EFFECT OF DIFFERENT METHODS OF PLACEMENT OF ORGANIC MATERIALS ON LEACHING LOSSES OF NITROGEN FROM INUNDATED SOILS

> Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY WORAPOTE RUMPANININ 1973

ABSTRACT

EFFECT OF DIFFERENT METHODS OF PLACEMENT OF ORGANIC MATERIALS ON LEACHING LOSSES OF NITROGEN FROM INUNDATED SOILS

Ву

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The objective of this experiment was to evaluate sources of N and methods of organic matter placement in terms of nitrogen mobility in water percolating through flooded Two nitrogen sources, urea and finely ground alfalfa soils. (Medicago sativa L.), were used. Chopped oat straw (Avena sativa L.) was used as a source of organic matter and reducing Spinks parent material in small lysimeter columns, power. 10.2 cm in diameter and 1.5 meters long were set up in the greenhouse. Two sources of nitrogen were incorporated into the plow layer at 1/3 atm moisture condition, and allowed to react with the soil environment for a period of 4 weeks, to simulate the dry season under a monsoon climate. At the end of the dry period, straw treatments were imposed, in quadruplicate, on columns previously amended with urea or alfalfa. The four treatments included (1) a control, (2) straw applied on surface, (3) straw mixed through the depth of a conventional plow layer (17 cm), and (4) straw bedded under the plow layer.

After additions of straw, the columns were saturated from the bottom, then flooded to a depth of 20 cm. Water was allowed to percolate at the rate of 6.5 cm per day, but a 20 cm head was maintained for 14 days.

Nitrogen appeared in drainage as NO_3^- , NO_2^- , and NH_4^+ . Over 21-day percolation period, total N from control columns was equivalent to 86% of N input as urea and 35% of N input as alfalfa. Maximum concentration occurred on the seventh day. Total N from straw bedded was 59% and 13% of N input as urea and alfalfa columns, respectively. The corresponding values with straw mixed was 70% of urea-N and 16% of N as alfalfa. Straw on surface was 81% of urea-N and 31% of N as alfalfa.

The greater movement of N in drainage from urea is ascribed to its essentially complete mineralization and nitrification during the dry period. The greater effectiveness of mixed or bedded straw in removing N from percolating water is ascribed to assimilation and/or denitrification of N; in these placements the straw had a longer period of contact with soluble N in percolating water than in the surface placement.

Algae grew profusely in surface floodwaters. There may have been additions of N by N fixing organisms, giving rise to positive N balances equivalent to 44 kg N per ha for the urea control and 58 kg N per ha for alfalfa. It appeared that similar inputs of N may have resulted from biological

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fixation in columns which received straw, but that denitrification was enhanced in the presence of straw. The largest apparent losses due to denitrification occurred with the bedded straw placement in urea columns and the mixed placement in alfalfa columns.

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TABLE OF SYMBOLS

Symbol

Description

- A = Alfalfa, 1.58% N, used in the same manner and at the same rate of N application as for urea.
- S = Surface, straw 0.755% N, 8.97 metric tons/ha, applied on surface just before flooding.
- M = Mixed, straw mixed uniformly in plow layer (17 cm) at the same rate as surface just before flooding.
- B = Bedded, straw bedded under plow layer (17 cm deep) just before flooding, the same rate of surface application.
- C = Control, the control was consisted of N source but no straw treatment.

INTRODUCTION

During the monsoon season in the tropics, surplus rainfall causes flooding over the rice land for several months. Soil moisture decreases gradually after the rainy season, the soils dry out after the cool season. The fluctuation of the water-table can cause severe losses of nitrogen from soil by leaching and other processes. Large fluctuations in the moisture content of a soil have pronounced effect on the stability of nitrogen. Nitrate is a mobile ion in soil and is also unstable under reducing conditions associated with flooding.

Buckman <u>et al</u>. (23) stated that there is only one practical method for improving the structure of coarsetextured soils so as to maintain moisture holding capacity, increase retention of plant nutrients, etc.; this is to add organic matter to the soils. In northeastern Thailand soils are mostly coarse texture and low in fertility, consequently, there is low rice production. Nitrogen is an important element for plant growth and increase in yield production. Crop residue application can improve soil fertility and conserve nitrogen fertilizer for the crop.

When straw is added to the soil, the changes require 1 to 2 months in the field condition. Initially, carbon dioxide

in the soil solution and the soil air increases while oxygen decreases. Kohnke (51) stated that it has been found that surface applications of organic residues results in a lower oxygen content in soil than any other method of application. It was found that during the decomposition of straw, previously immobilized fertilizer N¹⁵ becomes available for plants. Net release of N is greater when decomposition occurs under waterlogged conditions than under well-aerated conditions (11,41). Yoshida and Ancajas (102) reported that atmospheric nitrogen is fixed, in the root zone of rice plants, by bacteria rather than root tissues. Nitrogen is inefficiently utilized in tropical paddy systems, due to the losses by leaching and denitrification.

The objective in the present study was to evaluate a fertilizer source of N (urea) and legume source (alfalfa), and different methods of returning cereal straw in relation to losses of N from flooded soil. It appears likely that losses are greater because of the general practice of farmers in the monsoon area to burn crop residues in the field or as fuel (10). Also this study is to observe the changes of organic material in soil. It is attempted to conserve nitrogen for rice production. It is hopeful that the preliminary findings reported here can be the basis for further research in rice-producing area of the Mekong River basin.

LITERATURE REVIEW

The Fate of Nitrogen in Soils

The fate of nitrogen in soils and nitrogen fertilizers applied to soils has been investigated by many workers. Lvsimeters have been used most frequently in such studies. Recoverable nitrogen reported most often has included only nitrogen found in harvested plants and in soils. The unrecoverable nitrogen has included gaseous loss and losses by In two comprehensive reviews, Allison (5,6) conleaching. cluded that nitrogen loss mechanisms include physical processes, chemical reactions in soil, and biological activities of microorganisms. He drew the conclusion that the chief channel of loss in normal agricultural practice is probably leaching, but data from most experiments indicate that volatile loss occurs, also.

Nitrogen losses depend on many factors. These were reviewed by Fried and Broeshart (36). They include amount of rainfall, crop management, and sources of nitrogen fertilizers. In fallow soil, nitrate and ammonia fertilizer lost larger amounts of nitrogen than the other N sources. Overrein (66) measured nitrogen losses through leaching and volatilization in lysimeters after the addition of different nitrogen carriers. He summarized his result by saying that total leaching losses

of nitrogen increased in a linear manner with increasing rate of fertilizer application, and the difference in leachability of fertilizer nitrogen and soil nitrogen was highly significant regardless of fertilizer application rate. The losses in gaseous form were 0.2, 0.6, 3.5, and 2.3 percent for the 10, 25, 50, and 100 gm urea-N per square meter application respectively.

Burning, as a cultural practice on farm land, can lead to the loss of gaseous nitrogen. DeBell and Ralston (29) reported that only minor amounts of nitrogen were released by forest fire in forms which could be returned readily to the soil for tree growth, and most nitrogen is volatilized as nitrogen gasses. Shantz (74), and Sweeney (84) pointed out that fire increases the amount of certain plant nutrients, but the increase, notably in the case of nitrate nitrogen may be only temporary because soluble compounds are subject to rapid leaching.

Conservation of Nitrogen

The chemical distribution of nitrogen in soils was investigated by Cheng and Kurtz (26). Over 90 percent of added nitrogen in soils was found in the hydrolytic products of soil organic matter, mainly as amino acid nitrogen, amino sugar nitrogen, and hydrolyzable ammonia. When fertilizers are added to soils, some of the nitrogen is immobilized by microorganisms and thereby becomes a part of the soil organic

matter. Huber and co-workers (43) found that "N-serve" applied with nitrogen fertilizer was able to deter nitrogen loss and increase yield of wheat. Donahue (31) reviewed the post works from Ohio in which superphosphate was added to balance plant nutrient content of animal manures and to absorb and conserve ammonia. When superphosphate was used properly and in adequate quantities, loss of ammonia by volatization might be reduced to as little as 3 percent.

Nyborg (65) found that organic soil fixed about 20 times the quantity of gaseous ammonia that was fixed in nonexchangeable forms by mineral soil. The presence of oxygen during treatment with gaseous ammonia approximately doubled fixation in each of several soils. The fixation of NH_3 in this study was due to strictly chemical reactions and not to assimilation by microorganisms during decomposition of organic matter (4).

The Effect of Rewetting and Drying

Agarwal and co-workers (3) studied soil nitrogen and carbon mineralization as affected by drying and rewetting. They observed that the temperature of drying as well as drying-rewetting cycles enhanced nitrogen and carbon mineralization. Greater nitrogen release was found when incubation after drying was included than when omitted. Patrick and Wyatt (67) studied nitrogen loss as a result of alternate submergence and drying. They found that the loss could be 15 to 20 percent of the total soil nitrogen. Most of the losses

occurred during the first three cycles of submergence and dry-For soils cropped to lowland rice, nitrogen loss after ing. waterlogging is an important problem because the soil may be flooded and drained several times during the season. They found that adding ground rice straw to the soil when it has been through several cycles of wetting and drying result in it's being able to again reduce nitrate nitrogen rapidly. They suggest that the fewer times soil is flooded and drained during the growing season, the less will be this loss of nitrogen. However, the nitrogen loss can occur in normally welldrained soils that are temporarily water-logged as a result of excess rain or impeded drainage. The results of this study show that the system of flooding and drying rice soils one to three times during the season is very wasteful of both native soil nitrogen and applied nitrogen. When the soil is aerated by draining the flood from the field, nitrate is formed from both mineralized soil organic nitrogen and ammonium fertilizers. When the field is subsequently flooded, this nitrate nitrogen is rapidly lost.

The Effect of Physical Properties of Soils

The relationships of texture and moisture phenomena in soils are frequently linear. Shaw (75) reported that the pattern of downward movement of nitrate in coarse soil is different from that in clay soil but that large amounts of rain are required to remove nitrate completely from either

coarse or fine soil. In laboratory experiments, Webster and Gasser (94) found that coarse soil lost nitrate more quickly than fine soil. The nitrate was first lost from the surface of the structural units and later from the soil mass as a whole.

Wilson (101) found a relatively lower recovery of incorporated green manure nitrogen in drainage from a fine soil than from a high organic peat. He presumed that the fine textured soil exerted a more effective protective action on the incorporated green manure, so that net mineralization of nitrogen did not proceed as far as in the peat soil.

Bates and Tisdale (12) studied the movement of nitrate nitrogen through columns of coarse-textured soil materials. They found that nitrate movement depended upon soil porosity and the amount of water passing through the soil column. They emphasized that the greater amount of small pore space in finetextured soils would have limited downward movement of nitrate because the greater amount of water held from the previous leaching treatment would have to be displaced. However, Smith (77) stated that nitrate which is leached from upper soil layers is returned by the upward movement of soil water through systems of small pores to replace that lost from the surface by evaporation and that the tension gradients and continuous water films necessary for upward movement are better maintained in fine-textured than in coarse-textured soils. Nitrate moving downward after leaching rains was often retained in subsoil layers.

Similar work was done by Boswell and Anderson (15). They found that, after 27 inches of rainfall during 20 weeks, applied nitrogen was retained in the top 2 feet of a sandy clay loam soil and a loamy sand soil. The mean movement of mineral N in both soils was related to the accumulated rainfall.

Carter and Allison (25) reported that gaseous losses of nitrogen from two silt loams were much smaller than from a sandy loam. Miller and Johnson (61) were interested in the processes of nitrification and mineralization of nitrogen as influenced by moisture tension. They observed that nitrification occurred in range of 0.5 to 0.15 bars tension and could proceed at tensions above 15 bars but at a very slow rate. Ammonification took place at a faster rate at both high and low tensions. Smith and Cook (76), and Stewart and Eck (82) studied the influence of soil moisture, aeration, and compaction on nitrate movement into soil. They reported that nitrate moved downward to greater depth when soils were at a higher moisture content, but nitrate accumulations were found at 1.5 inches when soil was at 8 to 15 atmospheres tension. Also Voigt and Steucek (88) reported a strong correlation between soil moisture content and nitrogen concentration.

Burns and Dean (24) studied the movement of water and nitrate around bands of sodium nitrate in soils and in glass beads. Shields were variously placed to alter the movement

of water around the fertilizer bands under leaching and static moisture conditions. They observed that excess sodium nitrate solution could literally drop out of the band under the force of gravity and then, being dissolved, it was moved through the system by leaching.

In tropical areas, high temperatures and seasonal fluctuations of moisture have a great deal to do with nitrogen distribution in soil. This subject was of particular interest to Wetselaar (95,96,97). In these series of studies, he reported that during the dry season, the peak nitrate accumulation was at 3/4 to 1 inch depth instead of at the surface. This accumulation was explained in terms of capillary movement upwards to the point where water films were no longer thick enough or continuous enough to support mass flow. During the rainy season nitrate was carried down to accumulate in subsoil. The rate of downward movement of nitrate accompanying rainfall was closely related to the amount of rainfall.

Willis and Green (100) worked on the movement of nitrogen in flooded soil planted to rice. They found that ammonium nitrogen accumulated in the flooded water on the planted soils during the first 2 weeks of flooding and then decreased during the next 3 weeks which coincided with the time of most vigorous growth of plants. They observed that the decrease in ammonium concentration did not occur on the unplanted soils. They noted a gain (fixation) of nitrogen which was equivalent

or greater than crop utilization. A large loss of nitrogen occurred in the absence of rice plants.

Wagner (92) estimated the leachable nitrate nitrogen movement in Putnam silt loam soil under sudan grass by porous ceramic cup assemblies which were installed along with access tubes to accommodate use of the neutron moisture meter. He reported that one month after treatment, nitrate was concentrated at a depth 1 foot in the profile, but there was a larger amount of nitrate in the fertilized plot than in the control at the depth of 2 and 3 feet.

Foth and Turk (35) summarized much past work showing that conservation practices can greatly reduce loss of nutrients by percolating water. White and Pesek (98) reported that residual unused nitrogen applied to corn was found in the form of nitrate within 6 to 12 inches depth at the end of the season. They noted that this nitrogen would be accessible to a vigorously growing fall cover crop.

A study of water relations to nitrate leaching losses in citrus watersheds has been conducted by Bingham, Davis, and Shade (14). They reported that about 45 percent of the nitrogen applied each year as fertilizer was lost. Linville and Smith (52), Stevenson (80), and Smith (77) studied soil nitrate distribution in profile. They stated that nitrogen accumulation and losses by either leaching or denitrification or both were related to soil texture. Silt loam soil had deeper accumulations of nitrate from applied N fertilizers than silty clay

loam. Nitrogen fertilizer additions which exceed nitrogen removal in crops increase the potential for downward movement of nitrate.

MacIntire and his colleagues (55) recovered annually nitrogen in rainwater leaching through a red clay subsoil over a 12-year period of a lysimeter study in which nitrogen was applied as ammonium chloride, phosphate, and sulfate. They reported that leaching of NH_4^+ was nil to meager; nitrites appeared in the leachings throughout the first 3 years. Largest outgo of engendered NO_2 occurred in the second, third, and fourth years, in descending order, and respective totals for the initial 6 years were virtually the same as the totals for the 12 years. The applied NH_{4}^{+} was recovered chiefly as engendered NO_3^- , but substantial fractions were lost through reduction processes and/or fixation. They stated that heavy applications of nitrogen as ammonium chloride, phosphate, or sulfate to a fine soil, in fallow, will not be recovered completely in the rainwater leachings that pass through clay subsoil strata.

Lal and Taylor (51), Moe and co-workers (62), White, <u>et al</u>. (99) reported the effect of surface runoff on nutrient loss. White and co-workers found that the loss of fertilizer nitrogen in surface runoff water was small. They stated that one might expect losses to be most severe when nitrogen fertilizers are applied to very wet soils or to fallow soils having a

surface seal. The actual measured losses of mineral nitrogen in their experiment were low, even at the intensive rate of rainfall studied. The greatest loss amounted to only 15 percent of the applied fertilizer nitrogen after 5 inches rainfall. They recognized that with increased usage of nitrogen fertilizer it is quite possible that the nitrogen content of surface runoff water could become a significant contributing factor to nitrate pollution of surface water supplies.

Stewart and co-workers (83) reported that in Colorado the average total nitrate nitrogen content in 20 feet of soil under corrals was 1,436 pounds per acre. However, Bower and Wilcox (16) noted that over a 30 year period of studying nitrate content of the upper Rio Grande, the application of nitrogen fertilizer to three adjacent irrigated areas had increased from a very low to a high level. Over the same time period, the overall NO_3^-N concentration of the river had not increased, indicating no significant stream pollution by $NO_3^- - N$ from applied nitrogen fertilizer.

Reaction in Soil and Gaseous Losses

Nitrogen losses as gas have been extensively investigated by many workers. Carter and Allison (25) studied the effect of rate of application of ammonium sulfate on gaseous losses of nitrogen. They found that gaseous losses increased with increase in ammonium sulfate additions, and were greater on limed than on unlimed soils. Temperature increased rates of reaction in soil, therefore increasing nitrogen losses (Ayres and Doil, 1963).

The mechanisms involved in gaseous losses include volatilization of NH3, soil reactions of nitrous acid and/or nitrite, burning, and microbial denitrification (8,29,32,39,56, The processes of nitrification followed by denitrifica-70). tion are known to lead to gaseous losses. The loss due to denitrification can occur in the form of N₂ or N₂O, possibly also as NO or NO2. Burning can release nitrogen gas to the atmosphere. Volk (89,90,91) found that, with surface application of 100 lbs of urea-N (pelleted urea) per acre on grass sod, gaseous loss of ammonia during 6 to 8 days was 20.6 percent, comparable to the range from 17 to 59% when urea was applied to moist bare acid soils. The loss was greater (29.3%) when crystal urea was applied. The losses averaged 29% for unlimed turf and 36% for limed turf. Losses from urea surface applied to bare sandy soil averaged 25% in 7 days. He also found 4% of gaseous loss of ammonia from prilled urea when applied to undisturbed dry organic residue over moist soil under slash pine. Harding and co-workers (40) found that volatile loss of ammonia from surface broadcast urea was 13.2 percent, during a 2 week experiment period from a slightly calcareous Sorrento silt loam. Macrae and Ancajas (56) reported that increased application of both ammonium sulfate and urea resulted in increased losses of ammonia through volatiliza-Incorporation of nitrogen into mud of the flooded soils tion. significantly decreased losses due to volatilization. They observed that soil reaction was closely related to the magnitude

of losses due to volatilization. The losses of nitrogen from urea-treated, flooded soil was greater than from ammonium sulfate-treated. Ewing and Bauer (33) developed an equation to predict nitrogen losses from soil due to the reaction of ammonium ions with nitrous acid. The prediction is related inversely to soil pH and soil moisture, and directly to the concentration of ions.

McLaren (58,59) stated that nitrification leads to growth of nitrifiers, but that NO_2 and/or NO_3 are also produced by both maintenance and waste metabolism. In established populations approaching steady state conditions, growth and waste metabolism are small compared to maintenance metabolism. He studied the rate of reaction in soil columns with a constant rate of entry of NH_4^+ solution and found that the rate of change of ammonium to nitrate by nitrifiers conformed essentially with a steady state. His equations take into account growth of nitrifying organisms, but it was assumed that diffusion and ion exchange within the soil and fixation of nutrients by the nitrifiers were of secondary importance.

Cropped, Uncropped, and Crop Residue

The idea of bringing organic residues back to the land has been based in the past primarily on the objective of improving soil physical properties. Goodding and McCalla (39) reported that there was little ammonia nitrogen lost from straw or cornstalks left on the surface under constant

moisture and temperature conditions. From this result, it was proposed that crop residue can be used on the surface of the soil, not only for increasing water intake and controlling water and wind erosion, but also to reduce loss of nitrogen as ammonia during the decay of residue in mulch application.

The composition of leachate through cropped and uncropped soils in lysimeters was measured by Low and Armitage (53). They found that nitrogen was drained from soil under actively growing clover, with and without removal of clover, in quantities about four times as great as from soil under actively growing grass sward. Benson and Barnette (13) found that NH_4CO_3 was retained very efficiently by soil until nitrification began; compared to urea, it was leached to the extent of 35% and 16% after 1 and 4 day incubation periods, respectively.

Brown and Dickey (22) studied the disappearance by decomposition of wheat straw under simulated field conditions. They discovered that buried straw was lost in distinctly greater amounts than straw on the soil surface. Compared to the original straw, both nitrogen and phosphorus percentages increased as much as sixfold in the burried samples during decomposition. Keeney and Bremner (46) reported that the average percent loss of total nitrogen on cultivation, as compared with virgin uncultivated soils was 36.2%, but the percentage in different nitrogen fractions varied.

van Schreven (71,72,73) has done a series of researches on transformations of nitrogen and organic residue, and on leaching losses of nitrogen. He reported that there was a certain correlation between the C:N ratio of plant material added to the soil and the level of nitrogen mineralization. Additions of plant residues and increases in temperature result in increased microorganism activities, thus in greater total amounts of nitrogen being released. The mineralization of nitrogen from organic materials is influenced by nitrogen content, C:N ratio, amount of material, and whether the organic material is fresh or dried. The fresh material mineralized faster and to a great extent than dried chopped or dried ground materials, but the fresh chopped material had a C:N ratio less than chopped dried material. He also studied the leaching losses of nitrogen, and found that the net annual losses of nitrogen in discharge water ranged from 18.9 to 33.2 kg-N per ha for areas drained by a number of pumping stations in Eastern Flevoland.

Broadbent (20) found that weight losses of organic matter during decomposition were 44 percent with no nitrogen added, and 40 percent with nitrogen added, as an average for 27 days incubation. Stewart and co-workers (81) found that during the decomposition of straw, previously immobilized fertilizer N¹⁵ becomes available for plants.

Relation of ODR, and REDOX Potential to Nitrogen Transformation

Nitrogen transformations in soil, as related to oxygen diffusion rate, were investigated by Brandt and coworkers (17). They found that oxygen diffusion measurements reflected significant fluctuation in metabolic demand for molecular oxygen and paralelled changes in concentration of NH_4^+ and NO_3^- . Maximum rates of NH_4^+ oxidation were directly related to the general level of oxygen availability as estimated grossly by the platinum electrode. They stated that enzymatic and chemical losses of nitrogen were undoubtedly influenced by pH changes associated with levels of oxygen supply.

Meek and co-workers (60) studied the relation of dissolved oxygen, soluble carbon, and redox potential to the movement of nitrate in soil columns and into submerged tile lines. They reported that nitrate accumulated at the 160 cm depth, but disappeared or very small amounts were found at 180 to 240 cm. They stated that disappearance of nitrate was associated with decreases in redox potential, oxygen content of the soil solution and oxygen levels in the soil atmosphere, and with increases in soluble iron and manganese.

Time as a Factor for Fertilizer Application

Season of nitrogen application is one of the factors that influences loss of nitrogen fertilizer. This has been investigated by several workers, Gasser (37,38), Moore (63), Nelson and Uhland (64). Gasser found that ammonium nitrogen

applied in October was lost from surface soil during the winter. He concluded that ammonium was nitrified quickly after application and that winter rainfall leached nitrate to below 36 inches. Moore summarized his work to the effect that appreciable movement of fall applied nitrate nitrogen was noted. Consequently, in an exceptionally wet fall and/or spring there may be some danger of loss from fall applied nitrogen.

Certain factors affecting fall application of fertilizers may be more important in certain climatic, topographic and soil situations than others. That was the statement of Nelson and Uhland. They explained that possibilities for leaching losses from fall applied fertilizers depend on percolation of mater, and relate to conversion of ammonium nitrogen in fertilizer to leachable nitrate form.

Effect of Flooding

The result of alternate submergence and drying in studies of Patrick and Wyatt (67) was the loss of 15 to 20% of the total soil nitrogen. They observed that most of the losses occurred during the first three cycles of submergence and drying. The soil oxidation-reduction potential decreased rapidly after initial submergence. More organic nitrogen was mineralized as NH_3 under conditions of continuous submergence than was mineralized as NO_3^- under conditions of optimum moisture. Srisen (79) observed that, as a result

of flooding, soil pH was increased about one pH unit, except in soil where initial pH was lower than 5.30.

Miller and Johnson (61) found that carbon dioxide production during the first day of incubation increased from a minimum in air-dry soil to a maximum at a tension of from 0.15 to 0.5 bars, and then decreased with further increases in soil moisture. There was little difference in the CO₂ evolved in the tension range from zero to 0.15 bars.

Maximum nitrification occurred in the tension range of 0.15 to 0.5 bars, and there was a peak in both nitrogen mineralized and nitrogen nitrified in this tension range, followed by a decline in NH_4^+ -N and No_3^- -N as tension was reduced further to about zero (4). Cho and Ponnamperuma (27) stated that the rate of denitrification is virtually independent of temperature in the range of 15 to 60 C.

Delaune and Patrick (30) studied the conversion of urea to ammonia in waterlogged soils. They reported that urea hydrolysis to ammonia proceeded at about the same rate in waterlogged soils and in soils kept at 1/3 bar moisture. It took place at an initial rate of about 8 to 12 ppm per hour and began to level off after about 24 hours. Maximum conversion of urea occurred at about pH 8 under both moisture conditions. Volatilization loss of ammonia hydrolyzed from surface applied urea was slightly greater at 1/3 bar than under waterlogged conditions. For topdressed urea in flooded

soil, urea was converted much more rapidly in the surface layer of soil than in the flood water. This could agree with an observation of Magdoff and Bouldin (57): they state that flooded soils usually consist of a surface aerobic phase a few millimeters thick underlain by an anaerobic phase. Aerobic microbial activities still proceed in the aerobic-anaerobic inter-facial area in flooded soils.

Jordan and co-workers (45) found that when soils were submerged, NO_3^-N was reduced to NO_2^-N , then assimulated or accumulated by bacteria. Adriano, <u>et al.</u> (2) found that nitrate concentration in the unsaturated zone (several feet below the surface) increased with increase in N application rate but was inversely related to the leaching volume. Herron <u>et al.</u> (42) studied the leachable nitrogen in silty soils. They reported that only with soils very high in nitrogen or with high application of fertilizer nitrogen was there any indication of appreciable leaching of NO_3^-N below 180 cm in the profile.

Gain and Loss of Nitrogen

Gain of nitrogen in a natural system is due to a fixation process usually carried out by microorganisms. Loss of nitrogen from the system occurs by denitrification, volatilization, and/or leaching. Magdoff and Bouldin (57) believe that fixation of nitrogen by aerobic microbes occurs in the aerobicanaerobic interfacial area in flooded soils. Kobayashi <u>et al</u>.

(48,49) studied N fixation by photosynthetic bacteria in wet and submerged soil. They found that nitrogen was fixed in quantities up to 64.1 percent of that initially present in the system after a 60-day incubation of submerged soil in the light, and over 100 percent after a 105-day incubation. They concluded that in cultivated soils under submerged condition, like in a paddy field, the fixation of nitrogen will increase the soil fertility.

Jensen (44) found that in sand soil with 1.5% oat straw, nitrogen gain in the system was 16, 73, and 93 ppm, after 28, 150, and 250 days of incubation, respectively. Pratt and co-workers (68) conducted a study over a 5-year period with cereal straw treatments. They found that, with no calcium nitrate added, there was a nitrogen gain of 1.2 percent and a gain of 0.4 percent with a 100 lb N per acre addition from calcium nitrate. There was an average net loss of 1.9 percent when calcium nitrate was added at 200 lb N per acre. Rinaudo and co-workers (69) reported that the rate of nitrogen fixation due to bacterial activity in paddy soil was 1 to 3 μg N per gram soil per day. Nitrogen fixation by bluegreen algae in a rice field, depending on species of algae, ranged from 1.01 to 5.2 mg N per 100 ml of surface flood water over a period of 2 months (Watanabe and Yamamoto, 1971). Abd-El-Malek (1) observed that free-living bacteria could fix nitrogen in sandy soil plus 1% maize stalk to the extent of only 10 ppm N when moisture content was 100 percent. Fogg

(34) found that rate of nitrogen fixation in temperate zone lakes, in situ, in the light, was 0.096 to 3.5% of total organic-N content of water per day.

Broadbent and Clark (21) stated that the annual nitrogen deficit in soils averages 15 percent; presumably, volatile losses of nitrogen are involved. They suggested that, in paddy or rice soils, the appropriate environmental conditions for denitrification do exist. Nitrate fertilizers are not used on such soils and management practices include precautions to minimize nitrification of ammoniacal fertilizers applied before flooding.

MATERIALS AND EXPERIMENTAL METHODS

Greenhouse Lysimeter Experiment

The experiment was conducted in the greenhouse in lysimeter columns constructed of polyvinyl chloride (PVC) pipe, 10.2 cm in diameter and 150 cm long. Each length of PVC pipe was glued firmly to an acrylic plastic square, using Epoxy cement. A 1 cm hole was drilled near the bottom of the pipe for connecting a 1.5 m length of tygon tubing for use in controlling the water level in the lysimeter column and for daily removals of water during the percolation period.

The parent material of a Spinks series (Psamentic Hapludalf) was used as the soil medium. The soil was air dried and screened through a 1 mm sieve before dispensing in the 32 columns used for the experiment. Important soil properties are given in Table 1.

Soil was first added to the columns to a depth of 113 cm, saturated with water from the bottom for several hours, then allowed to drain. This procedure was repeated on three consecutive days to settle the soil uniformly and to minimize entrapment of air within the soil column. After this settling procedure, the soil in parallel test columns had a bulk density (oven-dry) of 1.33 g/cc.

columns.				
Bulk density	1.33	g/	/cc	
Texture*				
Sand 1.0 - 0.5 mm 0.5 - 0.25 mm 0.25 - 0.10 mm 0.10 - 0.05 mm	8.3 2.0 78.0 9.0	00 00 00 00		
Silt (0.002 to 0.05 mm)	1.6	୫		
Clay (<0.002 mm)	1.1	€		
Water holding capacity (1/3 bar tension)	5.7	8		
Saturation water content	24	ð	by	weight
Saturation water content	40	g	by	volume
Nitrate-nitrogen	0.01	5	ppı	n
Kjeldahl-N	14.9		ppr	n
Total C†	1.47	℅		
pH§	7.9			
Available P (Bray P _l)	8.5		ppı	n
Exchangeable ** K	30		ppı	n
Exchangeable Ca	1570		ppı	n
Exchangeable Mg	31		ppı	n

TABLE 1.--Characteristics of Spinks parent material used as the soil medium in lysimeter columns.

*Mechanical analysis by hydrometer method, sieving.

†Total C by Leco carbon analyser.

\$pH by glass electrode in 1:1 soil/water slurry.

**NH4OAc-exchangeable; K by flame photometer; Ca and Mg by atomic absorption.
On the basis of this bulk density, the N sources in Table 2 (urea or alfalfa) were mixed with an additional quantity of soil calculated, for each column, to give a surface "plow layer" 17 cm thick. The alfalfa (<u>Medicago sativa L</u>.) was ground to pass a No. 18 (1 mm) sieve and was found by Kjeldahl analysis to contain 1.58% N. "Plow layers," containing 182 mg N as alfalfa or as urea (46.6% N), plus water to bring them to 1/3 bar tension were added on top of 16 columns for each N source. The N addition was equivalent to 100 ppm in the "plow layer," or 224 kg/ha. The final depth of soil in each column was 130 cm.

The N sources were allowed to equilibrate with the soil environment in the "plow layer" for 4 weeks with no further additions of water, to simulate the dry period under a monsoon climate.

After the dry period, the "plow layers" were removed and stirred to simulate tillage. As the worked soil was returned to the columns, oat straw (<u>Avena sativa L</u>.), 0.755% N content, was added in the placements shown in Table 1. Control columns previously treated with urea or alfalfa received no straw. The others received 7.27 g per column (8.97 metric tons per hectare). The straw was coarsely chopped (2 to 3 cm lengths) to permit recovery of undecomposed straw by sieving at the end of the experiment.

Four replicate columns were set up for each combination of N source and straw treatment. These were arranged in

Treatment Number	Treatment Code	N Source*	Straw† Placement
1	U/C	Urea	Control (no straw)
2	U/B	Urea	Straw bedded
3	U/M	Urea	Straw mixed
4	U/S	Urea	Straw on surface
5	A/C	Alfalfa	Control (no straw)
6	A/B	Alfalfa	Straw bedded
7	A/M	Alfalfa	Straw mixed
8	A/S	Alfalfa	Straw on surface
			•

Ta	ble	e 2	Sc	hedule	e of	treatments	•
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* 182 mg N per column (224 kg N/ha) mixed through "plow layer"
(0-17 cm) at beginning of "dry period" July 7, 1973.

+7.27 g oat straw per column (8.97 metric tons/ha) placed as noted at end of "dry period," August 4, 1973, just before conditions of flooded percolation were imposed. randomized blocks to minimize confounding by systematic temperature variation in the greenhouse (Figure 1).

Before returning the surface soil with the various straw treatments, the columns were saturated with water from the bottom. The replaced surface soil and added straw were then similarly saturated by capillarity and small additions of water from the bottom, after which the columns were flooded to a depth of 20 cm by adding water gently on top. This procedure minimized displacement of soluble N from the "plow layer."

After flooding, water was allowed to percolate through the columns at the rate of 6.5 cm per day (525 ml per column). Water was added daily at the top to maintain 20 cm of flood water above the soil surface. The 6.5 cm/day withdrawal rate is about 1.4 times greater than deep percolation losses of 30% observed in sandy terraces along rivers of northeastern Thailand during monsoon periods when rainfall (up to 150 mm/day) exceeds infiltration rate (85,86,87).

Drainage water from each column was analyzed daily for NO_2 and NO_3 . Ammonium was determined every other day on twoday composites accumulated in the refrigerator at 4 C.

Daily withdrawals and additions of water were continued until NO_3^- in the percolate had diminished to fairly constant, low values. When water additions were discontinued and after drainage of free water had ceased, soil samples were taken with a 2 cm diameter bog auger at 5 increments of depth through 130 cm. Undecomposed fragments of straw were removed from plow

Figure 1.--Showing Column Arrangement in the Greenhouse.



layer samples by screening through a No. 18 (1 mm) sieve. Additional core samples (3.3 cm diameter) were taken from the plow layer for quantitative separation of undecomposed straw to provide an estimate of the proportion remaining and for analysis to determine changes in N content.

Soil samples were frozen until they could be analyzed for Kjeldahl N, NH_4^+ and NO_3^- .

Analytical Methods

Drainage Water analysis

The leachates from each column were analyzed for NO_3^--N daily. A sample was mixed well, and a 40 ml aliquot transferred into a 50 ml beaker. The NO_3^--N was analyzed by selective ion electrode (ORION IONALYZER Model 801), using procedures described by Baker and Smith (9), Keeney, Byrness, and Genson (47), Lowe and Hamilton (54). Duplicate analyses agreed within 0.4 ppm over a range from 1 to 10 ppm of nitrate-nitrogen.

Daily determination of nitrite was accomplished by the colorimetric method of Bremner (19) and Lowe and Hamilton (54). A 0.3 ml aliquot was pipetted into a 50 ml beaker. After adding 2 ml of 1% sulfanilamide, and 2 ml of 0.2% N-(1-naphthyl)-ethylenediamine (NED), the reaction mixture was allowed to stand for 20 minutes to develop color. The determination of nitrite content in samples was by reference to a semi-log calibration curve which was nearly linear over a range of standards from 0 to 6 ppm N. Ammonium was determined in 2-day composites by the semi-micro distillation method of Bremner (18). A 10 ml aliquot of leachate was pipetted into a micro-Kjeldahl flask. Steam distillation with 10 ml of 0.1 N NaOH was used to transfer ammonium over into 5 ml of 2% boric acid in a 50 ml Erlenmeyer flask containing also 1 drop of methyl purple indicator. Thirty ml of distillate was collected and titrated with 0.01705 N H_2SO_4 .

The observation of pH was made every few days. The pH of water leachates was determined by glass electrode, using a Sargent pH meter Model DR supernatant liquid.

Soil sample analysis

The nitrate in 20 g of moist soil was extracted in 50 ml of saturated CaSO₄ by shaking on an automatic shaker for 30 minutes. The suspension was allowed to settle for a few minutes, and then the supernatant was decanted into a 50 ml beaker. The nitrate content was determined by selective ion electrode, by the same procedure used for drainage water. The results were converted to the basis of oven dry soil, as determined in a separate sample.

The determination of ammonium in soil samples was accomplished by extracting 10 g of moist soil with 25 ml of 2 M KCl, with shaking for 1 hour. The extract was filtered, using Whatman No. 42 filter paper. A 10 ml aliquot of the filtrate was used for determining NH₃ by the semi-micro distillation method, as in the procedure for drainage water.

Kjeldahl-nitrogen, as determined here, included organic nitrogen and ammonium. Moist soil samples, equivalent to 2 g of oven dry weight, were weighed into micro-Kjeldahl flasks. Two ml of concentrated H_2SO_4 , and 1 gm of catalyst were added. The catalyst consisted of 100 gm K_2SO_4 , 10 gm $CuSO_4$, and 1 gm selenium. The samples were digested for about 2 hr (or for at least 1 hr after the last flecks of carbonized organic matter had disappeared and the mixture turned to greenish-blue). After the digest had cooled, 10 ml of distilled water was added, together with 10 ml of 10N NaOH to give a 5:1 ratio of base to acid for neutralizing the conc. H_2SO_4 . Distillation and filtration were the same as for ammonium in drainage water.

Undecomposed straw recovered from 4 replicate columns was combined to give a composite sample for each treatment for estimating degree of decomposition and change in N content. A 0.5 g portion of straw was weighed for Kjeldahl-N; the remainder was dried in the oven to determine moisture content and the proportion of undecomposed straw remaining.

Statistical Analysis

Variation in analyses for NH_4^+ , NO_2^- and NO_3^- in drainage water was analysed for each collection separately in accordance with the randomized block design of the experiment (Snedecor and Cochran, 1967). Variation in analyses for Kjeldhal-N, NH_4^+ and NO_3^- in soil at incremental depths at the end of the experiment was analyzed according to a split-plot design in which the main plot factor was considered to be treatment and the sub-plot factor was taken to be depth (Cochran and Cox, 1950).

RESULTS AND DISCUSSION

Forms of N in Drainage Water

Nitrate was the principal form of N which appeared in drainage water (Table 3). The quantities of NO_3^- recovered over the 21-day percolation period were 2 to 5-fold greater for urea as N source than for alfalfa. Nitrogen entering drainage as NO_2^- was only 2 to 5% of that entering as NO_3^- , but the quantities of NO_2^- were greater with urea than with alfalfa. Ammonium appeared in similarly small quantities which were independent of the source of N.

Organic N was not determined in drainage water. The quantities present would have been small, since the percolates were not visibly colored.

Total N $(NH_4^+ + NO_2^- + NO_3^-)$ in drainage from control columns over 21 days was equivalent to 86% of N input as urea and 35% of N input as alfalfa. It is likely that the urea had been completely hydrolyzed prior to flooding, whereas a substantial proportion of the N added as alfalfa remained in partially decomposed residues and humified products. There may have been some volatilization of NH₃ from both N sources during the dry period. Additional soluble N may have been removed from percolating water by immobilization or denitrification; these removals would have been less in control columns

Treat-					Days o	f perc	olation				
code	1	2	3	4	5	6	. 7	8	9	10	11
				- NO_3	- N	pp m					
u∕c	3.4	3.3	3.3	2.0	13.7	67.5	101.0	45.8	17.1	5.1	2.9
U/B	3.4	3.0	3.4	1.1	7.5	39.0	74.5	35.0	4.0	1.3	2.1
U/M	3.2	3.2	3.6	1.1	13.1	53.9	96.8	34.4	1.3	0.9	1.1
U/S	3.1	3.1	3.2	0.9	7.9	60.8	113.8	47.5	4.4	1.0	1.0
A/C	3.8	3.3	3.7	1.1	6.4	27.5	י 40.	10.3	0.9	0.8	0.8
A/B	3.5	3.2	4.1	1.5	4.0	4.2	3.5	1.3	0.5	0.8	0.6
A/M	3.2	3.2	3.4	1.3	4.7	6.2	4.4	1.7	3.4	0.5	0.6
A/S	3.5	3.3	3.7	1.3	6.4	16.4	31 5	15.5	1.4	0.5	0.6
LSD ₀₅	ns*	ns	ns	ns	7	19	19	22	7	2	1
				N	10- N	ppm					
U/C	0	0	0	0.1	- 0.5	1.8	3.2	1.8	1.0	1.0	0.8
U/B	õ	õ	õ	0.1	0.4	3.4	6.0	1.3	0.3	0.2	0.2
U/M	õ	õ	õ	0.1	0.3	1.6	1.1	0.9	0.2	0.01	0.1
U/S	ō	Õ	õ	0.1	0.4	2.6	4.9	1.3	0.6	0.3	0.02
A/C	0	0	0	0.1	0.2	0.5	0.7	0.8	0.2	0.1	0.03
A/B	õ	ō	õ	0.1	0.2	0.2	0.2	0.1	0.3	0.1	0.02
A/M	õ	ō	õ	0.1	0.2	0.4	0.5	0.3	0.04	0.1	0.03
A/S	õ	Ō	Ō	0.1	0.2	0.4	0.1	0.9	0.4	0.1	0.03
LSD ₀₅	ns	ns	ns	ns	0.2	1.2	1.8	1.0	0.3	0.3	0.4

Table 3.--Forms of N recovered in drainage water.

*NS = not significant

ttr = trace

\$nc = not calculated

TABLE 3.--continued

Treat-				Days	of per	colati	on			То	tal	
code	12	13	14	15	16	17	18	19	20	21		
				N	10 ₃ - N	ppm			-		mg N pe: column	r KgN/ha
U∕C	0.1	0.7	0.7	0.5	0.6	0.6	0.6	0.6	0.6	0.8	142.7	176
U/B	1.3	0.8	0.7	0.5	0.6	0.5	0.6	0.6	0.5	0.9	95.2	117
U/M	1.2	1.0	1.0	0.7	0.7	0.5	0.6	0.5	0.5	0.9	115.6	143
U/S	0.8	0.7	0.8	0.7	0.9	0.7	0.8	0.8	0.6	0.9	133.6	165
A/C	0.8	0.8	1.1	1.0	0.9	0.7	0.7	0.7	0.6	1.0	56.2	69
A/B	0.6	0.5	0.7	.0.6	0.6	0.5	0.6	0.6	0.6	1.0	17.6	22
A/M	0.6	0.6	0.7	0.5	0.6	0.5	0.5	0.6	0.5	0.9	20.3	25
A/S	0.6	0.6	0.8	0.7	0.9	0.8	0.9 ·	0.8	0.7	1.3	48.3	6 0
LSD05	ns	0.2	0.3	0.2	0.2	0.1	0.1	0.1	ns	0.2	nc§	<u> </u>
	*****			NO	- N	ppm -					mg N per column	KgN/ha
u/c	0.5	0.2	0.02	0.02	0.03	0.01	0.07	0.2	0.2	0.1	6.1	8
U/B	0.2	0.1	0.03	0.01	0.03	0.01	0.03	0.1	0.1	0.1	6.6	8
U/M	0.1	0.1	0.03	0.02	0.02	0.04	0.1	0.1	0.1	0.1	2.6	3
U/S	0.2	0.1	0.02	0.02	0.03	0.03	0.08	0.2	0.2	0.1	5.9	7
A/C	0.1	0.1	0.03	0.01	0.03	Tr	0.06	0.2	0.2	0.1	1.8	2
A/B	0.04	0.03	0.02	Trt	0.02	Tr	0.04	0.1	0.1	0.1	0.7	1
A/M	0.05	0.03	0.03	0.01	0.03	0.01	0.04	0.1	0.1	0.1	1.1	1
A/S	0.06	0.02	0.02	0.01	0.03	0.01	0.07	0.2	Q.2	0.1	1.6	2
LSD ₀₅	5.2	0.01	ns	ns	ns	r		1.5	ns	ns	пс	

.

Table 3.--continued

Treat-						Days o	f perco	lation				Tot	al
code	1+2	3+4	5+6	7+8	9+10	11+12	13+14	15+16	17+18	19+20	21	_	
						NH ⁺ 4	- N p	pm				mg N per column	KgN per ha
U/C	1.0	0.2	0.3	0.3	0.1	1.0	0.8	0.9	0.5	0.4	0.2	6.9	8
U/B	0.9	0.0	0.6	0.9	0.2	0.5	0.9	0.7	0.4	0.8	0.4	6.4	8
U/M	1.2	0.1	0.4	1.2	0.2	1.5	0.7	0.8	0.5	1.2	0.7	8.5	10
u/s	0.9	0.1	0.8	0.9	0.2	1.3	0.6	1.0	0.4	0.6	0.8	7.6	9
A/C	0.6	0.04	0.5	0.7	0.4	0.5	0.8	1.0	0.4	0.1	0.3	5.5	7
A/B	1.1	0.0	0.4	0.8	0.1	1.0	0.5	0.4	0.3	0.6	0.2	5.6	7
A/M	0.6	0.4	0.4	0.7	0.1	1.7	0.7	0.8	0.4	0.3	0.6	6.7	8
A/S	0.5	0.05	0.2	0.7	0.2	2.4	0.7	0.6	0.3	0.7	0.3	6.9	8
LSD05	ns	ns	ns	ns	0.2	ns	ns	ns	ns	0.6	ns	nc	

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with urea than with alfalfa because the original soil contained very little organic matter to support microbial activity (Table 1).

When straw was placed as a surface mulch, added energy substrates had very little opportunity to interact with mineral N derived from urea or alfalfa. Total N recovered in drainage was almost the same as for the controls (81% of input for urea and 31% for alfalfa).

The addition of oat straw was equivalent to 8.97 metric tons per hectare. The calculated net removal of N from percolating water (Table 4) in the presence of a surface mulch was 1.2 kg N per ton of straw in the case of urea and 0.9 kg/T where the N source was alfalfa.

The interaction of added energy substrates with available N sources was greater when the straw was mixed through the "plow layer." Total N in drainage was 69.6% of input urea N and 16% of the N introduced as alfalfa. The indicated net removal was 4.0 kg N per ton of straw in urea columns and 4.8 kg/T in columns previously amended with alfalfa.

The bedded straw placement was most effective in removing N from percolating water. Recoveries in drainage were 59% and 13% of input, equivalent to net removals of 6.6 and 5.5 kg N per ton of straw, respectively, for urea and alfalfa as N sources.

Treatment	Total N in drainage	*N Removal by straw	†Removal by straw
	K	g/ha	KgN/ton
U/C	192	-	-
U/B	133	59	6.6
U/M	156	36	4.0
U/S	181	11	1.2
A/C	78	-	-
A/B	29	49	5.5
A/M	35	43	4.8
A/S	70	8	0.9

Table 4.--Nitrogen removal by straw from drainage water.

*N removal by straw: e.g. (192 - 133) = 59.

tRemoval by straw is based on 8.97 T straw/ha.

Nitrate Leaching Patterns

The pattern of nitrate appearance over time is shown in Figure 2.

Daily additions of water to replace losses by percolation and evaporation were made through the 14th day. At that point, it appeared that movement of soluble N into drainage had leveled off at a stable low level. No further additions of water were made, but percolation was allowed to continue at a rate of 6.5 cm per day (525 ml/day). It took four more days for the 20 cm of surface flood water to disappear, and another three days for free gravitational water to move out of the soil columns.

Most of the NO_3^- recovered in drainage appeared in a wave of high concentration between the fifth and eighth days. With most treatments, there was a sharp concentration peak on the seventh day, corresponding to displacement of the first leaching volume of water.

It is apparant that most of the NO_3^- which appeared in drainage was already present in the "plow layer" as NO_3^- at the time the soils were flooded. The proportion of initial $NO_3^$ appearing in drainage would have been related inversely to its residence time in the vicinity of microbial populations utilizing energy substrates supplied as oat straw or alfalfa. In relation to straw, this residence time would have been shortest with the surface mulch and longest where straw was placed at the bottom of the plow layer. Net removals of N

Figure 2.--Nitrate in drainage under conditions of flooded percolation as related to sources of N and different placements of oat straw.



per ton of straw in the previous section are consistent with this interpretation.

The NO_3^- initially present in the plow layer moved downward with percolating water. Calculation of displacement water volume indicated that the seven days should be required for NO_3^- to appear in drainage water. The nitrate which appeared on the 2nd, 3rd, and 4th days would be expected to have come from original soil. The NO_3^- appearance on the 5th day came from NO_3^- diffusion from plow layer plus NO_3^- in original soil.

Sufficient available energy materials may have been released from native soil organic material during the dry period to support denitrification through the entire depth of the soil columns for a short period after flooding. This is consistent with the fact that a small decrease in NO_3^- output occurred in all columns on the fourth day. This delayed disappearance of NO_3^- is consistent with the adaptive nature of enzyme systems involved in nitrate reduction. Denitrifying organisms do not synthesize nitrate reductase, even in the presence of nitrate, until available oxygen has been depleted to very low level (Alexander, 1967).

Nitrite was not detected in drainage until the 4th day (Table 3). This may be taken as additional evidence that an active denitrifying population was not present initially, but it developed after a period of adaptation when flooded conditions were imposed.

Nitrite concentrations followed a pattern similar to NO_3^- , reaching peak concentrations during the 5th through the 8th days. The fact that very low concentrations of both NO_3^- and NO_2^- were detected through the remainder of the percolation period indicates that conditions in flood water, perhaps also in surface soil layers, were sufficiently oxygenated for nitrification to continue, whereas reducing conditions at greater depths were favorable for denitrification.

Photosynthesis by algae in the flood water would have been an important source of oxygen for nitrifiers, as well as a source of soluble organics to support denitrifying populations at greater depths. Photosynthetic production may have been the principal source of reducing power in the urea control In other columns, alfalfa and/or straw were undoubtedly columns. more important. It would be expected that maximum reducing power would be generated where both alfalfa and straw were present and that conversion of NO_3^- and NO_2^- to N_2O and/or N_2 would be more complete. In fact, the lowest maximum concentrations on the fifth through eighth days and the lowest total delivery in drainage of both NO_3 and NO_2 occurred with alfalfa plus straw treatments (Table 3). The effective contribution of straw to reducing power in the soil, however, was much less when it was placed under relatively well-aerated conditions on the surface.

pH of Drainage Water

The pH of input water was 8.1. The pH drainage water ranged from 7.9 to 8.5, tending to increase with time, but with no consistent differences among treatments. This range of pH is favorable for most microbial processes, including nitrification and denitrification.

Mineral Nitrogen Recovered in Soil

The data for NH_4^+ and NO_3^- in Table 5 show that essentially all of the mineral N in these systems had been removed in drainage and that very little net mineralization or net nitrification occurred during the last three days as free water was removed and air allowed to enter the soil columns.

The Spinks very fine sand used in this study had a very low clay and organic nitrogen content (Table 1). Thus, it would have been low in cation exchange capacity and would not be expected to retain much NH_4^+ against the leaching action of water. It is possible that some NH_4^+ may have been released from decomposing organic matter as air entered the columns during the last three days but there were no significant differences among treatments. There is some evidence that an active nitrifying population may have begun to develop, since slightly but significantly larger quantities of NO_3^- were recovered from alfalfa controls and alfalfa with surface straw placement. It is unlikely that nitrate reduction by denitrifying organisms was fully inhibited by the degree of aeration achieved during the 3-day drainage

Treat-			Dept	h (cm)		Total
ment	0-17	17-45	45-75	75-105	105-130	0-130 cm
			Kg	N/ha		
			Kjeld	<u>ahl - N</u>		
U/C U/B U/M U/S	56.6 74.4 94.6 64.7	62.2 57.6 62.3 62.2	72.4 86.3 81.3 91.7	75.0 76.5 80.4 74.0	64.0 66.9 70.6 70.2	330 362 389 363
A/C A/B A/M A/S	138 187 158 166	71.3 75.4 65.6 72.9	86.6 85.6 87.7 86.3	87.7 86.3 78.3 75.6	74.4 68.6 68.0 69.7	458 503 458 471
LSD ₀₅	12	15	ns	ns	ns	46
			NH	$\frac{+}{4} - N$	<u></u>	
U/C U/B U/M U/S	0.13 0.18 0.24 0.10	0.21 0.21 0.21 0.16	0.27 0.32 0.27 0.27	0.37 0.20 0.18 0.22	0.22 0.39 0.24 0.30	1.2 1.3 1.1 1.1
A/C A/B A/M A/S	0.13 0.19 0.14 0.18	0.12 0.23 0.11 0.24	0.24 0.37 0.31 0.38	0.16 0.31 0.42 0.47	0.22 0.14 0.16 0.15	0.9 1.2 1.1 1.4
LSD ₀₅	ns	ns	ns	ns	ns	ns
			NO	$\frac{1}{3}$ - N		
U/C U/B U/M U/S	0.05 0.05 0.04 0.05	0.06 0.05 0.05 0.06	0.08 0.08 0.07 0.08	0.08 0.07 0.07 0.09	0.07 0.07 0.08 0.08	0.33 0.33 0.31 0.35
A/C A/B A/M A/S	0.12 0.10 0.06 0.15	0.10 0.06 0.06 0.09	0.09 0.07 0.08 0.09	$0.11 \\ 0.04 \\ 0.08 \\ 0.10$	0.09 0.07 0.06 0.90	0.50 0.34 0.34 1.3
LSD ₀₅	0.02	0.02	ns	0.03	0.02	0.05

Table	5Forms	of	nitrogen	in	soil	at	the	end	of	the
	percol	lat	ion period	1.						

period. Continued use of nitrate in respiration by the denitrifiers would have contributed to the very low recoveries of mineral N in soil at the end of the experiment.

Organic Nitrogen Recovered in Soil

The Kjeldahl N values in Table 5 include NH_4^+ -N. Since NH_4^+ was found in such small quantities, Kjeldahl N is essentially equivalent to organic N.

These soil analyses do not include undecomposed straw, which was removed by screening and analyzed separately. Therefore, Kjeldahl N would have included N in humified materials and undecomposed plant structures less than 1 mm average diameter.

Much larger quantities of organic N were retained in soil of the "plow layer" (0-17 cm) of columns amended with alfalfa than in those which received urea. In the 17-45 cm layer, significantly more organic N was retained under the alfalfa amendment than under urea only where straw was bedded under the "plow layer." There were no significant differences among treatments at greater depths.

More N was immobilized in humified organic forms and finely divided plant structures in the "plow layer" when straw in any of the three placements was added after alfalfa. With urea as the N source, only the bedded and mixed placements of straw resulted in significantly increased retention of organic N. After the urea addition, the largest quantities of N were immobilized when straw was mixed through the "plow layer." After alfalfa, the bedded straw placement was most effective in retaining organic N. There is no readily apparent explanation for this interaction, but it was highly significant statistically (P = 0.01).

Although there were no significant differences among treatments at depths below 45 cm, the quantities of N recovered in soil at the end of the experiment were greater at every depth than were present in the original soil before treatment (Table 6). The total increase in soil N to a depth of 130 cm was equivalent to 34 to 46% of the N added in urea or urea plus straw and 70 to 91% of that input in alfalfa or alfalfa plus straw.

The profile distribution of Kjeldahl N is presented graphically in Figure 3 (also see Table 5).

Undecomposed Straw

Undecomposed straw was separated from soil by screening on a 1 mm sieve. The straw retained on the sieve was weighed in part (0.5 g) for Kjeldahl-N analysis, the remainder was dried for estimating percent moisture and the degree of the decomposition.

It appeared that percent loss of dry matter was not influenced by nitrogen source, but it was very different for different placements of straw (Table 7). The straw had decomposed most extensively (48%) when it was bedded below the "plow

Table 6N	et chang	ges in so	il N from	the begir	ning to the	end of th	e experimen	t.	i
Treatment	Input		Incre increm	ease in sc ents of d	oil N by lepth (cm)		Total in 0-130	crease cm	i
	к Д	0-17	17-45	45-75	75-105	105-130	Kg N/ha	% of input N	
			Kg	/ ha					i
(N in soil treatment)	before	(33)	(22)	(59)	(29)	(49)	(254)		
Increase									
u/c	224	23	8	14	16	15	76	33.9	
U/B	292	41	£	28	18	19	109	31.9	48
W∕n	292	61	8	23	22	22	136	46.6	}
u/s	292	32	ω	33	14	22	110	37.9	
A/C	224	105	17	28	29	26	205	91.5	
A/B	292	154	21	27	28	20	250	85.6	
A/M	292	126	11	29	20	19	205	70.2	
A/S	292	134	18	28	18	21	219	75.0	
*Input N in	cludes 2	224 kg N a	is urea or	alfalfa	incorporate	d to 17 cm	prior to d	ry period	

plus 68 kg N in straw added 4 weeks later, just before flooding.

Figure 3.--Distribution of Kjeldahl-N retained in soil columns.

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Key: C = control (no straw) S = oat straw on surface M = oat straw mixed through "plow layer" (0-17 cm) B = oat straw bedded under "plow layer"



Treatment	Undecomposed straw*	Percent decomposition	Kje undecom	ldahl N in posed straw
	T/ha		% N	KgN/ha
U/C	-	-	-	-
U/B	4.6	48.7	0.28	13
U/M	7.3	18.6	0.21	15
U/S	8.4	6.4	0.15	13
A/C	-	-	_	_
A/B	4.7	47.6	0.26	12
A/M	7.4	17.5	0.62	46
A/S	8.4	6.4	0.15	13
•.				

Table 7.--Percent decomposition of straw, and Kjeldahl-N in undecomposed straw at the end of the experiment.

*8.97 metric tons/ha of oat straw was added, containing 0.755% N or 68 kg N/ha.

layer." The least decomposition (6.4%) occurred in the surface mulch. Where the straw was mixed through the "plow layer," the disappearance of fragments greater than 1 mm was about 18%. This experiment shows that the decomposition of straw was greater where the straw had the greatest opportunity to interact with percolating nutrients and the soil environment.

The N content of the straw (initially 0.755%) decreased during decomposition. This result is contrary to much published literature in which it is reported that the N content of plant materials initially low in N increases during decomposition (Bartholomew, 1965; Harmsen and Kolenbrander, 1965). However, there do not appear to have been any systematic studies of changes in residual N content under anaerobic conditions of constant percolation.

The large reductions in N content observed for most treatments in Table 7 can be attributed to leaching of soluble N compounds present in the original straw or released during decomposition of proteins in the straw. The greatest reduction in N content occurred in the surface application where the decay population developing on the straw would have had the least access to N previously incorporated into the underlying soil as urea or alfalfa.

The smallest reduction in N content accurred where alfalfa residues and straw were mixed together through the

"plow layer." The greater retention of N in undecomposed straw here may be due partly to the fact that finely ground alfalfa residues tended to adhere to the coarse chopped straw in the straw analysis. However, this intimate association would also have given the decay population direct access to nitrogen released as the alfalfa decomposed. This would have favored a larger population and immobilization of more N in microbial tissues than in urea columns where NO_3^- formed by hydrolysis and nitrification would have moved quickly out of the "plow layer" with percolating water.

Soluble N and other nutrients moving through the bedded straw layer promoted very rapid decomposition under both urea and alfalfa treatments. A larger decay population developed in the bedded layer than in the surface applied straw, as evidenced by the greater N content of the residual straw. Because more N was immobilized by microbes, total N retained in the bedded straw was the same as in the surface application, in spite of the six-fold greater loss of dry matter.

Nitrogen Balances

In Table 8 shows the calculated nitrogen balances for the different treatments.

The values in columns (5) and (6) show that the sum of N recovered in drainage plus that in soil at the end of the experiment exceeded N initially present or input as urea or

Treatment	Initial N (1)	Total N in Drainage (2)	Total N in soil at the end of the expt. (3)	N in Indecomposed srraw (4)	Gain or of N in (5)	(loss) system (6)
		Kg	N/ha		Kg/ha	ang
u/c	478	192	330	I	44	9.2
U/B	546	133	362	13	(38)	(1.0)
M∕u	546	156	390	15	15	2.7
n∕s	546	181	363	13	11	2.0
A/C	478	78	458	ı	58	12.1
A/B	546	29	503	12	(2)	(0.4)
A/M	546	35	458	46	(2)	(1.3)
A/S	546	70	472	13	6	2.4
(1) Initial N added	l N = Sum of K l as urea, alf	jeldahl-N + NO alfa and/or sti	$\frac{1}{3}$ -N + NO $\frac{1}{2}$ -N + NH $^{+}_{4}$ -N raw, plus N added ir	in original soi n input water.	l, plus	
(2) Total N	l in drainage	does not inclu	de organic -N.			
(3) Sum of	Kjeldahl-N +	$NH_4^+ - N + NO_3^ N$	in soil to a depth o	of 130 cm.		
(4) Kjeldař	il N in undeco	mposed straw a	t the end of experir	ment.		

Table 8.--Nitrogen balance for the experiment.

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(5) N gain or (loss); column (5) = (2) + (3) + (4) - (1).

(6) Percent of initial N.

alfalfa in control columns by about 10 percent (9.2% in urea columns, and 12.1% in alfalfa columns).

These calculations suggest that there was a substantial input of N by biological nitrogen fixation. Increases in nitrogen due to biological fixation are frequently reported in surface flood water or at the soil-water interface of flooded soils (Magdoff and Bouldin, 1970; Fogg, 1971; Pratt <u>et al</u>. 1960). Responsible organisms have been reported to include blue green algae, photosynthetic bacteria and heterotrophic bacteria (Azotobacter, Clostridia).

In the present study, algae grew profusely in flood water in all columns. No attempt was made to examine this flora for the presence of N-fixing organisms. There were no visible differences in the quantity of algal growth in different columns, nor in the general appearance of populations which developed in the floodwater or on the surface of soil or straw. Net water movement was downward into the soil and this would have minimized differential effects of soil treatment on aquatic populations in the surface water. Thus, as a first approximation, it may be assumed that, if N-fixation occurred in control columns, then the quantity fixed in columns receiving straw treatments may have been similar.

Net gains in N occurred in urea and alfalfa systems where straw was placed on the surface and in the urea system where straw was mixed (Table 8). The increases were less than in the controls, however. In other straw systems, net losses of N occurred.

The lower total N recoveries for straw treatments imply that denitrifying organisms were involved in the decomposition of the straw. The apparent loss of N by denitrification varied with N source and with straw placement.

Apparent Immobilization and Denitrification Due to Straw

The data in Table 8 suggest that straw contributed to removals of N from percolating water in two ways: (1) by promoting immobilization of N in soil and (2) by supplying energy to support denitrification.

The apparent contribution of straw to these two mechanisms of N interception has been calculated in Table 9 for each straw treatment. The ratios in the last column indicate that denitrification in the presence of straw may have equalled or exceeded immobilization in all systems except urea with straw mixed or placed on the surface.

In both urea and alfalfa systems, the indicated total interception by immobilization plus denitrification was greatest where straw was bedded and least where it was placed on the surface. Both immobilization and denitrification by microorganisms involve the expenditure of energy. The order of increasing effectiveness in intercepting N for the three straw placements was the same as the order of increasing degree of decomposition (Table 7).

There can be no simple explanation for the indicated variation in the proportion of NO_3^- utilized in respiration by

	Apparent	immobili:	zation		N İ	ntercepte	¢d	
		In		Apparent	per t	on of str	aws	Ratio:
Treatment	In Soil*	undecom- posed straw	Total	denitri- fication†	Immobi- lized	Denitri- fied	mu S	Denitrified immobilized
		Kg N /ha				Kg/T		
U/B	32	13	45	82	5.0	9.1	14.1	1.8
M∕N	60	15	75	29	8.4	3.2	11.5	.4
n∕s	33	13	46	33	5.1	3.7	8 8	57 -
A/B	45	12	57	60	6.4	6.7	13.1	1.1
A/M	0	46	46	65	5.1	7.2	12.3	l.4
A/S	14	13	27	49	3.0	5.5	8.5	1.8
*Difference	in N found	d in soil	to 130 c	m: Straw tr	eatment mi	nus contr	ol (colur	nn 3, Table 8).
			•		-	• •	-	

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Straw +Difference in total N recovered in soil, undercomposed straw and drainage water: treatment minus control (column 5, Table 8).

8.97 metric tons/ha. [§]Straw applied: denitifiers to nitrogen immobilized in the presence of straw. Some relationships do appear to be important to mention.

Anaerobic conditions necessary for denitrification favor net mineralization rather than immobilization (Bartholomew, 1965). At the time of straw addition and flooding, a larger microbial population was probably present in soils treated with alfalfa than in those which had received urea, since the carbon in urea cannot serve as an energy source. This larger population would have exerted a greater oxygen demand, so that oxygen in percolating water would have been depleted more rapidly. As a result, it might be expected that denitrification due to straw would be greater and immobilization less in alfalfa than in urea columns.

This expected relationship is borne out by the calculations in Table 9 for the surface and mixed straw placements. In the case of the bedded placement, apparent denitrification was greater in urea columns (82 vs 60 kg N/ha). If one refers to Figure 2, it is apparent that denitrification in alfalfa columns was limited by the much lower concentrations of $NO_3^$ present as compared with the urea systems. This limitation was similar for bedded and for mixed straw, since the total quantities of NO_3^- appearing in drainage (Table 3) and apparent denitrification (Table 9) were very similar for these placements in alfalfa systems.

In urea systems, much more N was apparently denitrified in the presence of bedded than mixed straw, and less N

was retained in the soil. Thus, it would appear that less oxygen was available to the decay population at the bottom of the "plow layer." Also, previously accumulated NO_3^- , moving with percolating water, would have had a longer mean residence time in the vicinity of the bedded straw, so that a larger denitrifying population could develop.

With the surface placement, apparent immobilization was less with alfalfa than with urea, and denitrification loss was greater as expected. However, apparent denitrification was less than with the bedded or mixed straw placements and substantial quantities of NO_3^- did escape into drainage (Figure 2). In this case, it can be visualized that soluble energy materials from the straw moved behind NO_3^- in the percolating water column. The extent to which denitrification could proceed would have been determined by the extent to which energy material and NO_3^- were mixed by diffusion or convection.

It is recognized that denitrifying bacteria would have found additional sources of energy in alfalfa residues and possibly also in native soil organic matter. Actual losses by denitrification may very well have been greater than calculated for the different straw treatments in Table 9. This would imply that actual inputs of N by biological fixation were also greater.

The results obtained in this study suggest that atmospheric nitrogen exists in a very dynamic equilibrium with
organic and mineral N in flooded soils. Tracer studies with 15 N will be necessary to characterize this equilibrium under different conditions of climate, soil and management so that the most efficient use can be made of N cycling through the soil system.

In future research, it appears important to consider choice of crop residues and their placement. Time of residue application in relation to time of flooding should also be considered. For example, if the straw had been allowed to interact with the soil environment for a period before flooding, more N may have been immobilized and losses both by leaching and by denitrification may have been reduced.

SUMMARY AND CONCLUSIONS

A lysimeter experiment was conducted to evaluate the effect of positional placement on the effectiveness of cereal straw in reducing losses of nitrogen from soils under conditions of flooded percolation. Columns 10.2 cm in diameter, containing 130 cm of a Spinks parent material which is low in organic matter, were used. Nitrogen equivalent to 224 kg/ha was introduced as urea or alfalfa and incorporated into the "plow layer" (0-17 cm) during a drying cycle one month before flooding. Just before flooding, quadruplicate columns, previously treated with urea or alfalfa, received oat straw (8.97 metric tons per ha) in (1) a surface application, (2) mixed through the "plow layer," (3) bedded under the "plow layer," or (4) no straw (controls). The soils were then saturated from the bottom and flooded to a depth of 20 cm by surface additions of water. Percolation was allowed to occur at 6.5 cm per day, with daily surface additions to maintain 20 cm of floodwater through the 14th day. Seven more days were required to remove surface and gravitational water at the 6.5 cm/day percolation rate.

The results may be summarized as follows:

1. In the absence of straw, total N recovered in drainage $(NH_4^+ + NO_2^- + NO_3^-)$ over 21 days of percolation was equivalent

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to 86% of input urea-N and 35% of N input as alfalfa. Most of this N appeared as NO_3^- in a wave of high concentration on the 5th through 8th days, with a sharp peak on the 7th day.

2. In the absence of straw, the total increase in soil N to a depth of 130 cm was equivalent to 34% of the N input as urea and 92% of the N input as alfalfa. In the case of alfalfa, half of this increase was associated with residues retained in the "plow layer."

3. Algae grew profusely in surface floodwaters. It appeared that nitrogen may have been fixed biologically, giving rise to positive N balances equivalent to 44 kg/ha for urea control columns and 58 kg for alfalfa. It appeared that similar inputs of N may have resulted from biological fixation in columns which received straw, but that denitrification was enhanced in the presence of straw. N balances calculated for the straw treatments indicate that the potential for denitrification was enhanced by deep placement and by the presence in alfalfa columns of a large microbial population at the time the soils were flooded. These same conditions favored net mineralization so that less N was retained (immobilized) in the soil.

4. The effectiveness of straw in removing N from percolating water was related directly to the degree of decomposition of the straw (based on dry weight recovered by screening at the end of the experiment). The degree of decomposition

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was not affected by N source but increased with depth of placement of the straw: surface placed (6%), mixed (18%), bedded (48%). For these same placements, total N found in drainage represented 81, 70 and 59% of input urea N, and 31, 16 and 13% of N input as alfalfa. Calculated removals due to immobilization plus apparent denitrification ranged from 8 kg N per ton of straw for the surface mulch to 14 kg per ton for the bedded placement.

It was concluded that studies of management practices in relation to efficient use of N in paddy culture must take into account the equilibrium between flooded soils and the atmosphere due to biological fixation and denitrification. It appears that this equilibrium can be influenced significantly by choice and placement of crop residues, and by time of application in relation to time of flooding.

This study indicates that nitrogen may be conserved by mixing crop residues into the soil, either using urea or a legume as source of nitrogen fertilizer. Bedding the residue may be the best practice. However, further research in the field should be done: (1) to determine if organic materials applied after the monsoon period or during the long dry season on fallow land and cropped land may help to maintain nitrogen in soils, (2) to study the effect of residual straw on nitrogen movement in the next season, (3) to see if there are effects of straw on other factors, e.g., diseases, insects

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etc., and (4) to try incorporation of straw at varying periods of time prior to application of nitrogen fertilizer.

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