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Nitrification and Denitrification Processes in Rice (Oryza Sativa), with an Emphasis on Reduced Water Irrigation Regimes in USA

Michael T. Aide

Southeast Missouri State University, Cape Girardeau, MO, USA
Email: mtaide@semo.edu

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Abstract

The nitrogen cycle is the basis for understanding nitrogen dynamics in soil fertility and ecosystem health. Nitrification and denitrification are key nitrogen cycle components that influence nitrogen uptake in food crops, thus critical to food security. Rice (*Oryza sativa*) is comparatively unique in that the nitrification-denitrification sequence is a perceived loss of available nitrogen for plant uptake and the production of nitrous oxide (N_2O) has severe implications in climate change. This review focuses on recent research involving nitrification and denitrification, with an emphasis on rice. The review also focuses on the emerging irrigation strategies associated with furrow irrigation and alternating wetting-drying irrigation. With growing global interest in reducing irrigation water application, new research paradigms are emerging to perfect these reduced water applications systems to guarantee food security and farm profitability.

Keywords

Nitrification, Denitrification, Rice Modeling, Climate Change, Furrow Irrigated Rice

1. Introduction

Recent research in reducing water allotments for irrigating rice (*Oryza sativa*) has been published because of water shortages, aquifer overdraft, climate change, food security, environmental stewardship, and production economics [1]-[15]. An emerging rice production practice is furrow irrigation. Furrow irrigation requires graded land with groundwater application provided using a "flexible polypipe" along the upper field border. Bed configurations vary in-row spacing and bed height; however, the raised beds provide furrows that act as watercourses across the field [16]. In the Mid-South USA, the emerging irrigation practice of alternate wetting and drying has not been producer accepted and therefore of alternate wetting and drying has not been extensively investigated.

In the Mid-South USA rice belt, rice is an intensely irrigated crop, with aquifer overdraft an increasing concern [15] [16]. Furrow irrigation has conferred the advantage of water conservation; however, other potential advantages include: 1) Potentially equivalent yields compared to delayed flood; 2) Reduced levee construction given the requirement of graded land; 3) Potentially greater yields from rotation crops given the reduced soil structure slaking observed with delayed flood; 4) Greater use of ground-based equipment than airplane fertilizer and agrichemical applications. Furrow irrigation disadvantages include: 1) Reduced nitrogen use efficiencies; 2) Changes in weed management; 3) Reduced crop insurance options; 4) Necessity for land that is appropriate for land-grading. The objective of this review is to: 1) Discuss the current literature addressing nitrification and denitrification in rice; 2) Discuss emerging nitrogen fertilization practices associated with rice furrow irrigation.

1.1. The Basics of Oxidation-Reduction Processes in Soil

Denitrification is one component of the nitrogen cycle, and its ecosystem importance is associated with limiting excessive nitrate accumulation in the soil. Nitrification and denitrification are oxidation-reduction reactions based on the reactants' and products' free energies of formation [17] [18]. As soil reactions, nitrification and denitrification are critical to the operation of the nitrogen cycle. Half-cell reactions are customarily written as: Ox + ne^- = Red, where Ox refers to the oxidized species, Red refers to the reduced species and n is the number of electrons (e^-) involved.

The Nernst Equation may be written as: $Eh = Eo - (RT/nF)\ln\prod a_i v_i$, where Eo is the standard electromotive force of the cell, R is 8.3145 J·K^{-1}·mol^{-1}, J is energy (Joules), T is temperature in Kelvin (K), F is the Faraday constant (96,485 C·mol^{-1}) and n is the number of electrons transferred. The symbol v_i is the stochiometric coefficient for species i within the reaction, where the stochiometric coefficients v_i are negative for all reactants i and positive for all products i. The symbol a_i is the activity for species i.

Eh is the energy transfer associated with an oxidation-reduction reaction. Frequently *Eh* (the electromotive force, with oxidized and reduced species expressed as activities, and commonly presented as volts) is alternatively expressed as the electron activity (unitless). The electron activity (*pe*) is equated to *Eh*/0.059 [17]. At a given pH and with specified activities of the oxidized and reduced species, the half-cell reactions may be ranked for their reactivity in oxic, suboxic and anoxic regimes (**Table 1**).

Well-aerated soils may have Eh values near 700 mV, with oxygen reduction occurring largely in the 380 to 320 mV range. Nitrate reduction to N_2, NO and

Table 1. Selected denitrification half-cell reactions.

Reaction	logK	*pe* (pH5)	*pe* (pH7)
$\frac{1}{2}N_2O + e^- + H^+ = \frac{1}{2}N_2 + \frac{1}{2}H_2O$	29.8	22.9	20.9
$NO + e^- + H^+ = \frac{1}{2}N_2O + \frac{1}{2}H_2O$	26.8	19.8	17.8
$\frac{1}{2}NO_2^- + e^- + \frac{3}{2}H^+ = \frac{1}{4}N_2O + \frac{3}{4}H_2O$	23.6	15.1	12.1
$\frac{1}{5}NO_3^- + e^- + \frac{6}{5}H^+ = \frac{1}{10}N_2 + \frac{3}{5}H_2O$	21.1	14.3	11.9
$NO_2^- + e^- + 2H^+ = NO + H_2O$	19.8	9.8	5.8
$\frac{1}{4}NO_3^- + e^- + \frac{5}{4}H^+ = \frac{1}{8}N_2O + \frac{5}{8}H_2O$	18.9	12.1	9.6
$\frac{1}{2}NO_3^- + e^- + H^+ = \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	14.1	9.1	7.1
$\frac{1}{4}O_2 + e^- + H^+ = \frac{1}{2}H_2O$	20.8	15.6	13.6
$e^- + H^+ = \frac{1}{2}H_2$	0	−5	−7
$\frac{1}{12}C_6H_{12}O_6 + e^- + H^+ = \frac{1}{4}C_2H_5OH + \frac{1}{4}H_2O$	4.4	0.1	−1.9

Source: [20]. Note: *Pe* values calculated with oxidized and reduced species at 10^{-4} mole L^{-1}, partial pressures for trace gases at 10^{-4} atmospheres, and partial pressures for O_2 at 0.21 and N_2 at 0.71 atmospheres.

N_2O occurs in the suboxic Eh range of 280 to 220 mV range [17]. Similarly, oxides of MnO_2 and Fe_2O_3 are reduced to Mn^{2+} and Fe^{2+} in the 220 to 180 mV and 110 to 80 mV ranges, respectively. Sulfate (SO_4^{2-}) reduction to sulfide (S^{2-}) occurs at −140 to −170 mV anoxic range, whereas CO_2 reduction to methane occurs at −200 to −280 mV anoxic range [17] [18] [19]. Soil reduction typically proceeds in a continuous and frequently over-lapping sequence involving first O_2 depletion, followed by nitrate reduction, then ultimately culminating with methane production. However, soils are heterogenic systems with different oxidation-reduction environments co-existing because of soil texture, water content, pH, and soil structure variations.

The acid-base reaction of ammonium is $NH_4^+ = NH_3 + H^+$ with the Ka = 5.6 × 10^{-10}. Ammonium volatilization increases progressively with increasingly alkaline pH levels [17] [18].

1.2. Mineralization and Immobilization

Mineralization is a general term indicative of the microbial decomposition of soil organic matter and the subsequent production of ammonium (NH_4^+), phosphate ($H_2PO_4^-$) and sulfate (SO_4^{2-}). Immobilization refers to a complex series of biotic and abiotic processes that synthesize humus from particulate soil organic matter and inorganic soil constituents [21]. Soil organic matter may be operationally partitioned as: 1) Particulate matter (plant residues, manure, and animal remains); 2) Living organs (roots) and organisms (microbial, invertebrate and vertebrate populations); 3) Humus (partially decomposed and stabilized organic materials). Properly, mineralization pertains to the microbial assisted decomposition of humus; however, the decomposition of particulate matter also provides ammonium, nitrate, phosphate, and sulfate to the soil's aqueous phase and replenishes the soil's fertility.

Commonly, particulate matter decomposes relatively rapidly in moist (near field capacity), aerated (well-drained and permeable soils), and warm (25˚C - 35˚C) soils. Materials having smaller amounts of N relative to their total carbon content (a high C/N ratio) decompose more slowly because of limitations of nitrogen availability [21]. The C/N ratios for some crops are sweet clover (12), green rye (36), corn residues (60), grain straw (80), oak wood (200) and humus (9 to 12) [21]. Typically soil organic materials having a C/N ratio of 9-15 decompose without removing substantial quantities of easily available nitrogen from the soil environment.

Yang *et al.* [13] investigated factors instrumental in describing the role of soluble organic nitrogen within the nitrogen cycle, with an emphasis on rice soil fertility. Soil microbial biomass carbon and the initial soil organic matter content directly influenced protease and glutamine activities. Soil pH also influenced glutamine activity. Thus, either indirectly or directly, microbial biomass carbon, the initial soil organic matter content, protease and glutamine activities and soil pH influenced soluble organic nitrogen utilization and plant nitrogen uptake. Nitrous oxide may be formed as a product of nitrification, where ammonium oxidation to nitrite and chemical decomposition of hydroxyl amine produces nitrous oxide. Nitrous oxide may also be formed when autotropic ammonia oxidizers convert ammonia to nitrite, followed by nitrite reduction to nitrous oxide and dinitrogen [22].

1.3. Nitrification

Nitrification is a nitrogen pathway involving the microbial mediated conversion of ammonium (NH_4^+) to nitrate (NO_3^-). Ammonium is converted to nitrite (NO_2^-) according to:

$$2NH_4^+ + 3O_2 = 2NO_2^- + 4H^+ + 2H_2O.$$

The aerobic bacteria Nitrosomonas is the primary microorganism responsible for the oxidation of ammonium. The H^+ production contributes to soil acidification. Subsequently Nitrobacter facilitates the kinetically rapid oxidation of nitrite to nitrate:

$$2NO_2^- + O_2 = NO_3^-.$$

The entire process may be completed within three days if the soil moisture is near 60% of field capacity and the soil temperature approaches 30˚C.

Tan *et al.* [23] observed the influence of temperature and soil moisture on overall nitrification and denitrification in a lowland paddy field having an alternate wetting-drying irrigation regime, which was compared with a continuous flood irrigation regime. The grain yield was not significantly different based on the irrigation regime; however, the water productivity was nearly 17% improved with the alternate wetting-drying irrigation regime. Nitrification and denitrification rates were measured at three rice growth stages (early-vegetative, early-tillering and panicle initiation) and four temperature regimes (20˚C, 25˚C, 30˚C and 35˚C) and at three soil depths (cultivated, plow pan and illuvial horizon). Nitrification was greatest in the cultivated horizon at early tillering and increased with increasing soil temperature, whereas denitrification was more prominent at early-tillering, slightly greater in the cultivated and plow pan layer than the illuvial horizon, and slightly increased with increasing soil temperatures. Across all treatments, the rate of nitrification varied from 12.3 to 23.2 $mg \cdot N \cdot m^{-3} \cdot h^{-1}$, whereas the rate of denitrification varied from 3.6 to 5.8 $mg \cdot N \cdot m^{-3} \cdot h^{-1}$.

Lan *et al.* [22] observed soil processes leading to N_2O and NO emissions in two different Chinese soils under different soil moisture contents. Nitrous oxide emissions were greater in clay-textured soil than a silty-textured soil. Nitrification at reduced soil water contents was shown to be the principal source of nitrous oxide emission, with the exception at 90% water holding capacity, where the nitrous oxide emissions were equally attributed to nitrification and denitrification.

Blackburn *et al.* [24] modeled oxygen diffusion through a water layer overlying partitioned layers of a sediment bed to predict nitrification and denitrification among the layers in the sediment bed. Oxygen was consumed by nitrification and decomposition of dissolved organic carbon. The sediment layers representing zones of nitrification overlying zones representing denitrification were closely positioned together, with the underlying denitrification sediment zones supplying ammonium to the overlying nitrification zones via upward diffusion.

1.4. Denitrification

Denitrification is the microbial reduction of nitrate to nitrogen gas (N_2), nitric oxide (NO) or nitrous oxide (N_2O), typically during anoxic soil episodes, a feature that frequently occurs during periods of soil water saturation [25]. Robertson *et al.* [26] demonstrated that denitrification may occur because of aerobic denitrifiers. The process is typically mediated by facultative aerobic bacteria (Pseudomonas, Bacillus and Paracoccus) and autotropic bacteria (Thiobacillus denitrificans and Thiobacillus thioparus) according to half-cell reaction:

$$2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O.$$

Interestingly, denitrification consumes H^+, thus acts to decrease soil acidity.

Denitrification is usually presumed to occur in warm, suboxic to anoxic soil conditions; however, suboxic to anoxic zones may exist within otherwise oxic soil conditions, especially in heavy-textured soils or in the interiors of soil organic matter enriched soil structures [27] [28]. Denitrification is most likely to occur at soil temperatures greater than 4˚C and less than 60˚C. At pH levels greater than pH 6, N_2 is the dominant bi-product, between pH 5.5 and pH 6 the dominant bi-product is N_2O, and at pH levels less than pH 5.5 the dominant product is NO [29].

$$2NO_3^- \xrightarrow{K_1} 2NO_2^- \xrightarrow{K_2} 2NO \xrightarrow{K_3} N_2O \xrightarrow{K_4} N_2,$$

where K_1 is nitrate reductase, K_2 is nitrite reductase, K_3 is nitric oxide reductase, and K_4 is nitrous oxide reductase. Primarily in response to the partial pressure of oxygen (P_{O2}), soil pH, and the substrate C:N ratio, each denitrification enzyme is formed sequentially, causing a time lag between the conversion of nitrate to nitrite, nitrite to nitric oxide, nitric oxide to nitrous oxide, nitrous oxide to dinitrogen. Given that the induced enzymes degrade more slowly than they are synthesized, their continued existence over a short time interval implies that a more rapid sequential conversion of nitrate to dinitrogen may occur if recently preceded by a previous denitrification episode [30].

The availability of a bioavailable carbon source having an appropriate C:N ratio effectively improves the intensity of denitrification [31] [32]. Erler and Eyre [33] documented the maximum rate of denitrification in wetlands was estimated to be 956 ± 187 $\mu mol \cdot m^{-2} \cdot h^{-1}$ and the maximum nitrification rate was 182 ± 28.9 $\mu mol \cdot m^{-2} \cdot h^{-1}$. The release of N_2O from constructed wetlands has been reported to range from −16.7 to 188 mg N_2O $m^{-2} \cdot day^{-1}$ [28]. Smith and Delaune [34] investigated nitrification and denitrification in soil cores with and without rice plants. They documented that the denitrification rate (N_2O + N_2)-N declined with time progression in both the planted and not planted soil cores. The rice planted core denitrification rate after two days was 101 μg (N_2O + N_2)-N $m^{-2} \cdot h^{-1}$, whereas the unplanted rice core denitrification rate after two days was 86 μg (N_2O + N_2)-N $m^{-2} \cdot h^{-1}$. The level of ammonium in the upper 2 cm of soil was 46 μg N g^{-1} for the rice planted core, whereas level of ammonium in the upper 2 cm of soil was 132 μg N g^{-1} for the planted rice core. The authors concluded that the oxidized root rhizosphere did not appreciably influence soil denitrification rates.

Cai *et al.* [35] observed methane and nitrous oxide emissions from rice paddy fields having intermittent flooding and fertilized at three rates with either ammonium sulfate or urea. Ammonium sulfate and, to a smaller extent, urea reduced methane emissions at the higher amendment rates compared to the untreated check. Nitrous oxide rates increased with progressively greater nitrogen fertilization rates, with ammonium sulfate yielding greater N_2O emissions at comparable nitrogen rates. Nitrous oxide emission rates were comparatively small during the continuous flood and increased during the imposition of intermediate flooding, whereas methane emissions were appreciably greater during flood conditions and up to water draining for the imposed intermittent watering.

Leffelaar and Wessel [30], in a compelling manuscript, prepared laboratory-based incubation vessels to document the glucose amended soil's denitrification process. Model development included microbial growth, based on the presence of strict aerobes and denitrifers, where the microbial populations were never limited towards their respective population expansion. Population growth rates were a function of carbon availability and the presence of electron acceptors and were modeled using double monod kinetics. Their model also considered mineralization-immobilization, denitrification, and gaseous diffusion to simulate the nitrate, nitrite, nitrous oxide, and dinitrogen activities. At the beginning of the incubation experiment, the measured nitrate concentration was 325 mg NO_3-N kg^{-1}, whereas at 200 hours the N_2O-N peak was 50 mg N_2O-N kg^{-1} and cumulative dinitrogen emission was 200 mg N_2-N kg^{-1}.

Malique *et al.* [36] conducted a pot experiment to document the denitrification potential of two soils that differed in clay and soil organic matter contents and were subsequently planted to three different grain crops and a fallow (not planted check) as the main treatment and having two different soil moisture contents as a 2nd order treatment. The clay loam soil with a greater soil organic matter content exhibited a greater denitrification rate than the silt loam soil with a smaller soil organic matter content. All three-grain crops exhibited greater denitrification rates than the unplanted treatment. Rye grass (*Lolium multiflorum*) supported greater denitrification rates than barley (*Hordeum vulgare*), which, in turn, supported greater denitrification rates than wheat (*Triticum aestivum*). Denitrification for all crop treatments was optimized 10 days after transplanting, suggesting that root and biomass became more competitive sinks for soil nitrogen at later growth stages, thus reducing the nitrogen supply for enhanced denitrification. Oxygen consumption and root exudates (organic acids or xylose) may have sufficiently altered the rhizosphere, for which the authors suggested is an area of needed research. For each soil, denitrification was greater at the higher water content.

Tropical soils frequency presents variable charge exchange surfaces, rather than permanent charge surfaces, which possibly may be an important influence on the rate of denitrification. Severely weathered soils that exhibit desilicification and relative enrichment of aluminum and iron oxides because of phyllosilicate weathering may have a greater redox potential under comparable moisture contents. Xu *et al.* [37] reviewed the literature on denitrification in tropical and subtropical soil, noting that tropical, and subtropical soils typically have a reduced rate of denitrification than corresponding soils in temperate climates. Organic carbon content and its mineralization rate may be of greater consequence in tropical and subtropical soils than total nitrogen content and the associated C:N ratios. Additional reasons for low denitrification rates in tropical, and subtropical soils include: 1) Larger oxidation capacity; 2) Smaller quantities of organic carbon and nitrogen; 3) Low pH values that are not as favorable for denitrifier growth and expression; 4) Well formed soil structures that support percolation and limit water retention.

1.5. The Soil Processes of Methane (CH_4) Synthesis in Rice Systems

Methane emissions arising from rice production is a global concern, with considerable emphasis focusing on the role of soil texture [38], rice residues [39], water management [1] [35] [40] [41] [42] and cultivar selection [39] [43] [44] [45]. Methane generation requires an absence of oxygen and other electron acceptors, such as nitrates, Fe-oxyhydroxides and sulfates. Flooded soils alter key soil properties, such as gaseous diffusive and convective flux [19] [28] [46] [47]. Tiedje [48] discussed denitrification and the dissimilatory reduction of nitrate to ammonium. The rice plant's root, culm and leaf structures possess aerenchyma tissues having connected pore spaces which facilitate gas exchange and permits methane emission rates that frequently exceed soil diffusion rates [49] [50] [51] [52].

1.6. Mass Balance Approach

A mass balance budget model attempts to quantitatively document input, outputs and changes within the system, the system being small to large land areas [27]. Boyer *et al.* [53] documented N inputs into 16 large watersheds in the northeastern USA. They explored inputs (fertilization, biological nitrogen fixation, and atmospheric deposition), outputs (stream water export, volatilization, and in-stream denitrification) and changes in watershed storage (soils and vegetation) and inferred that denitrification best explained N losses within the watershed.

1.7. Modeling Long-Term N Cycling

Mechanistic models such as CENTURY simulate long-term nitrogen dynamics across landscapes and DAYCENT simulates short-term nitrogen dynamics daily [24] [54]. The denitrification routine predicts N_2O and N_2 emission based on nitrate concentration, labile carbon bioavailability, and competing oxygen availability. The model first approximates the total N emission, then partitions the N emission as N_2O and N_2, noting that as soil becomes more anoxic, the proportion of the nitrogen emission as N_2 increases [55].

1.8. Denitrification and Decomposition to Quantify Nitrous Oxide Emission

The denitrification-decomposition (DNDC) model attempts to quantify N_2O emissions from agricultural soils [46] [56] [57]. The soil biochemistry core is an assembly of 1) Coupled biogeochemical cycles of carbon and nitrogen; 2) Primary drivers (climate, soil properties, vegetation and anthropogenic activity). The model estimates the soil Eh, and dissolved organic carbon. Using the primary drivers, the DNDC model predicts nitrification, denitrification, and fermentation intensity to yield estimates of ammonia, nitric oxide, nitrous oxide, dinitrogen, and methane by kinetically simulating the activity of nitrifiers, denitrifiers and methanogens.

1.9. Agricultural Management of Crop Growth with Nutrient and Carbon Cycling

In the CERES (Crop Environmental Resource Synthesis) corn and wheat model, the simulation of mineralization was partitioned into three carbon fractions: 1) Carbohydrate with an initial decay constant of 0.80; 2) Cellulose with an initial decay constant of 0.05; 3) Lignin with an initial decay constant of 0.0095. The three soil organic matter fractions and their stated quantities employed the Michaelis-Menten equation to predict ammonium availability (μg N g-soil^{-1}) based on temperature, soil water content and the respective carbon fraction's C/N ratios [58]. The rate of nitrification (kg N ha^{-1}·d^{-1}) is simulated based on the potential ammonium concentration, a series of zero to unity indices for oxygen concentration and temperature, coupled with pH and a nitrification capacity index if conditions prior to the time start of the simulation are unfavorable for nitrification.

The corn and wheat crop-soil model CERES supports the simulation of denitrification. Denitrification only occurs when the soil water content is greater than field capacity and the potential rate of denitrification linearly increases up to soil water saturation. The potential denitrification rate (kg N ha^{-1}·d^{-1}) per soil horizon is moderated to estimate the actual denitrification rate (kg N ha^{-1}·d^{-1}) by 1) An empirically-derived temperature factor; 2) The water extractable carbon content (μg-carbon g-soil-1) based on the soil organic matter content; 3) The soil nitrate-N concentration (μg N g-soil^{-1}); 4) A lag-time factor based on the previous short-term weather given the kinetic response involving enzyme activation.

Yang *et al.* [59] employed the HYDRUS-1D model to water and nitrogen in continuously ponded conditions. Nitrogen pathways simulated included 1) Urea hydrolysis; 2) Nitrification; 3) Ammonia volatilization; 4) Leaching; 5) Mineralization; 6) Denitrification. The soil profile contained a plow pan, which moderated downward water percolation. Nitrogen rice plant uptake was primarily ammonium (greater the 95%) and the soil ammonium concentration greatly exceeded the nitrate concentration. Denitrification and volatilization losses were 23% and 14.5% of the total nitrogen consumption, whereas leaching and surface runoff nitrogen losses were 10.3% and 2%, respectively. In a lysimeter project, Jha *et al.* [60] modelled water and nitrogen transport across soil-water and water-atmosphere interfaces. The nitrogen stored in the plant, lost through soil storage, lost to deep percolation, and other losses (including mineralization, denitrification) were approximately 1.6%, 0.2%, 12%, and 86% of the total applied nitrogen, respectively.

The model EPIC (Environmental Policy Integrated Climate) terrestrial ecosystem model simulates the influence of agricultural management on erosion and crop productivity [61]. The major nitrogen cycling processes, that are daily time-step estimated, include mineralization, nitrification, immobilization, ammonia volatilization, denitrification, runoff, and subsurface leaching. Like CERES, EPIC simulates denitrification as a function of nitrate availability, carbon availability, soil temperature and soil water content. The field-scale agricultural management model GLEAMS was developed from both EPIC and CREAMS [62].

Izaurraide *et al.* [63], using EPIC, developed an hourly time-step submodel that considered carbon oxidation to release electrons to satisfy the electron demand of acceptors, such as oxygen, nitrate, nitrite, and nitrous oxide. Spherical diffusion and cylindrical diffusion were employed to transfer oxygen to microbial sites and roots, respectively. Oxygen uptake by microbial populations and roots was conditioned using Michaelis-Menten kinetics. Oxygen, carbon dioxide and N_2O were soil transported using a gas transport equation and buddling equations were used to transport N_2O and N_2 through the liquid phase to the soil-atmosphere interface. The EPIC model appropriately simulated the timing and intensity of N_2O flux and nitrate concentrations post nitrogen fertilization.

2. Rice Production in Water-Reduced Irrigation Regimes

Recently, USA rice producers have employed furrow irrigation on graded land. Furrow irrigated rice occurs when groundwater is pumped and applied at the upper end of land graded fields, resulting in 1) Water conservation; 2) Reduced levee construction; 3) Lower production costs; 4) Smaller rice arsenic concentrations [16] [64] [65].

Consider a rice paddy with 15 cm ponded water. The partial pressure of oxygen (PO_2 = 0.21 atm) permits partial oxygenation of the water layer with a limited oxygen diffusion rate extending into the uppermost soil layer. Abiotic and biotic factors in the paddy water, some of which are temperature dependent, will consume a portion of the paddy water oxygen [25]; however, aquatic plant photosynthesis from algae and vascular aquatic weeds (duck salad (*Heteranthera limosa*)) may oxygen enrich the paddy water. The uppermost layer of soil will likely alternate from suboxic to anoxic soil environments, whereas deeper soil increments will be progressively and continuously become more anoxic. The presence of the rice plant will also encourage suboxic to oxic root rhizosphere intervals because of O_2 transport via the aerenchyma vascular system [50] [52].

In furrow irrigated rice and in alternate wetting and drying rice irrigation systems, with the greater likelihood of suboxic and oxic soil conditions having longer durations, encourage a more robust nitrification-denitrification sequence [12] [23] [32]. The microbial-mediated denitrification process is represented by the half-cell reaction: $2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O$. When the denitrification half-cell is paired with a proper electron acceptor half-cell reaction and in the presence of an appropriate bacterial community and with the application of LeChatelier's principle (the Equilibrium Law) infers than any process that increases the nitrate concentration will likely promote denitrification. Thus, for furrow irrigation and alternating wetting and drying irrigation, the specter of greater near-surface oxygenation and subsequent cycles of nitrification-denitrification supports a reduced nitrogen use efficiency.

In the Mid-South USA rice fertilization is almost exclusively urea (46-0-0) or ammonium sulfate (21-0-0)24S. Urea's conversion to ammonium (NH_4^+) is frequently constrained using urea-impregnated urease inhibitors to support a more controlled ammonium delivery, thus potentially limiting an excessive nitrification-denitrification cycle. During intervals where ammonium exists in a suboxic to oxic soil environment, nitrification will favor the sequential conversion of ammonium to nitrite (NO_2^-) and then to nitrate (NO_3^-). With the cyclic return to increasing anoxic soil conditions with water reapplication, denitrification supports nitrate reduction to either N_2, NO or N_2O.

In the USA mid-South, delayed flood nitrogen fertilization programs typically have a rice variety dependent nitrogen application rate at the 5th leaf stage, followed by an internode elongation application to support grain-fill photosynthesis. Flood imposition occurs immediately after the 5th leaf nitrogen application to inhibit nitrification (**Figure 1**).

Chlapecka *et al.* [7], in Arkansas, compared furrow irrigated and alternated wetting and drying rice systems, demonstrating that the alternate wetting and drying system favored water conservation and given that the yields were comparable, supported a greater water use efficiency. In Missouri, rice furrow-irrigation shows promise in maintaining rice yields; however, substantial issues remain in securing a management consistency involving: 1) Nitrogen fertilization regimes, 2) Weed management programs; 3) Irrigation timing protocols [3] [65] [66]. Nitrogen furrow irrigation management increasingly requires a fresh examination of 1) Nitrogen fertilizer product selection; 2) Timing of application; 3) Precision placement (banding on bed vs broadcast); 4) Rates of application.

In Missouri, Aide *et al.* [67] compared rice arsenic (As) concentrations in furrow and delayed flood irrigation regimes on silt loam and clay textured soils

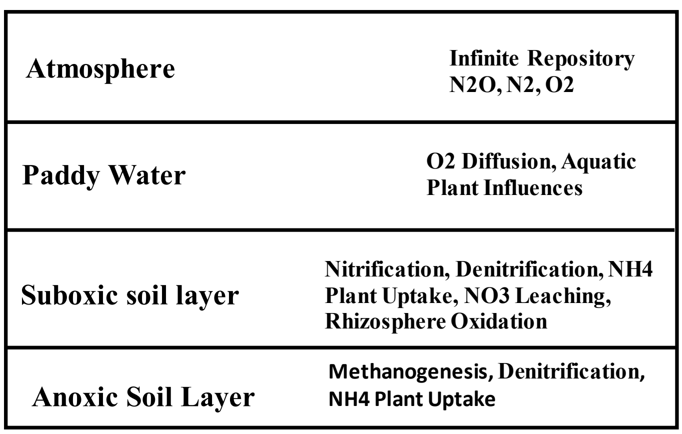

Figure 1. Illustration of nutrient pathways in an idealized Delayed-Flood Irrigation Regime.

for two years of rice production. At harvest, the arsenic concentration in leaf-stem material greatly exceeded brown and polished rice grain, with the furrow irrigated rice seed having arsenic concentrations at or smaller than 0.1 mg As/kg-dry-weight and the delayed flood rice seed having arsenic concentrations ranging from 0.2 to 0.3 mg As/kg.

Aide [3] investigated delayed flood and furrow irrigation on rice yield components across three cultivars in field sized research plots. Each cultivar treatment plot was greater than 100 meters in length at each plot was subdivided into three zones: 1) Zone one at the upper end of the field receiving water directly from side-inlet application; 2) Zone two in the middle of the field; 3) Zone three having tail-water accumulation (frequently ponded). Zone one had the greatest opportunity for water infiltration because of the longer duration of water application, and zone three had the greatest infiltration potential because of ponding. The three cultivars had rice yields of 9300 $kg \cdot ha^{-1}$, 11,950 $kg \cdot ha^{-1}$ and 9230 $kg \cdot ha^{-1}$ for the zone having tailwater accumulation, whereas the three cultivars had rice yields of 7310 $kg \cdot ha^{-1}$, 8010 $kg \cdot ha^{-1}$ and 6300 $hg \cdot ha^{-1}$ for the furrow irrigated subplots. Straw arsenic and seed arsenic concentrations were substantially greater for tailwater accumulation than furrow irrigated (not ponded) subplots. Seed arsenic concentrations were typically less than 0.05 mg As kg^{-1} for the furrow irrigated (not ponded) subplots, whereas seed arsenic concentrations were approximately 0.6 mg As kg^{-1} for the tailwater accumulation subplots across all cultivars.

Aide [65] evaluated six cultivars using similar plot design as used for the Aide [3] trial. Nitrogen mid-tillering rice concentrations were near 4.1% and there were no significant differences by field position (furrow irrigated versus tail water accumulation). At harvest, yields were greater where tailwater accumulation was present than furrow irrigation (no ponding) occurred. The yield differences are related to panicle weight, with higher yields having greater panicle weights. Late-season nitrogen deficiency was inferred to be associated with the furrow irrigated zones because of nitrification-denitrification cycles. Arsenic concentrations were appreciably greater where tailwater accumulation was present.

3. Photosynthesis and Reduced Water Applications

Wu *et al.* [68] performed gas exchange and chlorophyll fluorescence measurements of rice across irrigation regimes: 1) Flooding→midseason drying→flooding; 2) Flooding→midseason drying→saturation; 3) Flooding→rain-fed. Compared to the flooding→midseason drying→flooding regime; the flooding→rain-fed irrigation regime showed a decrease in the net photosynthetic rate. In contrast, the flooding→midseason drying→saturation regimes plants did not exhibit stomatal limitations and had comparable net photosynthetic rates with the flooding→midseason drying→flooding regime. The flooding→midseason drying→saturation regime exhibited 17.2% less irrigation water compared to the flooding→midseason drying→flooding regime and both systems had comparable yields. The results suggested that flooding→midseason drying→saturation regime can be an effective irrigation regime to reduce water application.

In an Arkansas field study, Barnaby *et al.* [69] evaluated seven rice cultivars, having diverse yield potential under water stress, using four continuous irrigation regimes varying from saturation to wilting point. Physiological and leaf metabolic responses were measured at the vegetative-reproductive growth transition. With increasing water stress, rice cultivars that did not exhibit significant yield losses accumulated fructose, glucose, and myo-inositol, even though a moderate reduction in stomatal conductance was observed. In contrast, cultivars that had significant yield loss showed lower accumulation of fructose, glucose, and myo-inositol. Thus, the existence of genetic variation in yield reflects physiological and biochemical responses to water stress.

In China, He *et al.* [70] investigated photosynthetic performance of rice during grain fill with the imposition of three water-reduced irrigation regimes: 1) Furrow irrigation with plastic mulch; 2) Furrow irrigation without plastic mulch; 3) Drip irrigation with plastic mulch. All three reduced water irrigation regimes were compared to conventional flooding. The three reduced water irrigation regimes exhibited reduced net photosynthetic rates, lower maximum quantum yield and lower effective quantum yield for pigment system II. The reduced photosynthetic responses were attributed to reduced nitrogen efficiency, suggesting the nitrogen use efficiency was critical to maintaining photosynthetic efficiency. In Australia, Silwal *et al.* [71] employed 13 aerobic rice cultivars with and without irrigation. Irrigation was associated with greater leaf area index, spikelet fertility, water use efficiency at anthesis. Interestingly, irrigation supported greater spikelets per panicle and effective tillers; however, kernel weight was not significantly different.

4. Research Needs

Key research needs are as follows to definitively support furrow irrigated rice across the Mid-South USA:

1) Greater understanding of nitrification and denitrification to improve nitrogen use efficiency;

2) Quantitative analysis of water used in furrow irrigation, including trials involving frequency of application and frequency of application with different bed widths;

3) Integration of item (1) and (2) to develop a comprehensive system of irrigation.

Secondary items for expanded research include:

1) Varietal selection (including Blast (*Magnaporthe grisea* and *Magnaporthe oryzae*, within the same M. grisea complex);

2) Assessment of irrigation on rice kernel quality components (milling, chalk, whiteness and others);

3) Yield;

4) Weed management;
5) Plant physiology, including photosynthesis and others;
6) Comparison of the performance of hybrid and non-hybrid varieties.

5. Conclusion

Rice research is increasingly focused on the nitrification-denitrification process because of emerging irrigation regimes that reduce water applications. The nitrification-denitrification process is critical to understanding nitrogen use efficiency, changing nitrogen fertilization practices, methane and nitrous oxide emissions and water quality.

Conflicts of Interest

The author has no conflict of interest.

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