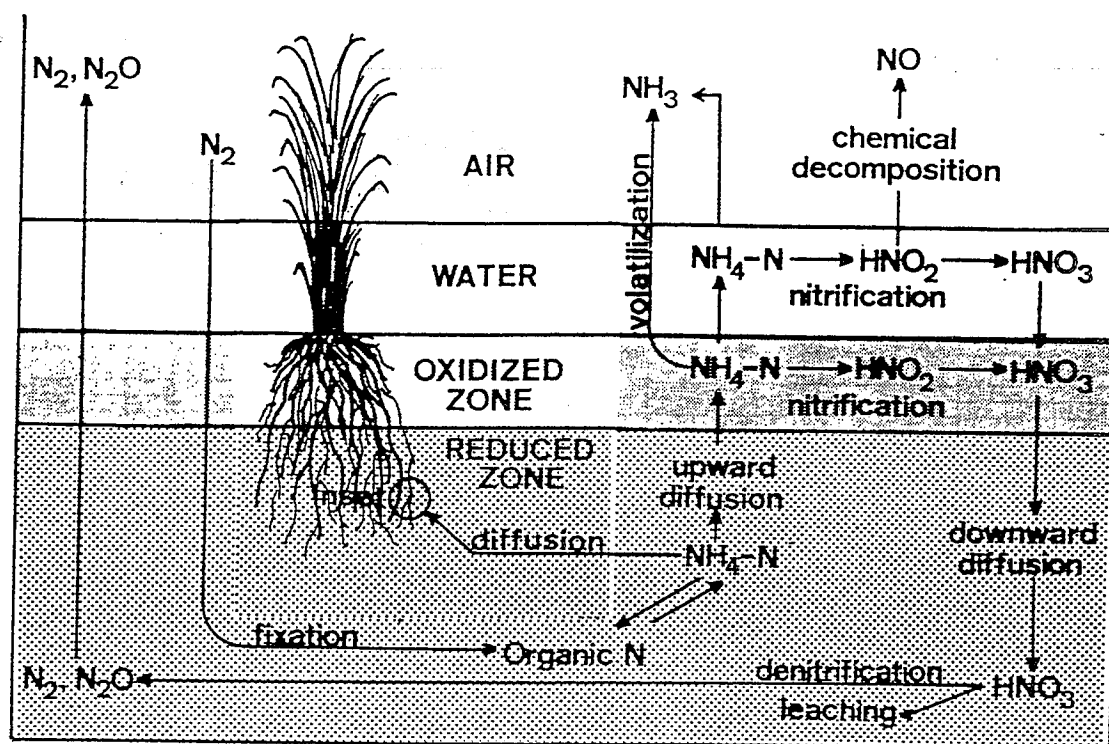
Agronomically, flooded soils are used for growing lowland rice, *Oryza sativa* L., the major food for approximately 50% of the world population. In the U.S., rice is grown with the application of heavy rates of inorganic N fertilizers. Recent increases in fertilizer costs as a result of energy shortage make it necessary to reduce the N loss from the flooded soil systems. In natural wetlands, nitrogen has been found to be the limiting plant nutrient.¹⁴⁸ The efficiency of N utilization in both agricultural and natural wetlands is reduced because of competition between plant uptake and biochemical processes functioning in the wetland soil-plant system. In recent years, a variety of wetland ecosystems, including freshwater marshes,^{70,231} hardwood swamps,³⁴ and cypress domes¹³⁷ have been investigated as waste water treatment systems. Nitrogen removal by natural processes is one of the major purposes of these treatment systems.

This review examines the agronomic and ecologic significance of N transformations involved in the transport of N from flooded soils and sediments to the atmosphere.

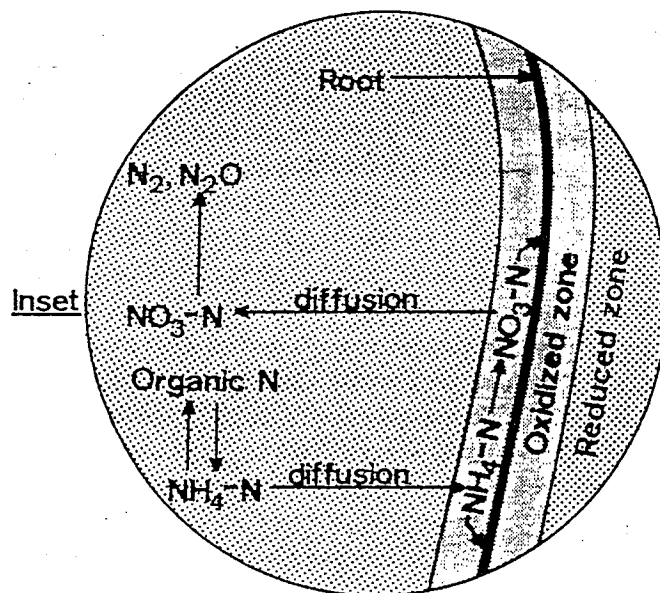
II. CHARACTERISTICS OF FLOODED SOILS AND SEDIMENTS

Flooded soils and sediments are generally characterized by the absence of oxygen compared to well-drained soils. In a well-drained soil, there is usually enough oxygen present in the soil atmosphere to act as an electron acceptor for microbial, plant root, and animal respiration. Upon flooding, the soil oxygen status is completely changed. In most rice fields and some water bodies, the dissolved oxygen content of the overlying floodwater remains relatively high due to: (1) a low density of oxygen-consuming organisms; (2) photosynthetic oxygen production by algae and possibly higher plants; and (3) mixing of water by wind action and

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A



B

FIGURE 1. Schematic presentation of nitrogen cycle in flooded soils and sediments.

convection currents. Though the oxygen demand is low in the overlying floodwater, the demand is usually high in the underlying soil layer, especially in those soils having an appreciable organic energy source which supports a high level of microbial activity. Turner and Patrick²¹⁰ could detect no oxygen in four soil suspensions within 36 hr after stopping the oxygen supply. No oxygen was detected in submerged lake muds and flooded rice fields by several research workers.^{19,108,133,134,230} Hutchinson⁹⁴ estimated an oxygen consumption rate of 2×10^{-10} to 2×10^{-9} g cm⁻² sec⁻¹ in lake and ocean muds, whereas Howeler and Bouldin⁹³ reported a value of 1×10^{-12} g cm⁻² sec⁻¹ in saturated soils. The low redox

potentials reported by Hutchinson⁹⁴ and Ponnamperuma¹⁵⁸ for lake muds and rice soils, respectively, also indicate the absence of oxygen. The redox potential at which oxygen disappears from the wetland soil system was found to be in the range of +320 to +340 mV.²¹⁰

Oxygen reaching the soil or sediment surface from the water column is consumed during the following biochemical processes:

1. Heterotrophic microbial respiration in the aerobic soil layer where oxygen is used as an electron acceptor
2. Chemical oxidation of reduced iron and manganese, and sulfides which diffuse from the anaerobic layer to the aerobic layer; these reduced components had previously served as electron acceptors in the respiration of facultative anaerobes.
3. Biological autotrophic oxidation of ammonium N; the organisms involved in the oxidation of ammonium N are strictly aerobic.

In a flooded mineral soil, approximately 50% of the total available oxygen is consumed in oxidizing the water-soluble ferrous iron diffusing upwards from subsurface reduced zones.⁹³ Recently, Patrick and Reddy¹⁴⁹ measured the total oxygen consumption in a flooded soil containing a high concentration of ammonium N. Most of the oxygen consumed initially was attributed to the oxidation of reduced iron and manganese, followed by oxygen consumption during the oxidation of organic carbon and ammonium N. Oxygen consumption by 37 anaerobic soils was found to be a two-phase process.¹⁷² The first phase represented chemical oxidation of water-soluble iron (Fe^{+2}), and the second phase represented chemical oxidation of exchangeable and soluble iron (Fe^{+2}) and manganese (Mn^{+2}), and biological oxidation of organic carbon and ammonium N. In this study, oxygen consumption was best described by a two-phase first-order reaction. The rate of oxygen consumption during phase I was approximately the same for all 37 soils ($k_1 = 0.15 \text{ hr}^{-1}$), whereas oxygen consumption during phase II ranged from 0.003 to 0.054 hr^{-1} . In soils with high organic matter (such as Histosols) and low Fe and Mn, rate of oxygen consumption will be determined by the ammonium N, sulfides, and easily decomposable fraction of soil organic matter.

The greater potential consumption of oxygen within the flooded soil or sediment profile, compared to the renewal rate through the floodwater, results in the development of two distinctly different soil layers: (1) an oxidized or aerobic surface layer where oxygen is present and (2) an underlying reduced or anaerobic layer in which no free oxygen is present (Figure 2). This profile differentiation has been described for lake and ocean sediments and flooded soils by several research workers.^{5,60,74,75,91,131,134,153-155}

Thickness of the aerobic surface soil or sediment layer is determined by the net oxygen consumption rate in the soil and the oxygen renewal rate through the floodwater. The thickness of this layer generally varies from a few millimeters in soils of high biological activity where there is greater demand for oxygen to 1 or 2 cm in soils of low biological activity where there is less demand for oxygen.^{66,93,145} To calculate the thickness of the aerobic zone and the amount of oxygen that diffuses into the soil, six mathematical diffusion models were proposed by Bouldin.³⁰ Patrick and DeLaune¹⁴⁵ characterized the oxidized (aerobic) and reduced (anaerobic) soil layers by measuring the redox potential at different depths and by the distribution of reduced components such as sulfide and soluble iron and manganese. The sulfide profile indicated the thickest aerobic zone, and the iron profile was intermediate in thickness. Reddy et al.¹⁶⁸ have shown experimentally that the increase in the depth of aerobic layer was a square root function of time. In this study, the depth of aerobic layer was determined from the thickness of the reddish brown ferric oxide layer in the soil column.

Increasing the concentration of oxygen over the flooded soil increased the thickness of

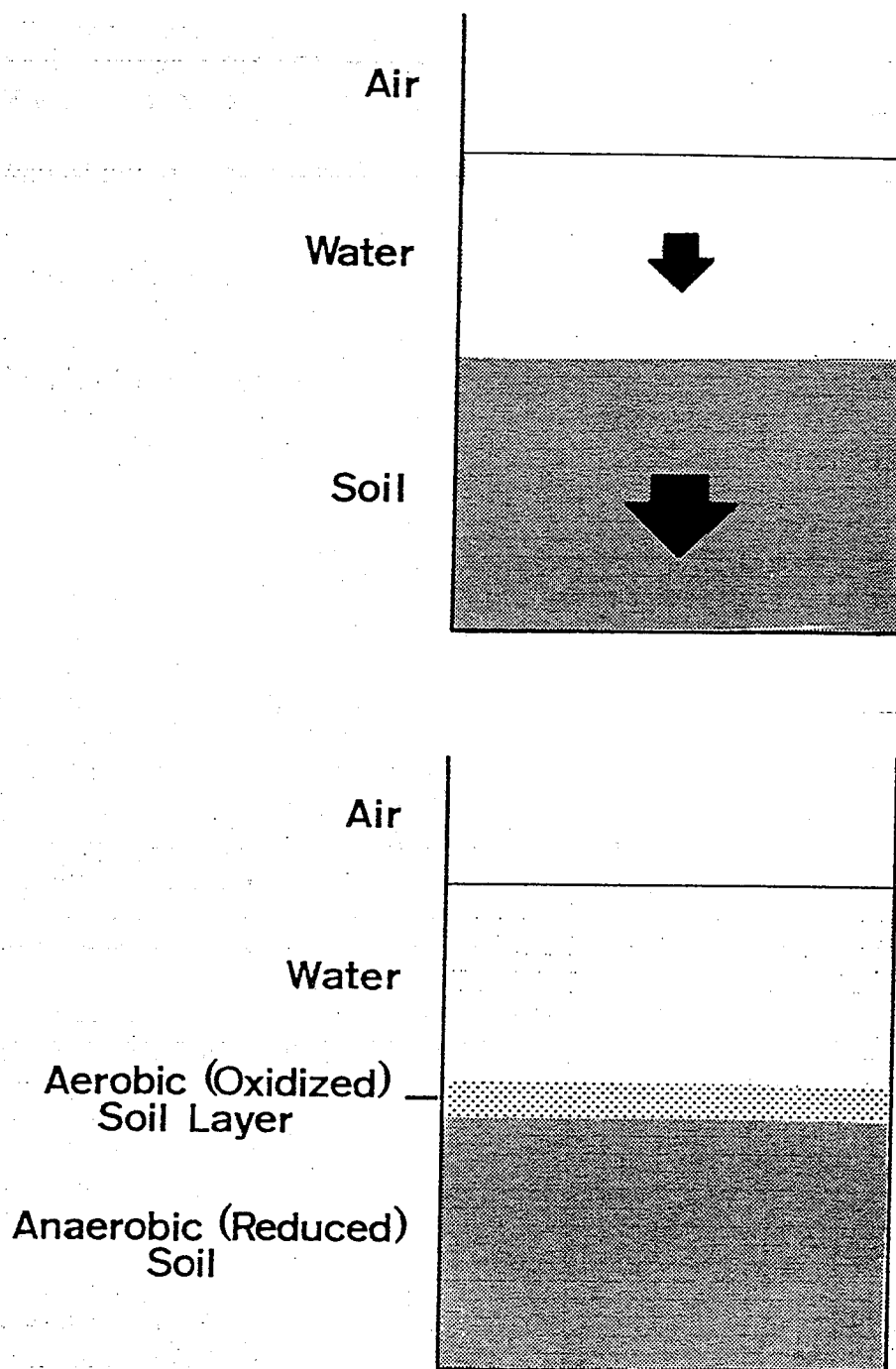


FIGURE 2. Development of aerobic (oxidized) soil layer.

the aerobic layer and increased the amount of oxygen consumed.¹⁴⁹ Increasing the concentration of ammonium N also increased the thickness of the aerobic layer.¹⁶³ This increase in thickness of the aerobic layer was probably due to the accumulation of nitrate in the surface layer as a result of nitrification of applied ammonium N. Data in Figure 3 present the Eh profiles of the intact soil cores obtained from a rice field. Thickness of aerobic layer (<1 cm) was characterized using an Eh value of 300 mV as a separation point between aerobic and anaerobic soil layers.

The development of two distinct soil layers favors the simultaneous occurrence of nitrification and denitrification in a flooded soil or sediment. The thin surface aerobic (oxidized)

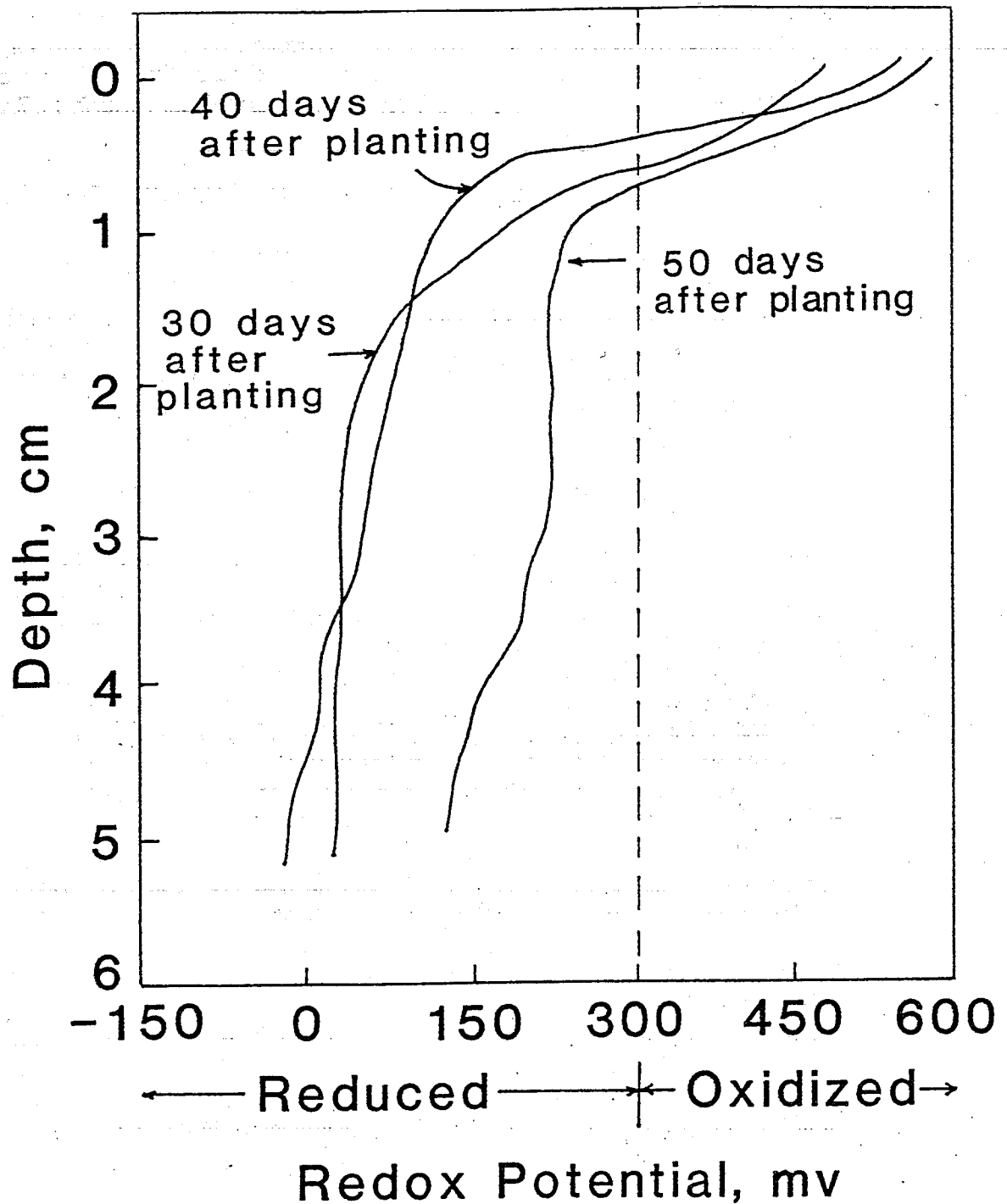


FIGURE 3. Thickness of oxidized soil layer, as shown by Eh profile in an undisturbed flooded soil column planted with rice.

layer promotes the oxidation of ammonium to nitrate, and the subsurface anaerobic (reduced) layer supports the reduction of nitrate to N_2 and N_2O .

Rice and other marsh and swamp plants have a unique feature of transporting atmospheric oxygen through the stem to the roots, and some of this oxygen subsequently diffuses from the root into the adjacent soil layer. This mechanism is undoubtedly one of the major factors enabling these plants to survive the anaerobic toxic environment of a flooded soil or sediment.^{4,5,12,17,18,180} Oxidation of the rhizosphere appears to serve as a protective mechanism

in preventing high concentration of reduced substances from coming into contact with the root surface. Besides oxidizing the reduced microzone around the root surface, the diffused oxygen will also enhance the development of a predominantly aerobic microflora in this zone.⁶ The formation of these two distinct layers around a root surface (Figure 1B) can also favor nitrification-denitrification reactions.

III. FORMS AND SOURCES OF NITROGEN

Nitrogen in flooded soils and sediments and water columns occurs in inorganic and organic forms with the organic form predominating. Organic N consists of compounds from amino acids, amines, proteins, and humic compounds with low N content. Inorganic N consists of ammonium N, nitrate and nitrite N. In sediments, both nitrate and nitrite N occur in trace quantities. Ammonium N is the predominant form of inorganic N in the sediments and is mainly derived through mineralization of organic N. The gaseous forms of N that occur in flooded soils and sediments include ammonia (NH_3), dinitrogen (N_2), and nitrous oxide (N_2O).

Sources of N include (1) precipitation on the surface of flooded soils and sediments; (2) nitrogen fixation in the water and the sediments; (3) inputs from surface and ground water drainage; (4) application of fertilizers to flooded rice soils; (5) nitrogen release during the decomposition of dead aquatic plant and animal community; and (6) discharge of waste water effluents. The contribution from each source to an aquatic system depends on the conditions that exist at the specific site.

A series of biochemical and physicochemical processes are involved in transforming one form of N to another form. Organic N is converted to ammonium N through ammonification process, while conversion of ammonium N to nitrate N occurs through nitrification process. The special conditions under which nitrate is formed in predominately reduced flooded soils are discussed in greater detail in the latter part of this review. The transport of N from flooded systems to the atmosphere occurs through (1) NH_3 volatilization and (2) denitrification of nitrate N to N_2 and N_2O . For NH_3 volatilization processes to occur, ammonium N must be formed (ammonification) in the system followed by favorable optimum soil and environmental conditions. For denitrification process to occur, ammonium N should be oxidized to nitrate N (nitrification) followed by conversion to N_2 and N_2O . For both nitrification and denitrification processes to function at a maximum rate, soil and environmental conditions must support both processes.

The transformation processes to be discussed in this paper are (1) ammonification; (2) NH_3 volatilization; (3) nitrification; and (4) denitrification. The transport processes to be discussed are (1) diffusion of ammonium N from anaerobic soil layers and (2) diffusion of nitrate N from aerobic soil layers and from the overlying water column.

IV. AMMONIFICATION

Ammonification is the first step in mineralization of organic N. Ammonification is defined as the biological conversion of organic N to ammonium N. Under anaerobic soil conditions, ammonium N accumulation occurs because of complete suppression of nitrification in soil zones which are devoid of oxygen. The breakdown of soil organic N or the organic N in crop residues or the organic wastes in a flooded soil which leads to the release of $\text{NH}_4\text{-N}$ into soil solution proceeds at a much slower rate in anaerobic environments than in aerobic environment.^{1-3,208} This is because organic matter decomposition in an aerobic system is caused by general-purpose heterotrophic bacteria and fungi.⁸ In an anaerobic system, a less efficient and more restricted microflora which do not require oxygen for respiration are involved in the breakdown of organic matter. Hence, the ammonification rates are consid-

erably retarded. The characteristic features of anaerobic bacterial decomposition of organic matter in flooded soils and sediments, therefore, comprise; (1) incomplete decomposition of carbohydrates into methane, organic acids, hydrogen, and carbon dioxide; (2) low energy of fermentation, resulting in the synthesis of fewer microbial cells per unit of organic carbon decomposed; and (3) low N requirement of the anaerobic metabolism.

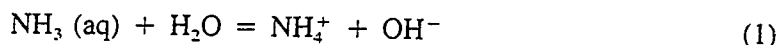
Net release of ammonium N during ammonification and immobilization processes in anaerobic systems is dependent on the N requirements of anaerobic microbial populations, nature of organic material, and several soil and environmental factors. The ultimate ammonium N formation is controlled by ammonification and immobilization balance in anaerobic systems, which can be interpreted through the ratio of carbon to nitrogen (C/N) of the decomposing residue. Sircar et al.¹⁹³ and Williams et al.²²³ concluded that minimum N needed for the net release of ammonium N from the rice straw decomposition in flooded soils was about 0.5% N compared to about 1.7% N for aerobic systems. If we assume the carbon content of the rice straw is about 40%, the critical C/N ratio for the net release of ammonium N into soil solution is about 80 for anaerobic systems. Under anaerobic conditions, organic residues with C/N ratios lower than 80 favor the ammonification process and those higher than 80 favor nitrogen immobilization. Under aerobic systems, these processes are balanced at a C/N ratio of approximately 23. This explains why ammonium release is higher under anaerobic conditions than under aerobic conditions during the decomposition of a plant material with wide C/N ratio, despite its greater extent of decomposition under aerobic conditions. Several research workers^{144,211,219} found that considerably more N was mineralized under flooded soil conditions compared to well-drained conditions.

The rate of ammonification in flooded soils is dependent on temperature, pH, C/N ratio of the residue, available nutrients in the soil, and soil conditions such as texture and structure. The effect of these factors on ammonification in well-drained soils is fairly well understood, but very little is known for flooded soils. It is possible that these soil and environmental factors may have different effects on ammonification rates, since different types of organisms are involved. The rate of ammonification was shown to increase with increasing temperature. In contrast to most of the microbiological processes, optimum temperature for conversion of organic N to ammonium N is between 40 to 60°C. These temperatures are seldom encountered under field conditions. Reddy et al.¹⁷⁰ concluded from the literature data that the rate of aerobic ammonification doubles with a temperature increase of 10°C. Mitsui,¹³¹ Kawaguchi and Kyuma,¹⁰⁰ and Cho and Ponnamperna⁵⁰ have reported a virtual doubling of ammonia production when the temperature of anaerobic soils was raised from 15 to 40°C. The optimum pH range for ammonification process is between 6.5 and 8.5. Under flooded conditions, pH is buffered around neutrality, whereas under well-drained conditions, pH of the soil decreases as a result of nitrate accumulation during mineralization.¹⁴⁴

Rate of ammonium N accumulation in flooded soils and sediments has considerable agronomic and ecologic significance. Agronomically, the accumulation of ammonium N supports about 60% of the N requirement of rice. A fairly good estimate of the amount of N available to the rice crop can be obtained by measuring the amount of ammonium N mineralized under anaerobic conditions.⁶⁴ Ecologically, ammonium N released from lake and river sediments into overlying water supports the life of aquatic plant communities and algal growth. In coastal marshes and swamps, ammonium N supports natural plant productivity. A number of marine studies have suggested that mineralization of sediment organic N is primarily responsible for maintenance of high rates of primary productivity and high standing crops of phytoplankton in nearshore and estuarine water.^{87,89,118,119,199} A few studies have been reported on the direct measurement of ammonium N mineralization in ocean bottoms⁸⁸ and lake bottoms.^{9,40,209}

V. AMMONIA VOLATILIZATION

Ammonia volatilization is a physicochemical process where ammonium N is known to be in equilibrium between the gaseous and hydroxyl forms as indicated below:



This reaction is pH dependent with alkaline pH favoring the presence of aqueous forms of NH_3 in solution, while at acidic or neutral pH the ammonium N is predominantly in the ionic form. Once converted to the gaseous forms, the transfer of ammonia N dissolved in aqueous solution to the atmosphere above the solution is a function of the relative difference in partial pressures of the NH_3 gas present in each medium. If the partial pressure of the dissolved gas within the liquid is greater than that due to the partial pressure of the gas in the atmosphere above the liquid, a net transfer of gas from liquid to atmosphere will occur until equilibrium of partial pressures is reached, in accordance with Henry's law.

Losses of NH_3 through volatilization from flooded soils and sediments are insignificant if pH is below 7.5 and very often losses are not serious if the pH is below 8.0. As pH increases, the partial pressure of NH_3 in equilibrium with a solution of NH_3 increases rapidly in the pH range of 8.5 to 10.0. Hence, volatilization losses of NH_3 from the aquatic systems are high if the pH is in this range or above.

Ecologists have long been aware that the pH of water in natural systems rises to values as high as pH 10 in a regular diurnal pattern, which is determined by the chemical equilibria that exist between all aquatic organisms, their CO_2 metabolism, and the various solutes, solids, and gases in water systems. Park et al.¹⁴⁰ reviewed the diurnal pH variations in a variety of natural waters showing changes of as much as 3.5 pH units, rising in midday when the photosynthetic process is actively withdrawing CO_2 from the ecosystem and falling at night when respiratory activities liberate free CO_2 into water. The agronomic significance of the high pH that develops in ponds or rice floodwater has largely been neglected as a factor in the direct volatilization loss of NH_3 . In flooded soils and sediments, high pH conditions can exist only in the overlying waters, thus creating conditions favorable for NH_3 volatilization.^{129,217} The pH of the overlying waters in shallow ponds, reservoirs, lakes, and streams is also governed by the presence and type of aquatic plants. For example, water bodies with dense cover of floating plants (such as water hyacinth) are slightly acidic, resulting from the accumulation of carbonic acid. These water bodies exhibit very little or no diurnal changes in pH, and under these conditions, losses of NH_3 through volatilization are insignificant. The pH of the water containing submerged aquatic plants (such as *Egeria densa*) and algae generally exhibit significant diurnal changes in pH. Diurnal changes in pH of the water containing different types of aquatic plants are shown in Figure 4.

Several research workers^{31,105,171,195,203,216} have presented simple equations to predict NH_3 losses from aquatic systems and from soils receiving NH_3 -rich wastes. All these workers concluded that the rate of NH_3 loss is proportional to the difference in the activity of NH_3 in the atmosphere and in the solution. The fraction of undissociated (free) ammonia present in solution is dependent on pH and temperature (Figure 5).

Rate of NH_3 volatilization is also controlled by the ammonium N concentration in the water, temperature, wind velocity at the surface of water, solar radiation, the nature and number of aquatic plants, and indirectly, the CO_2 balance between photosynthesis and respiration. Several researchers^{69,195,203} observed that reaction rate was increased approximately from 1.3 to 3.5 times for each 10°C rise in temperature when the system temperature was between 0 to 30°C . First-order rate constants for NH_3 volatilization in stream water as a function of temperature and pH are shown in Figure 6A and B.²⁰³ Several studies have indicated that volatilization of NH_3 increased with increasing air movement.^{201,216,220} These

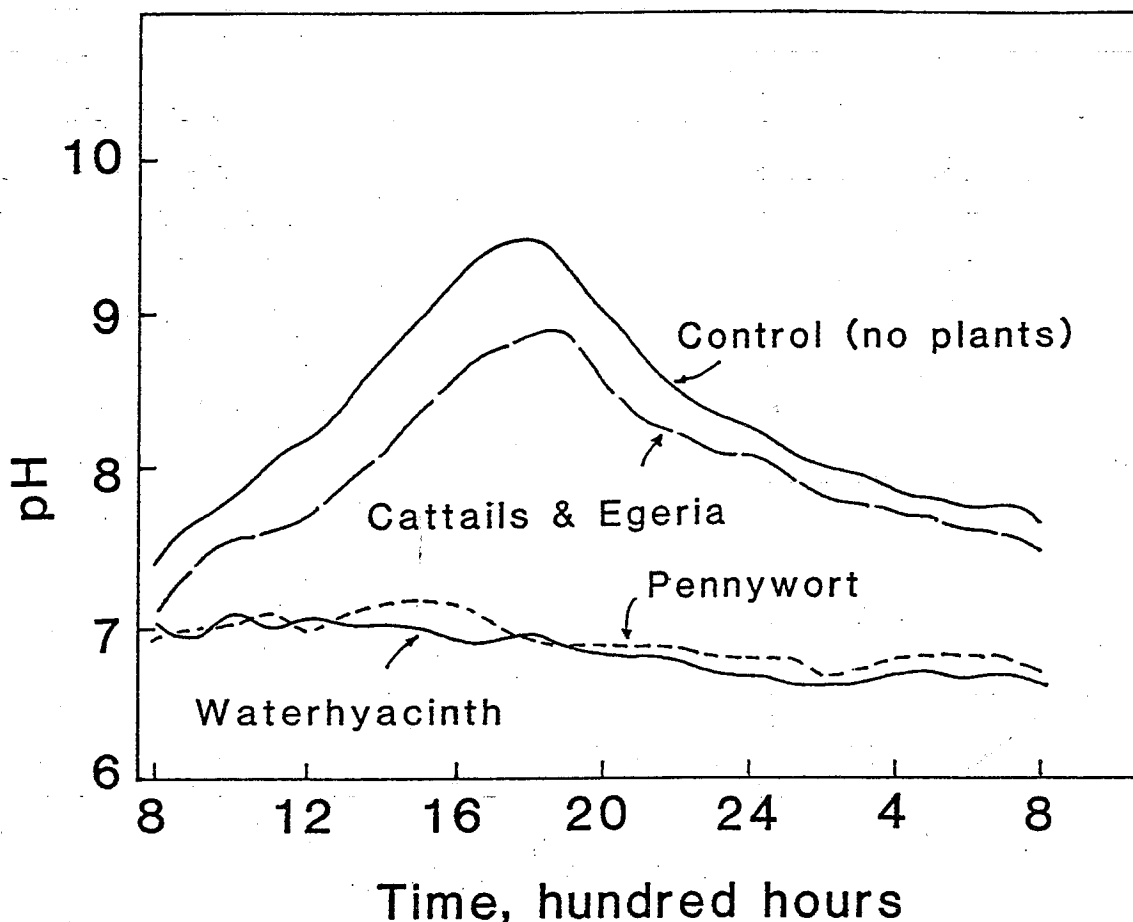


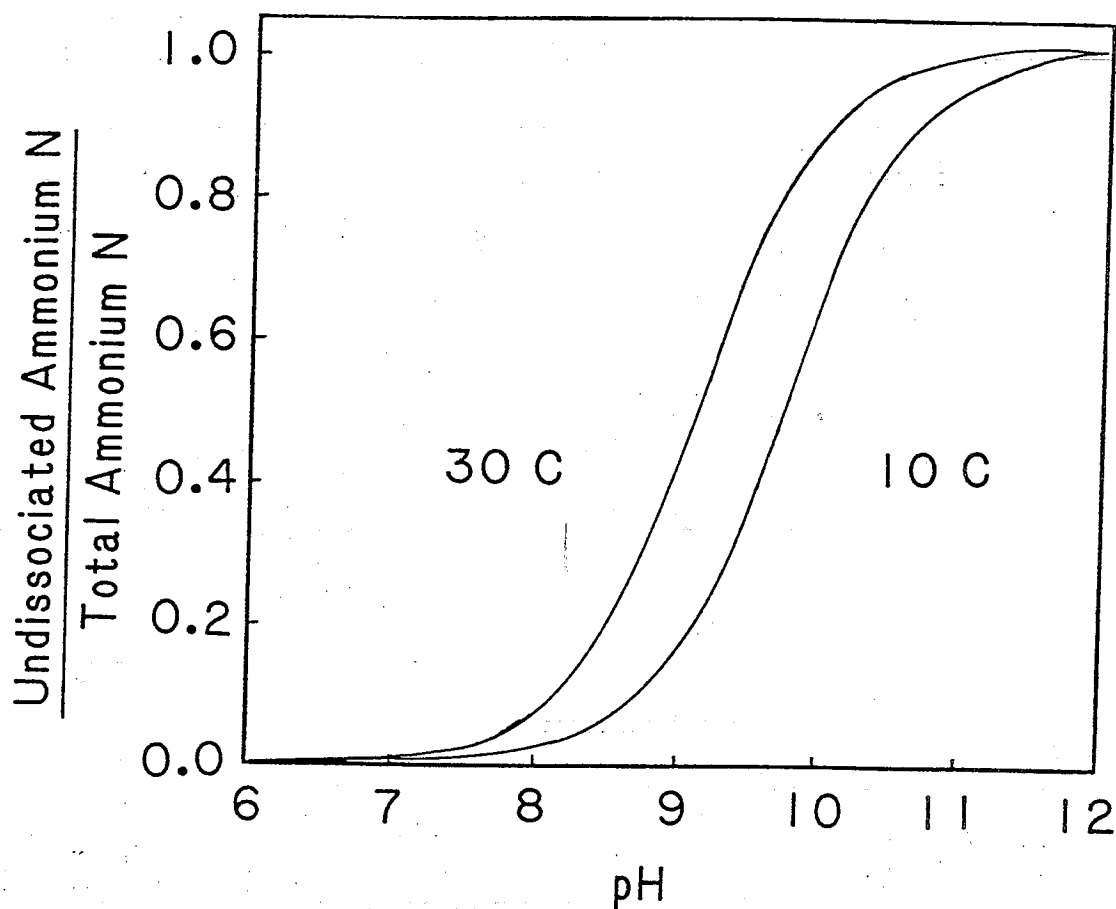
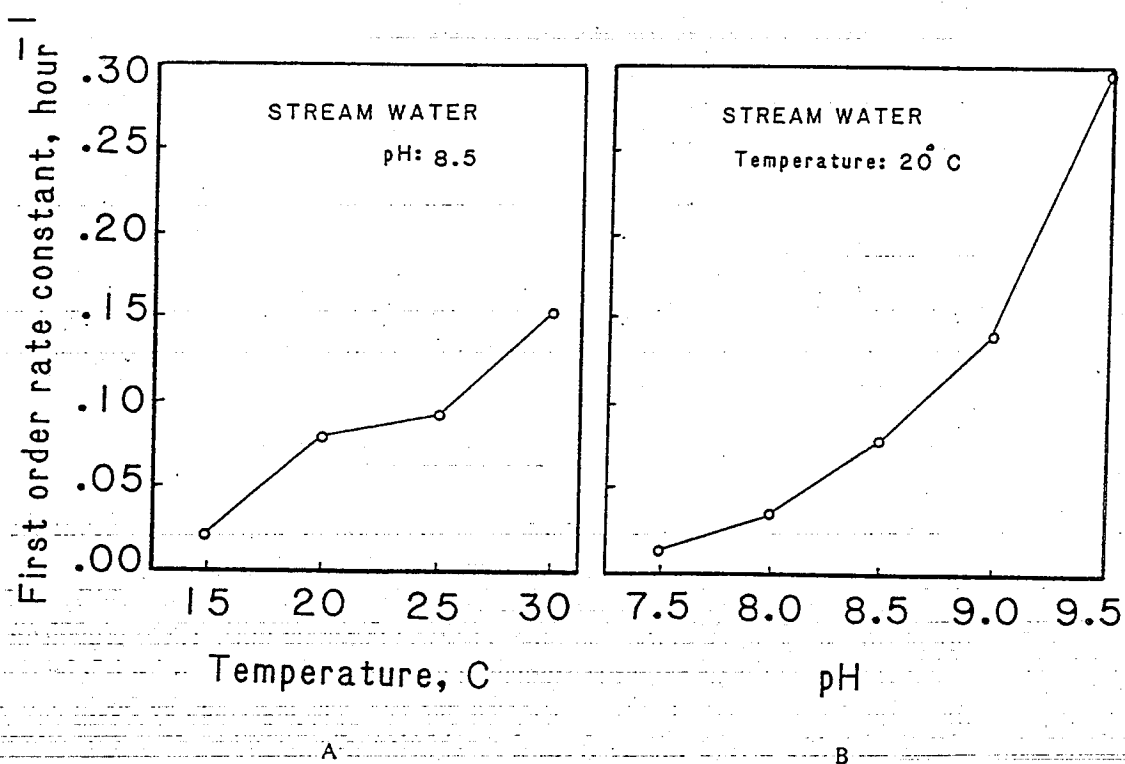
FIGURE 4. Diurnal variations in pH of water in selected aquatic systems containing pennywort (*Hydrocotyle umbellata* L.), waterhyacinth (*Eichhornia crassipes* [Mart] Solms), cattails (*Typha latifolia* L.), and egeria (*Egeria densa*), and control (no macrophytes but contained algae).

studies show that at air flow rates of 100 to 18,000 cm³/min, volatilization of NH₃ was proportional to the log of air flow velocity.

Ammonia and its ionized form (NH₄⁺) are readily identifiable products of the decomposition of soil organic matter and the micro- and macroplant residues in natural waters. Surface application of ammonium N and urea N fertilizers to a flooded rice soil also increase the ammonium N concentrations in the water. Depending on pH and other environmental factors, ionized NH₄⁺ can be rapidly converted to nonionized NH₃ which may escape from the water as gas. Relative losses of NH₃ as a result of volatilization in aquatic systems are discussed in the latter part of the paper.

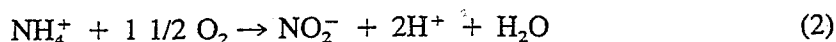
VI. NITRIFICATION

Nitrification is defined as the biological oxidation of ammonium N to nitrate N. Nitrification is known to take place in two stages as a result of the activity of chemoautotrophic bacteria of the genera *Nitrosomonas* (NH₄⁺ → NO₂) and *Nitrobacter* (NO₂ → NO₃). Both organisms are gram-negative, aerobic, chemoautotrophic rods. These organisms have been isolated from and their activities studied in a number of habitats. A list of chemoautotrophic nitrifying bacteria, isolated from selected habitats, was presented by Focht and Verstrate.⁷¹ These nitrifiers derive energy from the oxidation of ammonium N and/or nitrite N. These organisms require O₂ during ammonium N oxidation to nitrite N and nitrite N oxidation to

FIGURE 5. Relationship between NH_3 (aq.) and pH in an aqueous system.FIGURE 6. First-order rate constant for NH_3 volatilization shown as a function of temperature and pH.²⁰³

nitrate N. During ammonium N oxidation to nitrite N, oxygen is utilized by these organisms in two ways: by direct incorporation into the substrate and as the terminal electron acceptor, whereas oxygen is used only as the terminal electron acceptor by the organisms involved in the oxidation of ammonium N to nitrite N. Although there is evidence that some heterotrophic bacteria are involved in nitrification, it is generally believed that the contribution made by heterotrophs is negligible compared to autotrophs. Recent findings suggest that nitrification by heterotrophs might be qualitatively, as well as quantitatively, of major importance in acidic soils and highly alkaline soils where chemoautotrophic oxidation is inhibited. Oxidation of ammonium N to nitrate N is a two-step process.^{7,61}

Ammonium oxidation to nitrite:



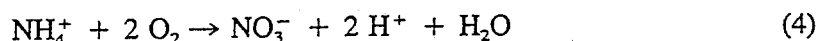
The organisms involved belong to the genus *Nitrosomonas* or related genera. The energy yield (ΔG) in the oxidation of ammonium to nitrite has been reported to be -65.2 to -84.0 Kcal/mol of ammonium.

Nitrite oxidation to nitrate:



The organisms involved belong to the genus *Nitrobacter* or related genera. The ΔG of the *Nitrobacter* reaction was reported to be -17.5 to -10.0 Kcal/mol.⁷⁸ These two dominant genera belong to the family Nitrobacteriaceae of the order Pseudomonadales. A detailed discussion of the auto- and heterotrophic nitrification in pure cultures and soils is presented by Focht and Verstraete.⁷¹

Combining these two reactions, we obtain:



This reaction involves a N valence change from -3 to the $+5$ oxidation state, a span involving eight electrons. Though oxygen is essential, nitrification will occur readily down to about 0.3 ppm dissolved oxygen. The actual limit is more dependent on the oxygen flux into the system rather than the oxygen level at a given time.⁸³ It takes 2 mol of oxygen to oxidize each mole of ammonium to nitrate. Stoichiometrically, these organisms require 4.57 g O_2 per gram of ammonium N oxidized. These reactions therefore potentially use large quantities of oxygen, and nitrification can at times produce oxygen-depleted water in lakes, streams, and estuaries subject to large amounts of high nitrogenous wastes. Oxygen depletion in this case is also due to the high BOD resulting from carbonaceous material in the waste water.

In a wetland system, nitrification can occur in: (1) the water column above wet soils, lake sediments, and stream sediments and (2) the surface-oxidized soil or sediment layer of the wetland systems, lake sediments, or ocean muds. Several researchers have documented the evidence of nitrification in the overlying water^{55,165,184} and in the surface-oxidized sediments.¹⁷⁴

To describe quantitatively the influence of nitrification on N transport from wetland systems, it is necessary to evaluate the activity and growth rate constants of nitrifying bacteria under various environmental conditions. Because of the complex nature of these biological reactions, it is difficult to describe nitrification by using one kinetic equation. Several rate equations have been proposed for the nitrification process. Among some of the kinetic rate equations used are (1) zero order; (2) first order; and (3) Monod equation of population dynamics. Nitrification reactions whose rates are independent of ammonium N (substrate)

Table 1
NITRIFICATION RATES EXPRESSED AS ZERO-ORDER CONSTANTS IN
SOIL-WATER SYSTEMS

System	Temperature (°C)	Zero-order rate ($\mu\text{g}/\text{m}\ell/\text{day}$)	Remarks	Ref.
Pure cultures				
<i>N. europaea</i> $\text{NH}_4 \rightarrow \text{NO}_2$	21	883	Pure culture systems with pH 7.8	196
<i>N. agilis</i> $\text{NO}_2 \rightarrow \text{NO}_3$	21	310	Pure culture system with pH 7.8	
Oxidation				
Ditch solids			Oxidation ditch containing poultry manure	196
$\text{NH}_4 \rightarrow \text{NO}_2$	21	6.2	pH 7.8	
$\text{NO}_2 \rightarrow \text{NO}_3$	21	8.6		
Aerobic soil layer of flooded soils			Nitrification rates measured in the surface aerobic layer of a flooded soil; pH of the soil layer ranged from 4.1 to 5.8	174
Crowley silt loam	30	2.1		
Midland silt loam		1.5		
Mhoon silty clay loam		2.8		
Commerce silty clay loam		2.3		
Gallion sandy loam		1.1		

concentrations are considered to be zero order. The rate equation for such reaction is given by:

$$-d \text{NH}_4/dt = k \quad (5)$$

where, k = rate constant for nitrification ($\mu\text{g}/\text{m}\ell/\text{day}$) and t = time (days). Several research workers observed nitrification to be independent of substrate concentration.^{11,49,62,104,196,222} The initial ammonium N concentration used in these studies ranged from 5 to 100 $\mu\text{g}/\text{m}\ell$. In a recent study, Reddy et al.¹⁷⁴ measured ammonium N oxidation in the surface aerobic layer of flooded soil. Their studies also showed nitrification to be independent of substrate concentration with relative rates ranging from 1.1 to 2.8 $\mu\text{g}/\text{g}/\text{day}$ (Table 1).

Equation 5 is a much simplified form for describing a complex microbially mediated nitrification process. This equation does not consider the changes in microbial population. McLaren^{122,123,125} emphasized the dependency of reaction rates on population densities of microorganisms involved in nitrogen transformations. Ardakani et al.¹⁴⁻¹⁶ also showed that nitrification rates were indeed dependent on microbial biomass.

McLaren¹²³ proposed a conceptual model based upon enzyme kinetics and bacterial growth, e.g.:

$$\frac{-d[S]}{dt} = A \frac{dm}{dt} + \alpha m \frac{K''B[S]}{K_m + [S]} \quad (6)$$

where S is the N substrate concentration; A is N oxidized per unit weight of biomass synthesized; M is biomass, α is N oxidized per unit weight of biomass per unit time for maintenance; K'' is specific rate constant, B is amount of enzyme per unit biomass involved in waste metabolism; and K_m is the saturation constant. The first term in Equation 6 represents the disappearance of substrate to microbial growth, the second term provides for maintenance, and the last term for that substrate oxidized but not needed for either growth or maintenance (waste metabolism). Saturation constant, K_m for ammonium N oxidation, ranges between

Table 2
FIRST-ORDER KINETIC RATE COEFFICIENTS FOR NITRIFICATION IN SOILS

Type of system and process	Temperature (°C)	First-order rate constant (k day ⁻¹)	Remarks	Ref.
Salinas clay	24		Laboratory incubation ⁴⁴	126
NH ₄ → NO ₂		0.22		
NO ₂ → NO ₃		9.0		
Milville loam	22		Laboratory incubation (Justice and Smith)	126
NH ₄ → NO ₂		0.14		
NO ₂ → NO ₃		9.00		
Tippera clay loam			Laboratory incubation at varying temperatures	56
NH ₄ → NO ₃	20	0.003		
Columbia silt loam			Steady-state flow through soil column maintained at -85-cm suction	56
NH ₄ → NO ₃		0.24—0.72		
Hanford sandy loam		0.76—1.11	Steady-state flow through soil columns, using ¹⁵ N	56
NH ₄ → NO ₃				
Webster silt loam	35	0.052	Laboratory incubation study with 35-day incubation	141
NH ₄ → NO ₃				
Marshall silt loam	35	0.048		
NH ₄ → NO ₃				
Colo silty clay loam				
NH ₄ → NO ₃	35	0.051		
Monona silty clay loam				
NH ₄ → NO ₃	35	0.047		
Grundy silt loam				
NH ₄ → NO ₃	35	0.072		
Aquatic Sytem			Field study conducted on the Clinton River between Pontiac, Mich. and Rochester, Mich. nitrification rates calculated based on changes in NH ₄ -N and NO ₃ -N concentration	
Clinton River		3.10		
NH ₄ → NO ₃				

1 and 10 µg/ml between 20 and 30°C,^{92,114,212} while Km for NO₂-N oxidation falls between 5 and 9 µg/ml in the same temperature range.^{82,113,212} Because Km is usually equal to or larger than substrate concentrations in nature, the rates of ammonium N and nitrite N oxidation tend to be dependent upon the substrate concentration. For enriched soil conditions, one in which the microbial population is at a maximum and the nitrogen substrate is low, dm/dt = 0 and S ≪ Km so that Equation 6 reduces to

$$\frac{-d[S]}{dt} = \propto m_{\max} \cdot K[S] \quad (7)$$

where m_{\max} is the maximum microbial population and K is the rate coefficient (day⁻¹). Equation 7 may be further simplified if the product m_{\max} is small compared to K[S], resulting in a first-order rate equation:

$$\frac{-d[S]}{dt} = K[S] \quad (8)$$

The above assumptions made to arrive at Equation 8 are reasonable for nitrification since the quantity of ammonium N that is available in the floodwater or surface aerobic soil layer to microorganisms is generally small. Ammonium N in the oxic zone of an aquatic system depends on the mineralization of organic N in the underlying sediments. Data in Table 2

show the first-order rate coefficients for oxidation of ammonium N in different soil-water systems.

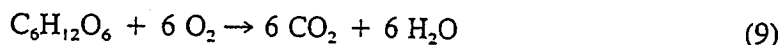
In an aquatic system, nitrification rate is influenced by: (1) temperature; (2) pH; (3) alkalinity of the water; (4) inorganic C source; (5) microbial population; and (6) ammonium N (substrate concentration).

The optimum temperature for nitrification in pure cultures ranges from 25 to 35°C and in soils ranges from 30 to 40°C.^{7,72,124} Lower temperatures (below 15°C) have a much more drastic effect on nitrification rate, compared to temperatures between 15 to 35°C. Oxidation of nitrite to nitrate proceeds at a faster rate than the oxidation of ammonium and thus nitrite does not accumulate in a soil or sediment system. However, nitrite may accumulate to some extent under conditions of high pH or low temperature.^{7,212} High concentrations of ammonium N have also been found to inhibit the activity of *Nitrobacter*, particularly at high pH values, probably due to production of free ammonia.^{6,68}

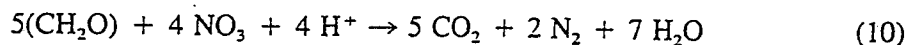
Since the process of nitrification depends on the metabolism of nitrifying organisms, it is imperative that they be present in adequate numbers to achieve the oxidation of ammonium N. Generally, fertilized soils have larger populations of nitrifiers compared to unfertilized soils.^{7,15,16} In a field study, Ardakani et al.^{15,16} estimated the population of *Nitrobacter* and *Nitrosomonas* microorganisms at different depths in an aerated soil. Profile distribution of nitrifiers showed higher density near the soil surface where concentrations of substrates and oxygen were always highest.^{15,16} In most of the flooded soils and sediments, large numbers of nitrifying organisms were shown to occur in the surface soil layers,^{55,56} and decreased with depth. Rate of nitrification was shown to be influenced by the presence or absence of CO₂ in the aquatic system. Reddy and Graetz¹⁶⁵ in a recent study observed rapid nitrification in a waste water column aerated with the air containing CO₂, compared to the water column aerated with CO₂ free air.

VII. DENITRIFICATION

Denitrification is defined as the biological reduction of nitrate or nitrite N to gaseous end products such as molecular N₂ or N₂O. This definition excludes the chemodenitrification (nonenzymatic) of nitrite N to nitric oxide and nitrogen dioxide, and the assimilatory reduction of nitrate N to ammonium N. Investigations by Goering and Dugdale,⁷⁹ Kuznetsov,¹¹¹ Brezonik and Lee,⁴¹ Keeney et al.,¹⁰¹ and Engler and Patrick⁶⁶ show denitrification to be an important process in removing N from lakes and floodwater. Under anaerobic or oxygen-free conditions and in the presence of available organic substrate, the denitrifying organisms can use nitrate as an electron acceptor during respiration. In a recent review Focht and Verstraete⁷¹ compiled a list of genera involved in denitrification process. Some of these genera include *Pseudomonas*, *Acinetobacter*, *Bacillus*, *Micrococcus*, *Gluconobacter*, *Alcaligenes*, *Halobacterium*, *Thiobacillus*, *Xanthomonas*, *Moraxella*, *Paracoccus*, *Spirillum*, and *Rhodopseudomonas*. When oxygen is available, these organisms oxidize a carbohydrate substrate to CO₂ and H₂O:



Under oxygen-free conditions, some microorganisms oxidize a carbohydrate substrate to CO₂ and H₂O using nitrate instead of oxygen as an electron acceptor and converting the nitrate to N₂ gas as shown by the overall reaction:



This reaction is irreversible in nature. The energy yield during nitrate reduction is about

Table 3
FIRST-ORDER RATE CONSTANTS FOR DENITRIFICATION IN SOILS AND
SEDIMENTS

Soil/sediment	Temperature (°C)	First-order rate constant (k day ⁻¹)	Remarks	Ref.
Peat soil	5—36	0.1—0.5	Laboratory incubation study conducted at various temperatures; rates based on NO ₃ -N loss	20
Florida organic soils (8 soils)	30	0.1—1.5	Organic soils obtained from several locations in south and central Florida, soils incubated under anoxic conditions, and stirred continuously; rates based on NO ₃ -N loss	
Huron soil (silty clay loam)	30 15 10	2.15 0.72 0.54	Soil obtained from cropped field	21
30 soil types	35	0.03—0.90	Soils collected from several locations in the U.S. rates are influenced by diffusion of NO ₃ -N from floodwater; rates based on NO ₃ -N loss	197, 198
8 soil types	30	0.03—0.76	Soils collected from several locations in the U.S. soils incubated under anoxic conditions, and stirred continuously; rates based on NO ₃ -N loss	
Crowley silt loam No floodwater 3-cm floodwater 6-cm floodwater	30	 0.37 0.18 0.13	Soil incubated in an O ₂ -free atmosphere, with NO ₃ -N present in both floodwater and underlying soil; rates based on NO ₃ -N disappearance	169
Hanford sandy loam Columbia silt loam Moreno clay loam	20—22	0.07 0.17 0.05 0.14	Rate constants measured under steady-state conditions	200 130
Yolo loam		0.004—0.03	Laboratory soil columns using ¹⁴ N	181
Norfolk sandy loam No waste added Beef waste added Poultry waste added Swine waste added	30	0.07 1.06—2.57 0.10—1.34 0.18—0.88	Laboratory incubation study with no excess floodwater; soils treated with organic wastes which underwent various degrees of decomposition	176
Danish lake sediments (Copenhagen, Denmark)		0.04—0.76	Sediments obtained from various times during seasons; ¹⁵ N was used to determine denitrification; rates measured based on N ₂ production	156

$$\frac{dN}{dt} = \frac{V_{\max} NC}{(N + K_n)(C + K_c)} \quad (11)$$

where N is the concentration of nitrate; C the concentration of carbon; K_n and K_c are the respective saturation constants, V_{\max} is the maximum rate; and t is time.

545 Kcal/mol of glucose if the nitrate is reduced to nitrous oxide and 570 Kcal if nitrate is reduced all the way to elemental gaseous nitrogen.⁶¹

In recent years many researchers^{22,53,106,107,152} have confirmed that the sequence $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$ is operating in true biochemical denitrification.

Several factors are known to influence the rate of denitrification directly or indirectly. Among these are absence of O_2 , presence of readily available C, temperature, soil moisture, pH, presence of denitrifiers, soil texture, and presence of overlying floodwater. In recent years, several studies have reported that increases in C content of the system increases the denitrification capacity of the soil, provided other factors are favorable for this process. Burford and Bremner⁴⁷ observed highly significant correlations between denitrification capacity of the soils and water-soluble organic C ($r = 0.99$). Similarly, Stanford et al.^{197,198} also observed a significant relation between nitrate loss and extractable C. Denitrification rate was shown to increase with increase in temperature. The optimum temperature for denitrification was shown to be between 60 to 75°C.^{86,136} From the results reported by several workers,^{20,21,136,198} it can be concluded that rate of denitrification increased 1.5 to 2.0-fold, with 10°C rise in temperature. The effect of moisture content of denitrification was shown by Jansson and Clark,⁹⁸ Nommik,¹³⁶ and Bremner and Shaw.³⁸ The effect of moisture on denitrification is largely in its effect on aeration. Pearsall and Mortimer¹⁵⁵ and Patrick¹⁴³ showed that denitrification would occur when the redox potential of the soil decreased to below about 340 mV. Rate of denitrification was also shown to be influenced by pH of the soil system. The optimum pH for the denitrification reaction was 6.0 to 8.5.^{136,214,221}

There is varied opinion on the kinetics of denitrification in soils. Several workers contend that the denitrification rate is independent of nitrate N concentration.^{38,42,57,136,143,221} Stanford et al.¹⁹⁷ used lower concentrations (below 32 $\mu\text{g NO}_3\text{-N}$ per milliliter) and subsequently found the reaction to be first order. Bowman and Focht³³ showed that the kinetics of denitrification fitted the standard Michaelis-Menton equation, providing the reductant (carbonaceous substrate) was not limiting. The usual experimental procedure for determining the order and rate of denitrification is to submerge the soil in a test tube or beaker and to then measure the disappearance of added $\text{NO}_3\text{-N}$ and/or the appearance of nitrogenous gases.^{33,103,197,198} Nitrate N in such a system is present in both the floodwater and the soil layer. Since denitrification occurs primarily in the soil layer,^{66,175} the diffusive flux of nitrate N from the overlying floodwater to the underlying soil layer will influence the apparent order and rate of reaction. To resolve this problem Reddy et al.¹⁶⁹ measured denitrification rates under diffusion-free conditions. Their results show that under conditions where carbon was not limiting and without floodwater above a soil column, denitrification rate in the soil followed zero order and proceeded at a faster rate compared to a slower reduction rate and apparent first-order kinetics when the soil was flooded with 3 cm of water. A number of studies have reported first-order kinetics as a result of not considering the limiting effect of diffusion of nitrate N from the floodwater to the soil. Reddy et al.¹⁶⁹ also showed that under carbon-limiting conditions the denitrification followed apparent first-order kinetics. Thus, the discrepancies between the first- or zero-order kinetics reported in the literature can be resolved when one considers that $\text{NO}_3\text{-N}$ concentration ranges used in the experiments, and whether the system is carbon or nitrogen limiting.⁷¹

Since rate of denitrification is dependent on several factors, it is very difficult to use a single rate constant to describe rate of nitrate N loss. Data in Table 3 show the relative rates of denitrification (expressed as first-order constants) in wide range of soils. The maximum denitrification rate of 2.57 day^{-1} was reported for organic soils and a minimum denitrification rate of 0.03 day^{-1} was reported for soils low in organic matter.

Since the rate of denitrification is also dependent on the available carbon, it is appropriate to describe denitrification kinetics in relation to carbon decomposition. Bowman and Focht³³ explained the kinetics of denitrification by the Bray-White³⁶ equation for the product of two simultaneous Michaelis-Menten expressions, such that

More recently, Reddy et al.¹⁷⁷ measured denitrification rates and the decomposition of available carbon simultaneously in the same system. Nitrate reduction coupled with organic carbon mineralization was best described as

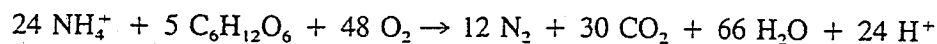
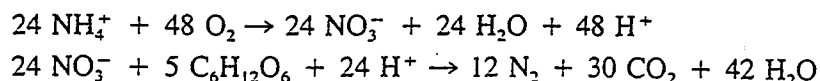
$$\frac{dN}{dt} = -k_n CN \quad (12)$$

where N is nitrate N concentration ($\mu\text{g N/m}\ell$); k_n is denitrification rate coefficient [day^{-1} ($\mu\text{g C/m}\ell$) $^{-1}$]; and C is ($C_{\text{max}} - \text{CO}_2$), i.e., the mineralization carbon remaining in the soil, C_{max} is the potentially mineralizable carbon and CO_2 is the carbon utilized during denitrification.

Traditionally, the denitrification rate was described either by zero- or first-order kinetics. Under both conditions, denitrification rates were measured under carbon-limiting conditions. If denitrification rates are expressed either as zero- or first-order rate constants without giving due consideration to the rate of soluble organic carbon availability in the soil, rate constants obtained will be of limited value in describing denitrification process. Significant relationships between the rate of denitrification and available carbon as assessed by glucose equivalent,^{197,198} water soluble carbon,^{47,176} and mineralizable carbon⁴⁷ were reported. When denitrification rate constants were adjusted for the available carbon (Equation 12), a single rate constant, which was independent of carbon and nitrate N, was obtained for mineral [$0.00147 \pm 25\% \text{ day}^{-1} (\mu\text{g C/m}\ell)^{-1}$] and organic soils [$0.00115 \pm 63\% \text{ day}^{-1} (\mu\text{g C/m}\ell)^{-1}$]. Agreement between predicted nitrate N loss as estimated by Equation 12 and measured nitrate N loss was good. Considering the practical usefulness of a single k_n value, the deviation between measured and predicted values is considered not too large. Equation 12, however, assumes that denitrifying population at an optimum level in all soils.¹⁷⁷

VIII. NITRIFICATION-DENITRIFICATION REACTIONS

These two reactions are known to occur simultaneously in flooded soils where both aerobic and anaerobic zones exist such as would be the case in a flooded soil or water bottom containing an aerobic surface layer over an anaerobic layer or in the aerobic root rhizosphere of a swamp plant growing in an anaerobic soil. The nitrification reaction occurs in the aerobic zone and denitrification reaction occurs in the anaerobic zone. By combining these two reactions, a balanced equation occurring in aerobic and anaerobic layers can be written as



These reactions involve both oxidation (nitrification) and reduction (denitrification), with a change in valence of N from -3 (for $\text{NH}_4\text{-N}$) to $+5$ (for NO_3), followed by a reduction to $+1$ (for N_2O) and zero (N_2). Four moles of oxygen are required to react with 2 mol of ammonium to produce 1 mol of N_2 gas. The nitrate N is an intermediate product in the reaction and does not appear in the final reaction. Where the surface aerobic layer is thin, little nitrate is likely to accumulate.¹⁴⁹

The major supply of ammonium N to the aerobic soil layer and floodwater comes from: (1) mineralization of organic N in the aerobic soil layer and floodwater and (2) diffusion of ammonium N from the underlying anaerobic soil layer. The majority of nitrate N in water-logged rice soils is derived from the nitrification of ammonium N in the surface aerobic layer. The nitrate formed in the aerobic layer is constantly supplied to the anaerobic layer by diffusion in response to a concentration gradient and removed by denitrification reaction.^{131,149,150,154}

In recent years, several researchers have used wetland ecosystems for inorganic N removal by nitrification-denitrification.^{34,70,194,231} Nitrification can occur in the aerobic floodwater and denitrification in the underlying sediment. Nitrification-denitrification has also been successfully used in reducing the inorganic N levels of secondary waste effluents^{32,122} and agricultural waste waters.¹⁶⁵

IX. AMMONIUM DIFFUSION

Ammonium N in the aerobic soil layer and overlying water is derived from: (1) decomposition of organic matter in the water column; (2) mineralization of organic N in the aerobic soil layer; and (3) mass transfer of ammonium N from the anaerobic soil layer to the aerobic soil layer and floodwater. The later process contributes a major portion of ammonium N to the overlying aerobic soil layer and floodwater. Mass transfer is accomplished by diffusion, bioturbation, and wave and current stirrings at and near the sediment-water interface. Several researchers^{25,35,90,132,135,159,192} have shown that sediments act as a potentially important source of nutrients, as indicated by determinations of high concentrations of dissolved N and P in sediment pore waters as compared to overlying waters.

To quantitatively evaluate ammonium N fluxes into the overlying waters, it is important to have an understanding of the mechanisms of ammonium N movement in aerobic soils and sediments. In flooded soils and shallow water bodies, ammonium N movement from the anaerobic soil layer into the aerobic layer is mainly due to diffusion, unless there is appreciable wave and current stirring at and near the sediment-water interface. Rate of ammonium N movement from the anaerobic soil layer is governed by: (1) the concentration gradient established as a result of ammonium N consumption in the aerobic zone during nitrification and NH_3 volatilization; (2) the ammonium N regeneration rate in the anaerobic zone; (3) the ammonium N concentration in the pore water; (4) other cations on the soil exchange complex; (5) cation exchange capacity of the soil; and (6) the relative volume of pore space which is the function of bulk density of the sediment.

The process of ammonium diffusion plays an important role in describing the transport of dissolved ammonium N into the overlying waters. The quantity of ammonium N transferred by diffusion phenomena per unit area per unit time is proportional to the diffusion coefficient and the concentration gradient. At the soil-water interface, concentration gradients can be relatively large and hence diffusion of ammonium N from the anaerobic layer can be rapid. Molecular diffusion is assumed to follow Fick's laws and is expressed in terms of the whole soil or sediment diffusion coefficient, D , which includes the effects of tortuosity but not those of adsorption. Data in Table 4 show the D values for ammonium N moving in several anaerobic soil or sediment systems. In a study reported by Reddy et al.,¹⁷⁴ D values were found to be lower ($D = 0.06 \text{ cm}^2/\text{day}$) for soils with high cation exchange capacity, as compared to the soil with low cation exchange capacity ($D = 0.17$ to $0.22 \text{ cm}^2/\text{day}$). These D values were not corrected for the adsorption of ammonium N. Krom and Berner¹⁰⁹ reported D values of $0.85 \text{ cm}^2/\text{day}$ in anoxic marine sediments, after adjusting D values for the effects of adsorption. The D values reported for wet soils and sediments are generally higher than the D values of 0.004 to $0.026 \text{ cm}^2/\text{day}$ obtained for well-drained soils containing 5 to 30% volumetric moisture content.⁵¹

Several research workers have reported data on the distribution of ammonium N in anoxic ocean and lake sediments^{46,102,192} and in flooded soils.¹⁶⁷ A typical ammonium N distribution in sediments and flooded soils is shown in Figure 7. All these studies show low ammonium N concentration at the sediment-water interface and the surface soil layer, while high ammonium N levels were observed in the lower sediment layers. These results suggest that ammonium N removal from the surface soil layers were probably due to upward transport of $\text{NH}_4\text{-N}$ into the overlying waters.

Table 4
DIFFUSION COEFFICIENTS FOR $\text{NH}_4\text{-N}$ MOVEMENT IN SOILS AND SEDIMENTS

Soil/sediment	Temperature (°C)	Diffusion coefficients (cm^2/day)	Remarks	Ref.
Flooded soil			Experiment conducted with an initial ammonium N concentration of 200 $\mu\text{g/g}$ of soil; incubation period of 2 days	174
Crowley silt loam	30	0.216		
Midland silt loam	30	0.172		
Mhoon silty clay loam	30	0.059		
Marine sediments (Long Island Sound)	20	0.850	Sediments with additional ammonium N added; diffusion coefficients adjusted for adsorption; incubation period of 5.9 days	109
Volumetric water content (cm^3/cm^3)			Experiment conducted with soils treated with 14.3 meq/l of $(\text{NH}_4)_2\text{SO}_4$ solution, and adjusted to various water contents; soils were sterilized using γ -radiation before use; incubation period of 5—17 days	51
Urrbrae	0.10 21	0.003		
loam	0.15 21	0.009		
	0.20 21	0.013		
	0.25 21	0.019		
Wanbi	0.10 21	0.019		
sand	0.15 21	0.022		
	0.20 21	0.030		
Volumetric water content (cm^3/cm^3)			Experiment conducted with an initial ammonium N concentration of 200 $\mu\text{g/g}$ of soil; nitrification inhibitor was used to prevent ammonium N oxidation; incubation period of 7 to 15 days	174
Crowley				
silt loam	0.06 30	0.004		
	0.11 30	0.010		
	0.27 30	0.050		
Flood Maahas clay			Laboratory of study conducted using undisturbed wetland soil cores; incubation period of 7 and 28 days	188
Prilled urea	25	0.019		
Super granule urea		0.022		
Sulfur-coated urea		0.016		

Ammonium N fluxes of about 0.104 g N per square meter per day from flooded rice soil were measured by Reddy et al. under laboratory conditions. In this study, more than 50% of the total ammonium N transported was due to diffusion from anaerobic soil layer to the aerobic soil layer. Using a D value of 0.216 cm^2/day and an ammonium N oxidation rate of 5 $\mu\text{g}/\text{cm}^3/\text{day}$, Reddy et al. also calculated the flux of ammonium N from the anaerobic soil layer to the aerobic soil layer. The calculated values were in close agreement with the experimental values. Using the pore water concentration of Long Island Sound sediment, Berner²⁸ calculated that about 70% of ammonium N liberated below 10-cm depth is lost from the sediment by diffusion and mixing. This value was in good agreement with the direct flux measurement made on the same sediments by Rosenfeld.¹⁸³

The transport of ammonium N by ionic diffusion from the anaerobic soil layer to the aerobic soil layer can be influenced by several factors such as organic matter status of the soil, cation exchange capacity of the soil, presence of reduced Fe and Mn, bulk density, and moisture content. The thicker the aerobic soil layer, the greater the nitrification of ammonium N because of the greater activity of nitrifying organisms in the surface soil layers.^{15,16,65} Since the anaerobic soil layer is devoid in oxygen and nitrate N, Fe^{+3} and Mn^{+4} will be reduced during microbial respiration. Large quantities of reduced Fe and Mn occupy most of the exchange complex^{80,81} enabling the ammonium N ions to be in the soil solution and therefore result in a high diffusion rate of ammonium N in flooded soils. Low cation exchange capacity of a flooded soil also increases the diffusion of ammonium N from the anaerobic soil layer to the aerobic soil layer. These factors have been discussed by several workers for diffusion of cations in well-drained soils.^{23,76,138}

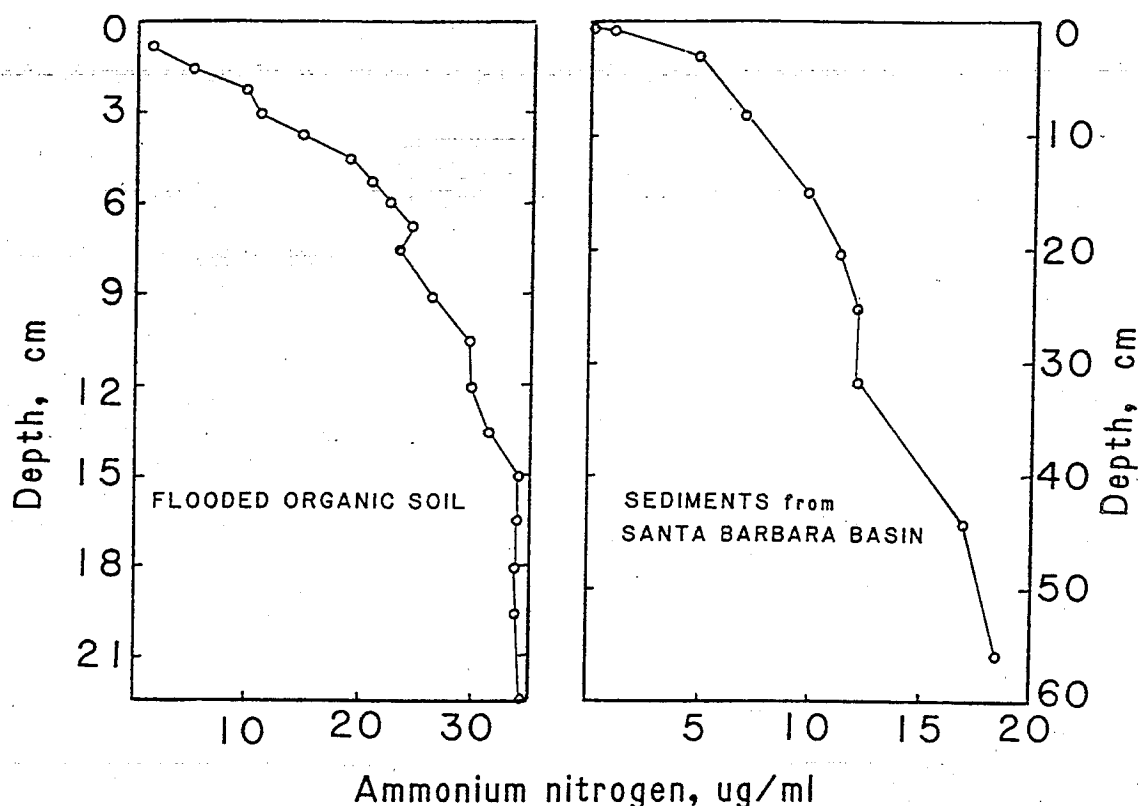


FIGURE 7. Distribution of ammonium nitrogen in flooded soils¹⁶⁶ and sediments.¹⁹²

X. NITRATE DIFFUSION

Nitrate N in the floodwater and in the aerobic soil layer is derived from: (1) nitrification of ammonium N in these zones and (2) input from drainage water effluents and from waste waters when flooded soils are used as a treatment system. In a natural system, oxidation of ammonium N is the major source of nitrate N in the floodwater and aerobic surface soil layer. In flooded soils and sediments, nitrate N present in the floodwater and aerobic soil layer readily diffuses into the anaerobic soil layer as a result of a downward concentration gradient. It has been shown that very little or no denitrification occurs in floodwater low in available carbon,⁶⁶ and under these conditions, floodwater nitrate N removal is dependent on the diffusion of nitrate N into the anaerobic portion of the sediment of flooded soil. However, the floodwater was the major site of denitrification where the floodwater contained a large amount of easily decomposable carbon source.¹⁷⁵

The flux of nitrate N from the floodwater and the aerobic soil layer into anaerobic zones of the sediment is controlled by: (1) available carbon supply in the anaerobic portion of the sediment; (2) thickness of aerobic soil layer; (3) floodwater depth; (4) nitrate N concentration in the floodwater; (5) temperature; and (6) mixing and aeration in the floodwater. Loss of nitrate N from the overlying floodwater was shown to increase with increased availability of available carbon in the underlying anaerobic sediment. Engler and Patrick⁶⁶ observed nitrate removal rates of 1.47, 2.60, 2.67, and 4.79 $\mu\text{g NO}_3\text{-N}$ per milliliter per day for the sediments receiving 0, 0.1, 0.5, and 2.0% rice straw. In a recent study, Krottje¹¹⁰ measured nitrate N removal rates from the floodwaters of 14 representative Florida wetland soils. His study showed that nitrate N removal rates from the floodwater were related to the square root of organic carbon and pH of the underlying anaerobic sediment, as shown below:

$$K = \sqrt{(8.9 \times 10^{-4}) (\text{OC}) - (3.9 \times 10^{-4}) (\text{OC}) (\text{pH } 6.5) + 0.002} \quad (13)$$

where K is the apparent first-order rate constant for $\text{NO}_3\text{-N}$ removal (day^{-1}) and OC is organic carbon by weight (%). Increased diffusive flux of nitrate N from the floodwater into the anaerobic soil high in carbon is due to greater demand for electron acceptors, because soils or sediments high in available carbon have greater potential to denitrify large amounts of nitrate N.

The thickness of the aerobic zone increases the path length for nitrate N diffusion from the overlying waters. High biological activity in the underlying sediment reduces the thickness of the aerobic zone and low biological activity in the sediment increases the thickness of aerobic zone.⁶⁶ The flux of nitrate N from the floodwater will be greater in the sediments with thin aerobic zone and high biological activity, as compared to the sediments with thick aerobic zone and low biological activity.

No experimental data are available to show the effect of floodwater depth on nitrate N removal. However, the factor of major importance is the ratio of surface area of the water sediment interface (S) to volume of water (V), with S/V increasing as the depth of the water decreases.³¹ Hence in very deep bodies of water, the flux of nitrate N will be reduced considerably relative to that in shallow bodies of water. Maximum nitrate N removal will occur in shallow water bodies. Reddy et al.¹⁷⁵ showed flux of nitrate N from floodwater containing high nitrate N concentration ($\approx 50 \mu\text{g}/\text{m}\ell$) compared to water containing low nitrate N concentration ($< 10 \mu\text{g}/\text{m}\ell$).

Flux of nitrate N from the floodwater into the underlying anaerobic soil layer was increased with increase in temperature with an average Q_{10} value ranging from 1.4 to 2.1 for 18 to 28° and 2.0 to 2.5 for 8 to 18°C.¹⁷⁵ This increase in flux was due to the dependence of denitrification on temperature. Reddy et al.¹⁷⁵ also showed that at low temperature (8°C) floodwater nitrate N diffused deep into anaerobic zone, compared to warmer temperature (28°C). These results suggest that when denitrifying activity was slower (cooler temperatures, soils with low available carbon) nitrate N can possibly diffuse into deeper soil layers.

Diffusive flux of nitrate N from the water column into the underlying anaerobic soil was shown to be increased by aerating the water column.¹⁶⁷ Aerating the water column probably disrupted the gradient within the water column, resulting in rapid movement of nitrate N into the underlying soil column. In a natural system, the nitrate N concentration gradient decreases due to convection currents and perturbation by wind, which tends to keep water columns well mixed in shallow water bodies.

To quantitatively evaluate the nitrate N flux from the floodwater, it is important to have an understanding of the diffusion coefficient (D) for nitrate N in flooded soils. Data in Table 5 present some of the D values reported in the literature. The measured D values for nitrate moving from floodwater into the underlying anaerobic soil column ranged from 0.25 to 1.33 cm^2/day in several soils.^{167,174} A D value of 1.15 cm^2/day for nitrate N moving in a soil (42.7% moisture by volume) was observed by Romkens and Bruce.¹⁸² The high D values for nitrate N are expected since nitrate N is anion and is not adsorbed on the exchange complex and tends to move in the soil water. Using the changes in chloride concentration of the flood-water, Krottje¹¹⁰ estimated D values for nitrate N which ranged from 0.26 to 1.8 cm^2/day . The D values for nitrate N are high compared to ammonium N D values, indicating that nitrate N diffuses at a faster rate in a flooded soil as would be expected because of the greater cross sectional area of water in the pores of a saturated soil.

To calculate the fluxes of nitrate N from the floodwater into the anaerobic soil layer, Bouldin et al.³¹ present a steady-state diffusion model, as described below. The nitrate N is considered to diffuse across the aerobic soil layer to the aerobic-anaerobic interface where it was assumed to be lost through denitrification.

Table 5
DIFFUSION COEFFICIENTS FOR NO₃-N MOVEMENT IN SOILS

Type of system	Temperature (°C)	Diffusion coefficient (cm ² /day)	Remarks	Ref.
Flooded soil			Experiment conducted with an initial nitrate N concentration of 300 µg/ml, incubation period of 24 hr saturated soil moisture content	174
Crowley silt loam	30	1.33		
Midland silt loam	30	1.94		
Mhoon silty clay loam	30	0.96		
Flooded organic soil	8	0.25	Experiment conducted with an initial nitrate N concentration of 100 µg/ml, incubation period of 78 hr	
	28	0.44		
Volumetric water content (cm ³ /cm ³)			Experiment conducted with the soils amended with 28.6 meq/l of KNO ₃ solution, and adjusted to various water contents; soils were sterilized using radiation before use; incubation period of 1—5 days	51
Urbræ	0.10	21	0.04	
loam	0.20	21	0.17	
	0.25	21	0.32	
Wanbi	0.05	21	0.13	
sand	0.10	21	0.23	
	0.15	21	0.34	
	0.20	21	0.42	
Saturated water content (cm ³ /cm ³)			Experiment conducted with silt, sand, or glass beads saturated with 0.1 NNaNO ₃	182
Silt	0.43	30	1.15	
Sand	0.42	30	1.20	
Glassbeads	0.38	30	1.21	
Flooded soils				
Everglades muck	25	0.51	Nitrate diffusion from floodwater into the underlying soil column was measured;	110
Floridana fine sand		0.33	diffusion coefficients for nitrate N were measured, using the changes in chloride concentration of floodwater	
Astor sand		0.68		
Surrency sand		1.80		
Samsula muck		1.70		
Pickney fine sand		0.81		
Riviera fine sand		1.30		
Delray fine sand		1.20		
Chastain silt loam		0.35		
Brighton peat		0.42		
Iberia silty clay		0.45		
Chobee fine sandy loam		0.38		
Eureka fine sandy loam		0.72		
Valkaria fine sand		0.26		

$$V \frac{dN}{dt} = SD \left(\frac{N}{L} \right) \quad (14)$$

where dN/dt is the rate of change of nitrate N concentration of the water with time, V is the volume of water, S is the surface area of the water-sediment interface, D is the diffusion coefficient of nitrate N in the aerobic portion of the sediment, and L is the thickness of the aerobic zone of sediment. The above-shown equation assumes zero nitrate N concentration at the aerobic-anaerobic interface in the sediments, and the concentration of the nitrate N in the water is assumed to be uniform throughout the volume V .

Integrating and setting $N = N_0$ when $t = 0$,

$$\ln N = \ln N_0 - (SD/VL)t \quad (15)$$

If we assume (SD/VL) is constant for a given system, then Equation 15 reduces to a simple first-order equation:

$$\ln N = \ln N_0 - Kt \quad (16)$$

where $K = (SD/VL)$.

Equations 15 and 16 are very simple forms of describing the fluxes of nitrate N from floodwater into the anaerobic soil layer. Data on nitrate N fluxes from ponds fitted well to Equation 15³¹ and to Equation 16.¹⁷⁵ In both systems, nitrate N fluxes at any given time were expressed as the fraction of initial concentrations (0.069 to 0.203 day⁻¹). Note the above equations do not use a sink term for nitrate N moving into anaerobic soil layers, but assumes that all the nitrate N diffused into anaerobic zone is lost through denitrification. In a recent study, Reddy and Rao used Fick's law of diffusion by adding a sink term for nitrate N diffusing into the anaerobic soil column:

$$\frac{d(NO_3)}{dt} = D \frac{d^2[NO_3]}{dX^2} - K[NO_3] \quad (17)$$

where, it is time (days); D is the diffusion coefficient for nitrate N (cm²/day); X is depth (cm); and K is the first-order rate constant for denitrification. Solution to Equation 17 was obtained by using numerical techniques, and simulated results were in agreement with the experimental values.

XI. LOSSES OF NITROGEN AS A RESULT OF NITRIFICATION-DENITRIFICATION AND NH₃ VOLATILIZATION

A. Nitrification-Denitrification

The importance of the nitrification-denitrification sequence in aerobic-anaerobic soil layers has been recognized by several research workers around the world. These reactions are undesirable in paddy soils, but may be ecologically beneficial in regulating excessive accumulation of nutrient forms of N in aquatic ecosystems, especially in wetland soils and sediment-water systems receiving large nitrogen inputs from waste discharge sources.

1. Flooded Rice Soils

As early as 1935, information began to appear on the importance of these aerobic and anaerobic layers in nitrogen transformations. Shiori and Mitsui¹⁹⁰ observed severe losses of applied ammonium N in flooded soils during extended incubations. The losses were apparently too great to be accounted for by direct volatilization or by other possible mechanisms of N loss known at that time. Further experiments led them to believe that even under flooded conditions ammonium was nitrified to nitrate when applied to the flooded soil surface. Nitrate thus formed moved down into the anaerobic zone by diffusion and was subsequently denitrified biologically and possibly chemically to gaseous end products such as nitrous oxide and nitrogen gas. Later, this process was confirmed by Pearsall,¹⁵⁴ Shioiri and Tanada,¹⁹¹ and Mitsui.¹³¹

Studies conducted with paddy soils in different parts of the world indicated that losses of N through nitrification and subsequent denitrification largely account for the low recovery of ammonical fertilizers by rice.⁹⁵ Several other workers reported similar N losses through these mechanisms.^{10,24,205,209,225} Patnaik,¹⁴² in a tracer study of N transformations in waterlogged soils, could not account for 24% of applied N. Tracer investigations in the fate of ammonium sulfate under submerged conditions⁹⁷ showed considerable losses of applied ammonium due to denitrification after 4 weeks of incubation.

Tusneem and Patrick,²¹¹ Broadbent and Tusneem,⁴³ and Patrick and Tusneem¹⁴⁶ in studies using ^{15}N reported that substantial N losses occurred in soils receiving N in a reduced form (ammonium sulfate) and maintained in a flooded condition throughout the experimental period. These studies demonstrated that nitrification and subsequent denitrification reactions were functioning simultaneously in a flooded system and controlling N loss. Similar results were also reported by Manguiat and Yoshida¹¹⁷ and Yoshida and Padre.²²⁸ In other recent studies, Patrick and DeLaune,¹⁴⁵ Patrick and Gotoh,¹⁴⁷ Takai and Uehara,²⁰⁶ Patrick and Reddy,¹⁴⁹ and Reddy and Patrick^{163,164} showed that more ammonium N was lost from a flooded soil than is actually present in the aerobic soil layer at any one time. Apparently, ammonium N diffuses from the anaerobic soil layer to the aerobic soil layer where it undergoes nitrification and subsequent denitrification.

Application of fertilizer ammonium N to flooded rice fields by deep placement has been shown to be superior to surface application.^{45,58,59,95,127,128,151,226} Recovery of applied fertilizer N in the soil-plant system under field conditions was determined by Patrick and Reddy¹⁵⁰ and Reddy and Patrick.¹⁴⁹ Their studies indicated that when labeled ammonium sulfate was applied by deep placement, an apparent loss of 25% applied N occurred, whereas 49% of applied N was recovered in the plant and 26% of applied N remained in the soil either in the roots or in the soil organic matter. It was suggested that at least part of the N losses were due to ammonium N diffusing from the anaerobic layer to the aerobic layer, where it underwent nitrification and subsequent denitrification.

2. Aquatic Sediments

The importance of the nitrification-denitrification sequence has also been recognized by researchers working with environmental quality. Graetz et al.⁸⁴ observed that during anoxic conditions, ammonium N was released to the water at a relatively constant rate. They estimated that these processes contributed approximately 30% of the nitrogen entering the lake from external sources. Aeration affected rapid nitrification, and the nitrate thus formed in the overlying water decreased with time, probably due to diffusion into the highly reduced sediment and subsequent denitrification. Kemp and Muodrochova,¹⁰² working with Lake Ontario sediments, indicated that nitrogen was returned to the atmosphere through nitrification-denitrification processes. Billen²⁹ showed that nitrification of ammonium N is the main source of increase in nitrate concentration in the upper layers of the sediment. When this nitrate moved below the 3-cm layer it disappeared by denitrification. Kemp and Muodrochova¹⁰² found that the upward diffusion of ammonium due to a concentration gradient in the interstitial water was active to a depth of approximately 150 cm. They also reported that the ammonification and nitrification of inorganic nitrogen in the top 6 cm of the sediment resulted in about 20% of the nitrogen loading into the Lake Ontario sediments being lost to the overlying water, either in a nutrient form or as N_2 or N_2O gas which would escape into the atmosphere. Chen et al.⁴⁸ showed that ammonium exchange with the overlying water column was considerable in the top 4 cm of the sediment studied, but negligible beneath the 8-cm depth. Recently, Curtis et al.⁵⁵ estimated that 80% of the oxidation of ammonium N occurred in the sediments only.

Apparently, ammonium N in the surface aerobic soil layer is readily converted to nitrate. Nitrate N thus formed in the aerobic layer readily diffuses down into the anaerobic layer, where it undergoes denitrification into gaseous end products such as N_2 and N_2O .¹⁴⁹ Immediately following nitrification in the aerobic layer, a concentration gradient of ammonium N is established across the aerobic and anaerobic layers. Additional ammonium N present in the anaerobic layer diffuses upward into the aerobic layer and is also subjected to nitrification-denitrification. This decrease in ammonium N the surface layer was demonstrated by Reddy et al. and for a Lake Ontario sediment core by Kemp and Muodrochova.¹⁰² The depletion of ammonium in the brown surface layer (oxidized) indicates nitrification, and

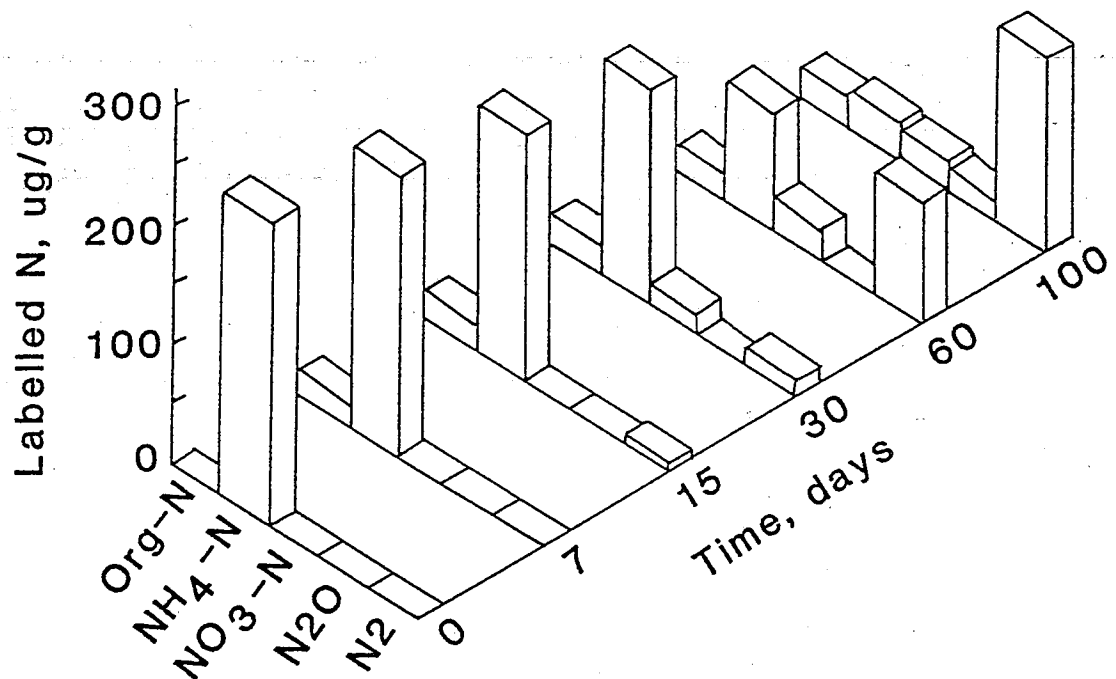


FIGURE 8. The conversion of ^{15}N -labeled ammonium to elemental nitrogen in a flooded soil. The distribution of labeled ammonium among various nitrogen fractions following incubation under 30% oxygen.

disappearance of ammonium in the gray mud layer (reduced) indicates diffusion of ammonium from the aerobic layer to the anaerobic layer. The low concentration of nitrate N in the surface layer indicates that the denitrification reaction prevents nitrate from accumulating. The sequential processes functioning in a natural flooded soil or a sediment system are ammonification, ammonium diffusion, nitrification, nitrate diffusion, and denitrification. All these processes were shown to occur in the flooded soils incubated under a 30% oxygen atmosphere. The ultimate conversion of ammonium N to N_2 gas by this sequence was shown by Patrick and Reddy¹⁴⁹ (Figure 8).

3. Effect of Alternate Aerobic and Anaerobic Conditions on Nitrogen Loss

Inorganic N transformations are greatly influenced by alternate aerobic and anaerobic conditions. Severe N loss has been shown to occur in soils subjected to alternate draining (aerobic) and flooding (anaerobic).^{116,144,185,221} Organic N is converted to ammonium N in both aerobic and anaerobic soils (though the N mineralization rate is likely to be greater in aerobic soils). The ammonium N thus formed is oxidized to nitrate under aerobic conditions and the resulting nitrate denitrified under anaerobic conditions. Loss of N due to sequential nitrification and denitrification is especially high in soils planted to lowland rice, where water management practices sometimes require draining and reflooding.

Russell and Richards¹⁸⁶ were probably the first workers to recognize the importance of alternate aerobic and anaerobic conditions in determining loss of N. Their studies showed large losses of N from farmyard manure under alternate wetting and drying conditions, but little loss when the material was maintained under either aerobic or anaerobic conditions. Wijler and Delwiche²²¹ noted that alternating aerobic and anaerobic conditions should result in greater total N loss from the soil than would be found under continuous anaerobic conditions. Patrick and Wyatt¹⁴⁴ observed a large loss of N (up to 20% of total N or 200 ppm) as a result of repeated cycles of flooding and drying to field moisture. Tusneem and Patrick²¹¹ showed that ammonium N was highly unstable under alternate flooded and moist conditions of several weeks duration, since only trace amounts of applied labeled ammonium N was recovered at the end of a 120-day incubation period.

The length of each aerobic and anaerobic period in the soil may vary, depending on the conditions at any given period. The effect of several variable length cycles of alternate aerobic and anaerobic conditions on native and applied N loss was demonstrated by Reddy and Patrick^{160,162} under laboratory conditions. Total N loss was as high as 24.3% in a soil system which underwent maximum number of alternate aerobic and anaerobic periods of 2 and 2 days during a 4-month incubation. Increasing the durations of the aerobic and anaerobic periods decreased the loss of N.

B. Ammonia Volatilization

Ammonia volatilization is not considered to be an important mechanism of N loss from flooded soils and sediments, except in specialized cases where high ammonium N concentration exists in conjunction with high pH in the soil-water system.

1. Rice Soils

The agronomic significance of the high pH that develops in rice floodwater has largely been neglected as a factor in the direct volatilization loss of NH_3 . Losses of volatile NH_3 from flooded rice soils reported by MacRae and Ancajas¹¹⁵ are calculated as 7% of the ammonium sulfate applied and as much as 19% of the urea within 7 weeks. Ventura and Yoshida²¹⁵ measured NH_3 volatilization losses from different N sources on a flooded Maahas clay soil and reported NH_3 losses occurred principally during the first 9 days after N application. Losses were small when soil pH was adjusted below pH 7.4. Their field experiments showed N losses of 3.8% from ammonium sulfate and 8.2% from urea during a 21-day sampling period when surface applied at 100 kg N per hectare. Incorporation of fertilizer N into a puddled soil decreased NH_3 volatilization losses by 50%.

Nitrogen losses from fertilizer broadcast into floodwater on a fertile, neutral pH Maahas clay were as high as 20% of the amount applied, but losses varied depending upon water pH, the nitrogen source, and rate, time, and method of application. Losses from an acid Louisiana clay, where the floodwater was not conducive to algal growth and did not exceed pH 6.8, produced NH_3 volatilization losses consistently less than 1% of the total N applied. Placement of N fertilizer in the soil at depths of 10 to 12 cm reduced NH_3 volatilization losses to less than 1% of the total N applied.¹²⁹ Vlek and Craswell²¹⁷ observed losses up to 50% of the surface-applied urea within 2 to 3 weeks, and losses from surface-applied ammonium sulfate occurred to a lesser extent (about 15% of the added N). This study also shows that soil pH had little effect on the pH of the floodwater, and thus on the ammonia volatilization process. The conclusions presented in this study were based on controlled experimental conditions and have not been extrapolated to field conditions.

2. Aquatic Sediments

The sources of ammonium N to the overlying water in lakes, shallow water bodies, marshlands are mainly: (1) inputs from external sources, waste water effluents, agricultural runoff, and rainfall and (2) ammonium N produced from the mineralization in the sediments. Volatilization of NH_3 in these systems is dependent on pH and ammonium N concentration. In experimental ponds, Bouldin et al.³¹ observed losses of ammonium N up to 38%/day (range 2 to 38%/day). They concluded that a major portion of these losses was due to NH_3 volatilization. These conclusions were based on the calculation of NH_3 losses using ammonium N concentration of water, pH of the water, and equilibrium reactions. The calculated values were in close agreement with the experimental results.

More recently, Reddy and Graetz¹⁶⁵ reported rapid NH_3 volatilization losses from waste water aerated with CO_2 -free air, while very little NH_3 volatilization occurred in the water aerated with CO_2 -containing air. In a natural water system containing algae and submerged aquatic plants, CO_2 can be depleted during photosynthesis, thus increasing pH, which will enhance NH_3 volatilization.

XII. NITROUS OXIDE EVOLUTION DURING NITRIFICATION-DENITRIFICATION

In recent years, concern has arisen that N_2O production by soils and natural waters might lead to a significant increase in the net global source of atmospheric N_2O .^{39,54,73,120} After transport to the stratosphere, N_2O may be converted to NO , and deplete the ozone layer. It is well established that N_2O is the intermediate metabolite during denitrification which under certain conditions may escape to the atmosphere. Recently, researchers^{179,227} have also observed small amounts of N_2O production during the oxidation of ammonium by intact cells and cell-free extracts of *Nitrosomonas europaea*. Under aerobic conditions (soils maintained at 60% of their water-holding capacity), production was higher in soils treated with ammonium sulfate or urea than soils receiving nitrate N.³⁹ In a field study, Breitenbeck et al.³⁷ showed that the emission of N_2O induced by application of calcium nitrate, but represented <0.2% of the fertilizer N applied. To our knowledge, no data are available on the significance of N_2O evolution during nitrification in the surface-oxidized layer and the overlying floodwater. With the current limited information, it is very difficult to assess the role of nitrification in N_2O evolution from soils and sediments.

The amount of N_2O evolution during denitrification varies greatly. Ratios of $N_2:N_2O$ can range from greater than 100:1⁶³ to less than 10:1. Wider $N_2:N_2O$ ratios were observed in the soils with high carbon content, poorly drained with low O_2 concentration, where more complete reduction of nitrate N to N_2 is expected,⁷¹ because of greater demand for electron acceptors. McElroy et al.¹²¹ measured N_2O evolution from the Potomac estuary receiving sewage effluent, and their studies concluded that between 1 and 5% of the total N input was converted to N_2O . Measurements of dissolved N_2O in fresh water ponds near Boston demonstrate that aquatic systems may provide both strong sources and sinks for atmospheric N_2O .⁹⁹ Graetz et al.⁸⁵ observed less than 0.2 to 6.5% of floodwater nitrate N resulted in N_2O .

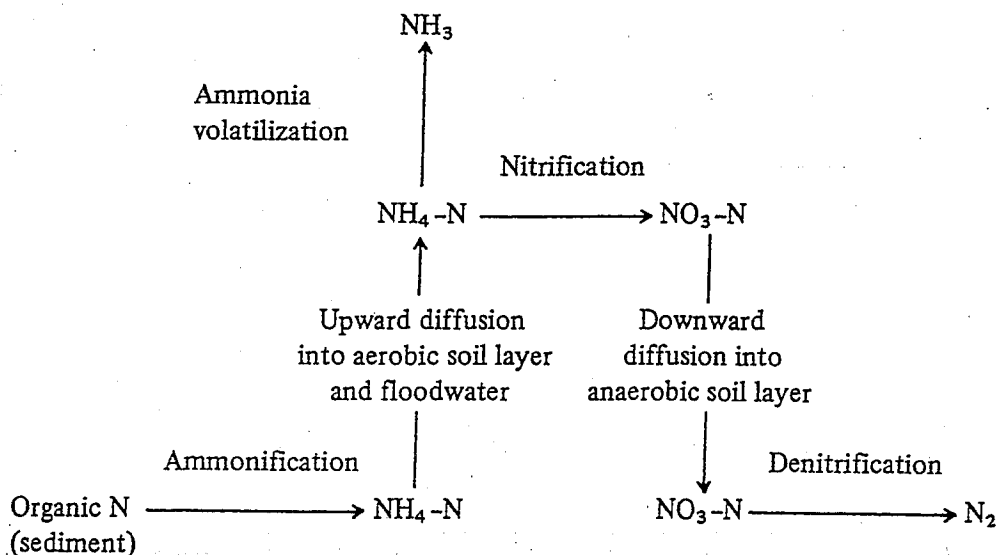
In flooded soils and sediments, N_2O can be formed in the surface aerobic layer during nitrification and in the anaerobic layer during denitrification. However, the extent of these processes on the significance of N_2O evolution from the aquatic system is still not well documented.

XIII. INFLUENCE OF PLANTS ON NITROGEN LOSS

Nitrogen losses in flooded soils and sediment can be greatly influenced by the presence of plants. The magnitude of N loss can be reduced by plant uptake of inorganic N present in soil solution. The N losses can be enhanced by the presence of the aerobic layer around the root zone. Ammonium diffusion from the anaerobic (reduced) layer into the aerobic (oxidized) root rhizosphere, nitrification of ammonium N to nitrate N in the aerobic layer around the root, diffusion of nitrate N from the aerobic layer to the anaerobic layer, and finally denitrification of nitrate N to gaseous end products can occur, although complete experimental verification of these reactions has not been carried out. Woldendorp²²⁴ suggested that plant roots can accelerate denitrification in the rhizosphere by taking-up oxygen and by secreting organic substances which can serve as hydrogen donors in the denitrification process. Several other research workers^{21,77,189,202,218} also reported the significance of plant roots on denitrification. Workers at IRRI⁹⁶ assessed the relative abundance of certain microorganisms occurring in the rhizosphere. Their data indicated the presence of nitrifying bacteria around the root zone. At present, no information is available on the activity of nitrifying organisms in the oxidized rhizosphere of predominately reduced soils. It is speculated, however, that the high root density of rice plants in flooded soil can increase the total area of the aerobic zone and create a favorable condition for nitrification to occur. These same reactions can occur in the aerobic root rhizosphere of swamp and marsh plants.

XIV. CONCLUSIONS

From the literature data reported by several research workers, it can be concluded that N loss mechanisms in flooded soils and sediments are governed by N transformations (ammonification, nitrification-denitrification, and NH_3 volatilization) and transport processes ($\text{NH}_4\text{-N}$ diffusion and $\text{NO}_3\text{-N}$ diffusion) and presence of plants; a schematic representation of the sequential processes functioning in the transport of N from flooded soils and sediments is shown below.



The processes shown above will function continuously in flooded soils, shallow water bodies, lake bottoms, and ocean muds. These processes will aid in returning N in the form of N_2O , N_2 , and NH_3 to the atmosphere. Vaccaro²¹³ estimated that without denitrification in aquatic sediments, atmospheric N_2 will be depleted as a result of fixation in 400 million years.

Inorganic N in aquatic sediments and waters is converted to gaseous forms by two processes: (1) nitrification-denitrification and (2) NH_3 volatilization. The former process seems to be more predominantly involved in the ammonium N loss from the sediments, whereas the latter process occurs under specialized conditions, mainly in the overlying waters. The processes involved in converting organic N to gaseous end products include ammonification of organic N to ammonium N, upward diffusion of ammonium N into the aerobic soil layer, oxidation of ammonium N in the aerobic soil layer, downward diffusion of nitrate N into the anaerobic soil layer, and reduction of $\text{NO}_3\text{-N}$ to the gaseous end products such as N_2 and N_2O . Under certain conditions, where nitrification rate is slower than the flux of ammonium N from the anaerobic soil layer, ammonium N may diffuse into the overlying waters. If the optimum conditions such as high pH and high temperature exist in the water column, ammonium N can be lost through volatilization. Studies have shown that under CO_2 -limiting conditions, NH_3 volatilization occurs at a fast rate compared to nitrification process.¹⁶⁵

To evaluate the overall N transport from aquatic sediments, it is important to know at what rates these processes are functioning and which of these processes are limiting the overall process. In flooded soils and sediments, ammonium N diffusion (0.06 to $0.85 \text{ cm}^2/\text{day}$) and nitrification (1.1 to $2.7 \mu\text{g}/\text{cm}^3/\text{day}$) were found to be functioning at a slower rate, while nitrate N diffusion (0.25 to $1.94 \text{ cm}^2/\text{day}$) and denitrification (0.03 to $2.57/\text{day}$) were functioning at a rapid rate in flooded soils. It can be concluded from these data that nitrate N diffusion and denitrification are not limiting in controlling N loss during nitrification-denitrification sequence. Ammonium diffusion was dependent on the ammonium N removal

mechanisms (nitrification and NH_3 volatilization) in the aerobic soil layer and floodwater to establish a concentration gradient. If ammonium N removal mechanisms do not occur in the aerobic soil layer or floodwater, there will be very little or no ammonium N loss from the flooded soils or sediments.

In shallow reservoirs or wetlands flooded with waste water, nitrification was shown to occur at a rapid rate in the overlying water column,¹⁶⁵ and the major limiting process in the removal of nitrate N from the overlying water was diffusion of $\text{NO}_3\text{-N}$ from the water column to the underlying soil column.

So far, no data are available on the volatilization losses of ammonium N that diffused from the underlying anaerobic soil. Laboratory experiments indicated that very little or no ammonium N was diffused into the overlying waters.¹⁷⁴ However, severe volatilization losses can be expected in certain rice soils, where fertilizer urea N is applied to the floodwater.²¹⁷

XV. RESEARCH NEEDS

It is well established from the reported literature that in flooded soils and sediments having established aerobic and anaerobic soil conditions, simultaneous occurrence of nitrification-denitrification reactions plays a significant role in determining the losses of applied and native soil N. These reactions were also found to be very significant in upland soils which are subjected to alternate draining and flooding. Critical evaluation of the literature presented in this paper suggests several future research needs. Even though these processes are fairly well understood under laboratory conditions, very limited information is available on the extent of these losses under field conditions. Future research should be directed to quantify N losses due to several processes under varying soil and climatic conditions with an objective of increasing efficiency of fertilizer N. Field studies are necessary using isotopic N to determine more precisely the N balance sheets under plant-soil-water systems. The data generated from these studies will be useful to the researchers to manipulate agronomic practices and improve varieties to maximize the yield potential by increasing the efficiency of applied fertilizer N.

Presence of plants may either increase or decrease losses of applied fertilizer N. The rate of N losses can be reduced by plant uptake. Simultaneous occurrence of nitrification-denitrification reactions can take place at the aerobic-anaerobic interface between aerobic root rhizosphere and adjacent anaerobic soil layer. Because of high root density in the soil, the aerobic soil layer around roots could play a significant role in N losses. So far, no data are available on the extent of N losses, through simultaneous occurrence of nitrification-denitrification reactions around the roots and future research should be directed to evaluate this important process to quantify N losses.

In upland soils, alternate drained and flooded environments provide favorable conditions for simultaneous occurrence of nitrification-denitrification reactions. These conditions also exist in the areas with heavy rainfall and soils with poor drainage. Aerobic soil atmosphere favor nitrification process and anaerobic microsites favor denitrification process. These conditions can contribute especially high N losses in the land areas receiving organic wastes (such as animal or municipal origin) and plant residues, where demand for oxygen is very high. Data are very limited on simultaneous occurrence of nitrification-denitrification under these soil conditions, and future research is necessary to quantify the extent of N losses. In the land areas utilized for crop production, simultaneous occurrence of nitrification-denitrification is not beneficial, and research should be directed to develop methods to control N losses under these conditions.

Significance and extent of NH_3 volatilization losses under field conditions need to be evaluated under various climatic conditions. The most important research need is to study volatilization losses by measuring the fluxes of NH_3 from an aquatic system, as related to

the temperature, surface wind velocity, sediment characteristics, alkalinity of the water, and biological activity in the soil-water system.

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