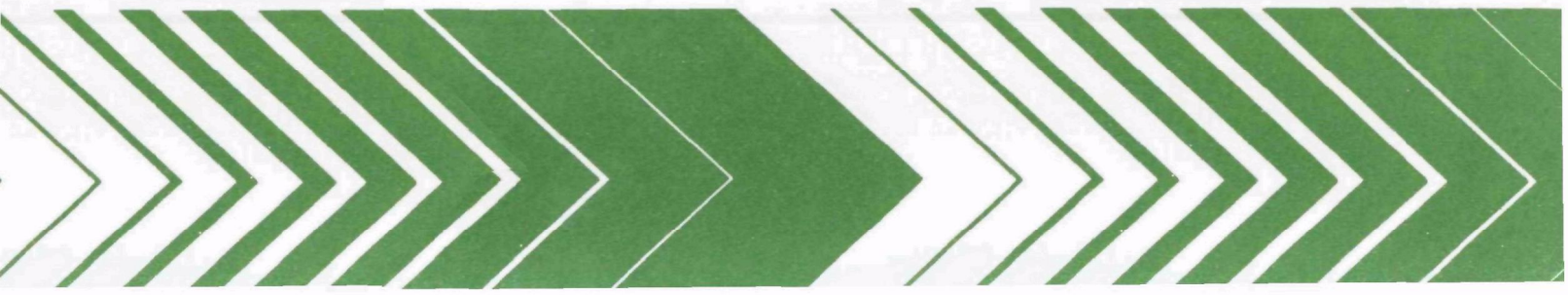


Research and Development



# Denitrification as Affected by Irrigation Frequency of a Field Soil



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DENITRIFICATION AS AFFECTED BY IRRIGATION  
FREQUENCY OF A FIELD SOIL

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## FOREWORD

Environmental protection efforts dealing with agricultural and nonpoint sources have received increased emphasis with the passage of the Clean Water Act of 1977 and the subsequent implementation of the Rural Clean Water Program. As part of this Laboratory's research on the occurrence, movement, transformation, fate, impact, and control of environmental contaminants, data are developed to assess the causes and possible solutions of adverse environmental effects of irrigated agriculture.

This report addresses the denitrification process as it affects the management of nitrogen and water in an agricultural production system. An understanding of the complete nitrogen cycle, including denitrification, is required to make sound management decisions regarding nitrogen use- and water use-efficiency in irrigated agricultural systems. This research should benefit environmental managers as they attempt to understand and solve pollution problems related to nitrogeneous compounds and wastes.



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## ABSTRACT

The amount of nitrogen (N) as nitrate ( $\text{NO}_3^-$ ) in irrigation return flow waters is dependent upon each of the components of the N cycle in soils. One of those components for which absolute amounts and rates are not well known is denitrification. Volatile denitrification products, primarily nitrous oxide ( $\text{N}_2\text{O}$ ) and dinitrogen ( $\text{N}_2$ ), are evolved whenever anoxic sites develop within the soil and when sufficient carbon (C) is available. Absolute amounts and rates of denitrification from a Yolo loam field profile at Davis, California, were studied in relation to the influence of irrigation frequency and soil incorporation of crop residue. Field plots were intensely instrumented with soil atmosphere samplers, soil solution samplers, tensiometers, neutron access tubes, and thermocouples. Two different C treatments were established by using plots to which no crop residues had been incorporated within one year prior to the experiment and plots to which 10 metric tons  $\text{ha}^{-1}$  of chopped barley straw were incorporated into the top 10 cm of soil two months prior to fertilization. Irrigation frequencies of three irrigations per week, one irrigation per week, and one irrigation every two weeks were established on areas cropped with perennial ryegrass. Fertilizer was applied at the rate of 300 kg N  $\text{ha}^{-1}$  as  $\text{KNO}_3$  enriched with 56 to 58%  $^{15}\text{N}$  to 1- $\text{m}^2$  plots. The flux of volatile gases at the soil surface was measured from the accumulation of  $\text{N}_2\text{O}$  and  $^{15}\text{N}_2$  beneath airtight covers placed over the soil surface for one to four hours at several times immediately after irrigation and at less frequent intervals as denitrification fluxes decreased.

Small rates of total denitrification were measured in this well-drained alluvial soil under normal cyclic applications of irrigation water. For plots without C addition, the largest denitrification of only 1.5% of the applied fertilizer was measured in the most frequently irrigated plot. For the least frequently irrigated plot of one irrigation every two weeks, only 0.7% of the fertilizer denitrified. For plots to which C was added as straw, denitrification was greatly increased over that of the plots not receiving straw. The greatest denitrification also occurred for the most frequently irrigated plots with denitrification being between 5 and 6.5% of the fertilizer applied. For the least frequently irrigated plot, only 1.8% of the fertilizer was denitrified. Denitrification rates decreased to near zero values within one or two days after irrigation. The amount of  $\text{N}_2$  produced was much greater than  $\text{N}_2\text{O}$ . The  $\text{N}_2\text{O}$  flux at the soil surface varied between 5 and 27% of the total denitrification over a 40 to 50 day period.  $\text{N}_2\text{O}$  mole fractions tended to be smallest immediately after irrigation and increased as the soil water redistributed and the soil profile became less anoxic.

The irrigation frequency of three irrigations per week gave higher  $\text{NO}_3^-$  concentrations as measured by both soil solution and soil samples within the root zone of the crop than those of the other two frequencies. Thus, frequent, small irrigations tended to result in less leaching losses than frequent, large irrigations.

Denitrification as measured using the  $^{15}\text{N}$  enrichment method compared reasonably well with that determined using the acetylene ( $\text{C}_2\text{H}_2$ ) inhibition method. However, rates of denitrification as measured by the two methods at any one sampling time varied considerably due to the lags in reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  and to possible development of organisms which may reduce  $\text{N}_2\text{O}$  in the presence of acetylene.

Denitrification of  $\text{NO}_3^-$  fertilizer was simulated using a mathematical model that included transport and plant uptake of water and N in soil. The rate of denitrification was considered to be a function of  $\text{NO}_3^-$  concentration, available C concentration, degree of soil-water saturation, and temperature. Available C concentrations were calculated from initial amounts of soil C and additions of plant residues or animal manure. The consumption of added C in the soil system was assumed to occur in two or three stages with different rate constants for each stage and C addition. A  $Q_{10}$  value of two was used to correct the denitrification rate constant and C consumption constants for temperature. Model simulations for total denitrification were compared with measured  $\text{N}_2$  plus  $\text{N}_2\text{O}$  gas fluxes during  $\text{NO}_3^-$  leaching in field plots of Yolo soil at different soil-water contents, C additions, soil temperature, and irrigation frequencies. Reasonable agreement was found between measured and calculated rates and total amounts of denitrification for all plots.

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# LIST OF ABBREVIATIONS AND SYMBOLS

## ABBREVIATIONS

cm	-- centimeter	ppmv	-- parts per million on a volume basis
m	-- meter		
ml	-- milliliter	cm <sup>3</sup>	cubic centimeters
°C	-- degrees Centigrade	g	-- gram
kg ha <sup>-1</sup>	-- kilograms (10 <sup>3</sup> grams) per hectare	µg	-- micro grams (10 <sup>-6</sup> grams)
mg	-- milligram (10 <sup>-3</sup> grams)	hr	-- hour
ppm	-- parts per million on a weight basis	ET	-- evapotranspiration
		MT	-- metric ton (10 <sup>3</sup> kg)

## SYMBOLS

C <sub>2</sub> H <sub>2</sub>	-- acetylene gas	G	-- sum of denitrification gases (N <sub>2</sub> + N <sub>2</sub> O) [µgN(g soil) <sup>-1</sup> ]
N	-- Nitrogen		
NH <sub>4</sub> <sup>+</sup>	-- Ammonium		
NO <sub>2</sub> <sup>-</sup>	-- Nitrite	C <sub>N</sub>	-- concentration of NO <sub>3</sub> <sup>-</sup> [µg N (cm solution) <sup>-3</sup> ]
NO <sub>3</sub> <sup>-</sup>	-- Nitrate		
N <sub>2</sub> O	-- Nitrous Oxide gas	C <sub>W</sub>	-- concentration of water soluble carbon [µg C (g soil) <sup>-1</sup> ]
N <sub>2</sub>	-- Nitrogen gas		
<sup>15</sup> N	-- Nitrogen isotope of mass 15	f <sub>W</sub>	-- water function for denitrification
CO <sub>2</sub>	-- Carbon dioxide gas	f <sub>T</sub>	-- temperature function
O <sub>2</sub>	-- Oxygen gas	k <sub>1</sub>	-- first-order denitrification constant [g soil day <sup>-1</sup> (µg C) <sup>-1</sup> ]
C	-- Carbon		
Na	-- Sodium	C <sub>S</sub>	-- concentration of total soil organic carbon [µg C(g soil) <sup>-1</sup> ]
Cu	-- Copper		
SO <sub>4</sub>	-- Sulfate	t	-- time (day)
Cl <sup>-</sup>	-- Chloride	k <sub>S</sub>	-- first-order constant for soil carbon decomposition (day <sup>-1</sup> )
H <sub>2</sub> O	-- Water		
<sup>63</sup> Ni	-- Nickel isotope of mass 63	g <sub>W</sub>	-- water function for carbon decomposition
K	-- Potassium	C <sub>I</sub>	-- concentration of total organic carbon from straw or manure [µg C(g soil) <sup>-1</sup> ]
Å	-- Angstrom	k <sub>I</sub>	-- first-order constant for straw or manure carbon decomposition (day <sup>-1</sup> )
x	-- distance (cm)		
h	-- soil-water pressure head (cm)	k <sub>O</sub>	-- zero-order denitrification constant [µg N day <sup>-1</sup> (µg C) <sup>-1</sup> ]
θ	-- soil-water content (cm <sup>3</sup> cm <sup>-3</sup> )		
θ <sub>s</sub>	-- saturated soil-water content (cm <sup>3</sup> cm <sup>-3</sup> )		
ρ	-- soil bulk density (g cm <sup>-3</sup> )		

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## SECTION 1

### INTRODUCTION

The amount of  $\text{NO}_3^-$  reaching the groundwater of irrigated lands is dependent upon each of the components of the N cycle in soils. One of the potential losses of N from the soil system for which absolute amounts and rates are not well known is denitrification. Volatile denitrification products, primarily  $\text{N}_2\text{O}$  and  $\text{N}_2$ , are evolved whenever anoxic sites develop within the soil and when sufficient C as supplied by soil organic matter, plant materials, and manure is available.

Simulation models of the N balance in soil systems attempt to predict the amount and concentration of  $\text{NO}_3^-$  in irrigation return flow water as a function of irrigation and cropping practices (Mehran and Tanji, 1974; Donigian and Crawford, 1976; Shaffer et al., 1977; Tanji and Gupta, 1978; and van Veen, 1977). In general, the denitrification component of the various mathematical models has not had adequate input data especially for the rates of denitrification. Total denitrification of applied fertilizers is used quite frequently such as 10 to 15% of the fertilizer N applied (Fried et al., 1976).

Very few experiments have evaluated the absolute amounts and rates of denitrification in the field. Rolston et al. (1976) demonstrated that the volatile gases from denitrification could be measured in a field profile. Total denitrification from gas fluxes compared reasonably with denitrification determined by difference for a small, intensely-instrumented field plot. Total denitrification was determined by integrating with time the flux of the gaseous denitrification products as determined from measured soil gaseous diffusion coefficients and concentration gradients. These studies only evaluated the amount of denitrification under one cropping or C input system and one soil-water content near saturation. Rolston and Broadbent (1977), Rolston et al. (1978, 1979) directly measured denitrification from the fluxes of  $\text{N}_2$  and  $\text{N}_2\text{O}$  at the soil surface of small, intensely-instrumented field plots.  $\text{NO}_3^-$  fertilizer was applied to plots which had a crop growing on the soil, to plots to which manure had been added, and to uncropped plots maintained at two different soil-water contents near saturation and at two different temperatures (winter and summer). These experiments were conducted for constant water content conditions over the entire period that denitrification measurements were made. These experiments defined the range over which denitrification might occur and gave the potential rates and total amounts that might be expected in field soils. However, the continual maintenance of high water content conditions for long time periods in the field is generally not the normal practice which might occur during irrigation or rainfall events. The wetting and drying cycles which would take place under

field situations, due to either rainfall or irrigation, may drastically change the rates and total amounts of denitrification that may occur. The rate that a microbial population can increase from a relatively small biomass in an air dry soil to a population which could effectively reduce  $\text{NO}_3$ , the length of time that irrigation water is maintained on the soil, and the rate of redistribution of applied irrigation water within the soil profile would all have a very dynamic effect on the denitrification process.

Ryden et al. (1979) directly measured denitrification in field soils of the Santa Maria Valley of California using the  $\text{C}_2\text{H}_2$  inhibition technique. The  $\text{C}_2\text{H}_2$  inhibition method is based upon evidence that  $\text{C}_2\text{H}_2$  completely blocks the reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  in the denitrification sequence. Thus, all denitrification yields  $\text{N}_2\text{O}$  which is easy to measure without the use of  $^{15}\text{N}$ .

The objectives of the research reported here were:

A. To directly measure fluxes of  $\text{N}_2$  and  $\text{N}_2\text{O}$  gases from a field soil as influenced by three different irrigation frequencies and two levels of C.

B. To compare denitrification obtained directly using  $^{15}\text{N}_2$  and  $\text{N}_2\text{O}$  gas fluxes from  $^{15}\text{N}$  enriched fertilizer with denitrification measured directly using the  $\text{C}_2\text{H}_2$  inhibition method.

C. To evaluate existing N simulation models to determine if such models could simulate the dynamic denitrification process that occurs during and after normal irrigation cycles and to develop or improve existing models to adequately consider denitrification.

The research was conducted on small  $1\text{-m}^2$  field plots because of the large cost of  $\text{NO}_3$  fertilizer tagged with high enrichments of the stable isotope  $^{15}\text{N}$ . The experiments were conducted at three different irrigation frequencies of three irrigations per week, one irrigation per week, and one irrigation every two weeks with the same total amount of water applied to each plot. The plots also had two C levels; one in which no plant materials (residues) were added to the soil for more than one year prior to the experiment and a second in which 10 metric tons per hectare ( $\text{MT ha}^{-1}$ ) of chopped barley straw were added approximately two months prior to fertilization.

## SECTION 2

### CONCLUSIONS

The following major conclusions were obtained from this research:

1. The results of this research demonstrate that denitrification rates and total amounts are generally small for normal irrigation practices in fairly well-drained, alluvial soil.

The greatest amount of fertilizer N lost through denitrification was only 1.5% of the total N applied ( $300 \text{ kg N ha}^{-1}$ ) for the situation where plant materials had not been incorporated into the soil for greater than one year prior to the experiment. For the plots to which straw was incorporated two months prior to fertilization, the greatest denitrification loss was still only 6.5% of the total fertilizer applied ( $300 \text{ kg N ha}^{-1}$ ). It is expected that these values would be similar for other well-drained, loam soils of similar C levels. Little denitrification is expected in sandy soils. Approximately two or three times the denitrification measured here might be expected in clay soils. The presence of hardpans, impeding layers, textural discontinuities or high water tables in the soil profile would all tend to increase the amount of denitrification over that given in this report.

2. Denitrification rates were largest immediately after the first irrigation and decreased for subsequent irrigations.

Denitrification fluxes tended to decrease quickly within one to two days after irrigation. The soil-water pressure head values for one to two days after irrigation corresponded fairly closely with those from experiments of Rolston *et al.* (1978) for constant water content plots. This very rapid decrease in denitrification fluxes soon after irrigation was most likely due to rapid redistribution of the soil water deeper into the soil profile resulting in oxygen ( $\text{O}_2$ ) diffusing into the soil pores and a decrease in the amount of anoxic soil volume.

3. The presence of added organic C greatly increases denitrification rates and total amounts due to the availability of C derived from the added crop materials.

The effect of C in the denitrification process is very important, especially that from crop or manure additions. However, simulations using the denitrification model indicate that soil C levels or organic matter levels can be increased by two or three times with only slight increases in

denitrification. This is due to the fact that only a small proportion of the total organic C is available for denitrification.

4. In general, the plots irrigated frequently, with small amounts of water, resulted in the greatest amount of denitrification.

Those plots receiving irrigation only once every two weeks resulted in very small amounts of denitrification and were much smaller than the more frequently irrigated treatments. This phenomenon of greatest denitrification under the most frequently irrigated plots is partially due to the initial distribution of the added  $\text{NO}_3^-$  fertilizer during the first irrigation.  $\text{NO}_3^-$  fertilizer was applied uniformly during the first irrigation so that the  $\text{NO}_3^-$  band was distributed over a much narrower depth interval for the frequently irrigated experiments than that of the less frequently irrigated experiments. Another important factor affecting the amount of denitrification for the least frequent irrigations was the fact that the soil profile was fairly dry at the initiation of each irrigation. There may have been some time lag in the development of anoxic conditions and microbial activity. However, the water applied to the initially dry profiles redistributed very quickly with little time available for the development of anoxic conditions conducive to denitrification.

5. Total denitrification for plots without straw additions compared reasonably well for the  $^{15}\text{N}$  and  $\text{C}_2\text{H}_2$  inhibition methods, although the rates measured at any one day were very much different between the two methods of directly measuring denitrification gases.

These differences in rates at any one time period were attributed to the lag in reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  for the  $^{15}\text{N}$  method and possibly to the development of organisms which could reduce  $\text{N}_2\text{O}$  in the presence of  $\text{C}_2\text{H}_2$ .

6. The  $\text{N}_2\text{O}$  mole fraction was generally small immediately after irrigation and then increased as redistribution of soil water resulted in less anoxic conditions within the wetted soil zone.

The mole fraction as measured by the  $^{15}\text{N}$  and  $\text{C}_2\text{H}_2$  methods compared reasonably well. There was some indication that the  $\text{N}_2\text{O}$  mole fraction tended to decrease with subsequent irrigations possibly due to the effect of  $\text{NO}_3^-$  concentration on the inhibition of  $\text{N}_2\text{O}$  reduction.

7. The addition of plant materials such as barley straw resulted in a decrease in the  $\text{N}_2\text{O}$  mole fraction over those experiments without the addition of barley straw.

This again would be expected since greater anoxic conditions would develop in the plots to which straw was added than those without straw, resulting in more favorable conditions for  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$ .

8. The data on  $\text{N}_2\text{O}$  mole fraction demonstrate that the proportion of  $\text{N}_2\text{O}$  produced during denitrification was very dynamic and variable.

Mole fractions varied from zero to one for treatments without C additions and varied from nearly zero to 0.4 or 0.5 for plots with C additions. The overall  $\text{N}_2\text{O}$  mole fraction throughout all irrigation cycles varied from 0.04 to 0.27.

9. The frequently irrigated plots with small applications of water resulted in higher  $\text{NO}_3^-$  concentrations in the root zone than those plots with less frequent, larger applications of water.

The most frequently irrigated plots also resulted in greater plant uptake of fertilizer N, most likely due to higher  $\text{NO}_3^-$  concentrations in the root zone, and soil-water contents potentially more conducive to plant growth. The most frequently irrigated plots also tended to lose less fertilizer by leaching than that in the least frequently irrigated plots. A water management program using small irrigations several times per week would tend to increase denitrification. However, the increase in denitrification may be more than compensated by less leaching and more plant uptake of applied N.

10. The denitrification simulation model was able to reasonably predict rates and total amounts of denitrification with a minimum amount of model calibration.

First order kinetics with respect to  $\text{NO}_3^-$  concentration gave the best prediction of denitrification rates and total amounts for all plots. This does not mean that denitrification per se followed first-order kinetics due to the fact that diffusion of  $\text{NO}_3^-$  to anoxic zones may be the primary mechanism resulting in a better fit using first-order than zero-order kinetics. The model is very sensitive to soil-water content, which is expected as previous data indicated that the very dynamic nature of denitrification is dependent upon the amount of water in the soil. It may be better to use an  $\text{O}_2$  diffusion and consumption component to directly describe the anoxic volume development. However, it is expected that this would also be a very sensitive parameter and the necessary input data to do such a calculation are complex and not available. The amount of organic C derived from manure and straw additions, which is available for denitrification, is still somewhat uncertain and needs to be researched.

### SECTION 3

#### RECOMMENDATIONS

The following recommendations for efficient management of water and nitrogen under irrigated conditions can be proposed from this research:

1. To decrease potential  $\text{NO}_3^-$  leaching and pollution of groundwater, small and frequent applications of irrigation water should be made instead of larger, less frequent applications. However, increased labor, equipment, and energy costs must be considered before recommending this management technique as a viable alternative to present irrigation practices.
2. To increase N-use efficiency of applied N fertilizers (decrease denitrification), incorporation of organic materials should be made at least two months prior to  $\text{NO}_3^-$  additions.
3. Future research should be directed at understanding the dynamic effects of C from crop and manure incorporation into the soil on denitrification rates and total amounts. The addition of C greatly increases denitrification, yet there is very little information on the proportion of the applied crop or manure C which is available for denitrification as a function of time after incorporation.
4. In simulation modeling of the denitrification process in field soils, the use of a water function based on relative soil-water saturation is the most useful and easily-determined parameter indirectly accounting for the degree of anoxic soil development. Some means of accounting for degree of anoxic soil development is essential in simulation of denitrification. The applicability of the soil-water function developed in this report to other soils needs further research.

## SECTION 4

### EXPERIMENTAL PROCEDURES

#### FIELD INSTALLATION

Six plots for the  $^{15}\text{N}$  method and three plots for the  $\text{C}_2\text{H}_2$  method were established on Yolo loam soil, a member of the fine-silty, mixed, non-acid, thermic, Typic Xerorthents family, at Davis, California. The Yolo loam soil is a deep, well-drained, alluvial soil in the Sacramento Valley. The soil is similar to other soils of extensive acreage. The schematic diagram of the experimental location and the treatment layout is given in Figure 1. Each of

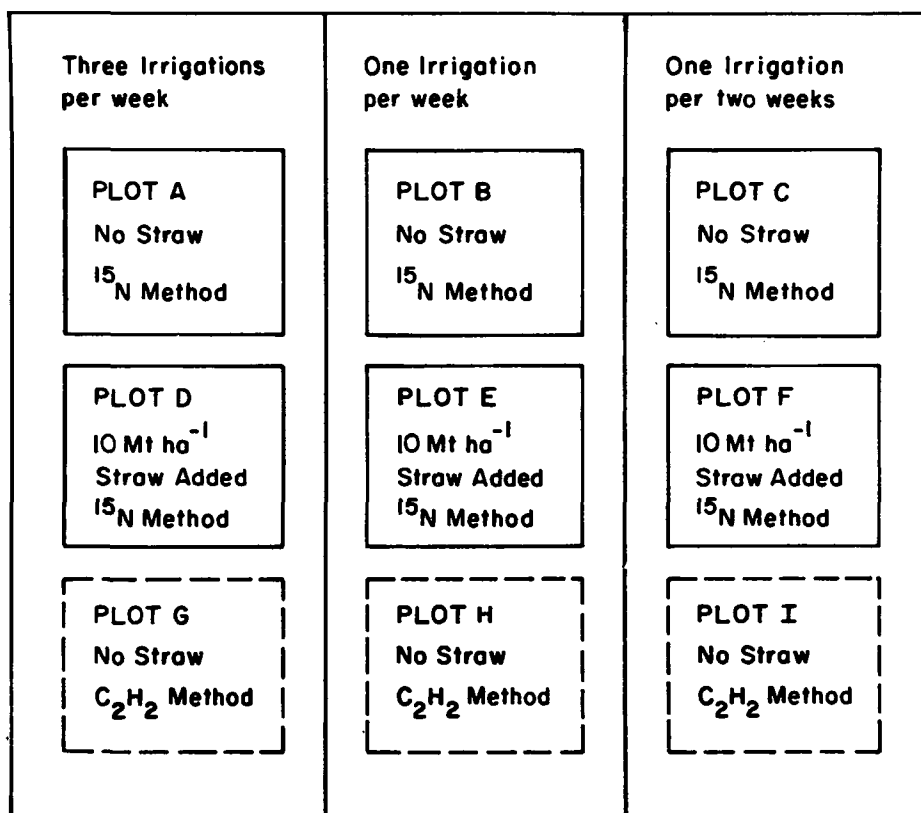


Figure 1. Schematic diagram of experimental location and the treatment layout. The area for measuring denitrification by the  $\text{C}_2\text{H}_2$  method did not contain wood borders placed in the soil to a depth of 60 cm.

the six, 1-m<sup>2</sup> plots (A through F) was established with a 60-cm deep redwood barrier around the outside edges of each undisturbed block of soil. Redwood barriers were installed by digging a trench around the 1-m<sup>2</sup> areas, slipping the redwood over the undisturbed block of soil, and backfilling the trench on the outside of the redwood. The space between the wood barrier and the soil on the inside was sealed by pouring melted paraffin into the small crack between the soil and the wood. Each of the six plots was instrumented with tensiometers, soil solution samplers, soil atmosphere samplers, thermocouples, and a neutron access tube. Triplicate soil atmosphere samplers were installed at the 2-, 5-, 15-, 45- and 60-cm soil depths. Triplicate samplers designed to function as tensiometers or solution extractors were installed at 30-, 45-, 60-, and 90-cm depths. Duplicate thermocouples were installed at the 5-cm depth. Soil solution samplers consisted of porous cups glued to polyvinyl chloride tubing. Soil atmosphere samplers consisted of 0.1 cm inside diameter nylon tubing glued into a 5-cm long, 0.25-cm I.D. perforated acrylic plastic tube. For the deeper soil depths, the small diameter nylon tubing was placed inside a 1.3 cm diameter polyvinyl chloride tube and the nylon tubing was glued into a milled plastic tip. For all samplers, the volume of the sampling tubes was very small (less than 1.0 cm<sup>3</sup>). Soil solution samples were obtained by evacuating bottles connected to samplers. Soil atmosphere samples were obtained by withdrawing 1 ml of gas with glass syringes. All gas samples were analyzed within a few hours after sampling.

In addition to the six plots with redwood barriers down to the 60-cm depth, three plots were also established to evaluate the C<sub>2</sub>H<sub>2</sub> method for directly measuring denitrification.

The plots were irrigated by three different irrigation frequencies. Irrigation frequencies were three irrigations per week, one irrigation per week, and one irrigation every two weeks. All plots received the same amount of water which was intended to be 15% greater than evapotranspiration (ET). The plots were irrigated with a spray irrigation system which consisted of spray nozzles on a traveling boom. The irrigation system applied water at a rate of 0.54 cm hr<sup>-1</sup> to Plots A, D, and G; 0.63 cm hr<sup>-1</sup> to Plots B, E, and H; and 0.71 cm hr<sup>-1</sup> to Plots C, F, and I.

In order to establish different C treatments within each of the three irrigation frequencies, three plots were used for which no C additions such as plant residues or weeds were incorporated for one year prior to the experiment. Three plots of each irrigation frequency had 10 MT ha<sup>-1</sup> of chopped barley straw added to the soil approximately two months prior to the initiation of denitrification experiments. Chopped straw was mixed in the top 10 cm of the soil surface. All plots and the surrounding buffer areas were planted with perennial ryegrass (Lolium perenne). The grass was planted on the plots approximately two months prior to the initiation of denitrification experiments. The C<sub>2</sub>H<sub>2</sub> inhibition plots did not have straw additions. Table 1 gives the plot labeling system and the irrigation frequency and C treatments for the plots.

Particle size analyses and texture as a function of soil depth for the Yolo loam soil are given in Table 2, and the average bulk density at the field site is given as a function of depth in Figure 2. The bulk density was



TABLE 1. LABELING SYSTEM FOR THE NINE PLOTS AT THREE DIFFERENT IRRIGATION FREQUENCIES AND TWO CARBON ADDITIONS

Plot	Denitrification method	Carbon <sup>*</sup> addition	Irrigation frequency
A	<sup>15</sup> N	0	3 per week
B	<sup>15</sup> N	0	1 per week
C	<sup>15</sup> N	0	1 per 2 weeks
D	<sup>15</sup> N	10 MT ha <sup>-1</sup>	3 per week
E	<sup>15</sup> N	10 MT ha <sup>-1</sup>	1 per week
F	<sup>15</sup> N	10 MT ha <sup>-1</sup>	1 per 2 weeks
G	C <sub>2</sub> H <sub>2</sub>	0	3 per week
H	C <sub>2</sub> H <sub>2</sub>	0	1 per week
I	C <sub>2</sub> H <sub>2</sub>	0	1 per 2 weeks

\* Chopped barley straw incorporated into the top 10 cm of soil.

TABLE 2. PARTICLE SIZE DISTRIBUTION AND TEXTURE WITH SOIL DEPTH

Depth	Sand (%)	Silt (%)	Clay (%)	Texture
0 - 15	41	37	22	Loam
15 - 30	40	37	23	Loam
30 - 60	42	38	20	Loam
60 - 90	38	42	20	Loam
90 - 120	38	42	20	Loam
120 - 150	32	46	22	Silt Loam
150 - 180	25	51	24	Silt Loam

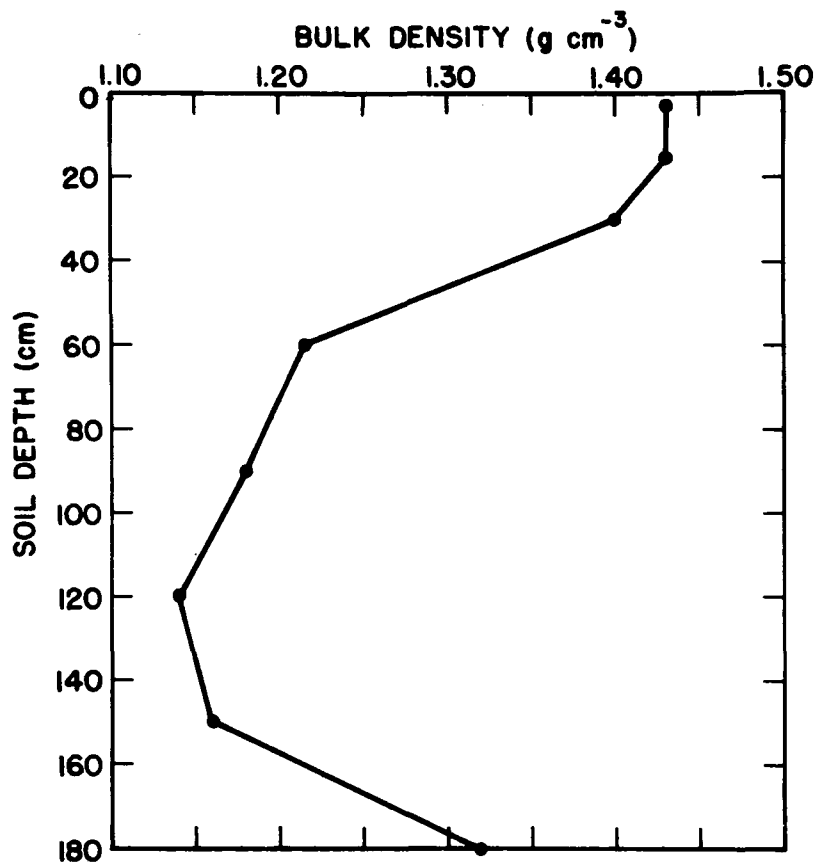


Figure 2. Mean bulk density as a function of soil depth at the experimental site.

greatest near the soil surface with a minimum at the 120-cm depth. Bulk density was determined on triplicate 7.6 cm long, 7.6 cm diameter undisturbed soil cores for each depth. The percentage of organic C as a function of soil depth is given by Figure 3. Organic C was determined on soil samples taken during the experiment conducted by Rolston *et al.* (1978, 1979).

#### EXPERIMENTAL PROCEDURES - FIELD

After the plots had gone through several irrigation cycles and the grass was well established,  $\text{KNO}_3$  solution was applied uniformly to the plots throughout one complete irrigation. Dry  $\text{NO}_3$  fertilizer was also applied to the surrounding border area. The total amounts of fertilizer and the  $^{15}\text{N}$  enrichment of the fertilizer applied to each plot are given in Table 3.

Immediately after irrigation, an airtight cover was placed over the plots. The cover consisted of a thick sheet of acrylic plastic with rubber tubing on the lower edge to make an airtight seal with the top of the redwood border. Samples of the atmosphere beneath the cover were taken after two to four hours with the lid in place and analyzed for  $^{15}\text{N}_2$  and  $\text{N}_2\text{O}$ . Soil atmosphere samples from within the soil profile were also taken soon after

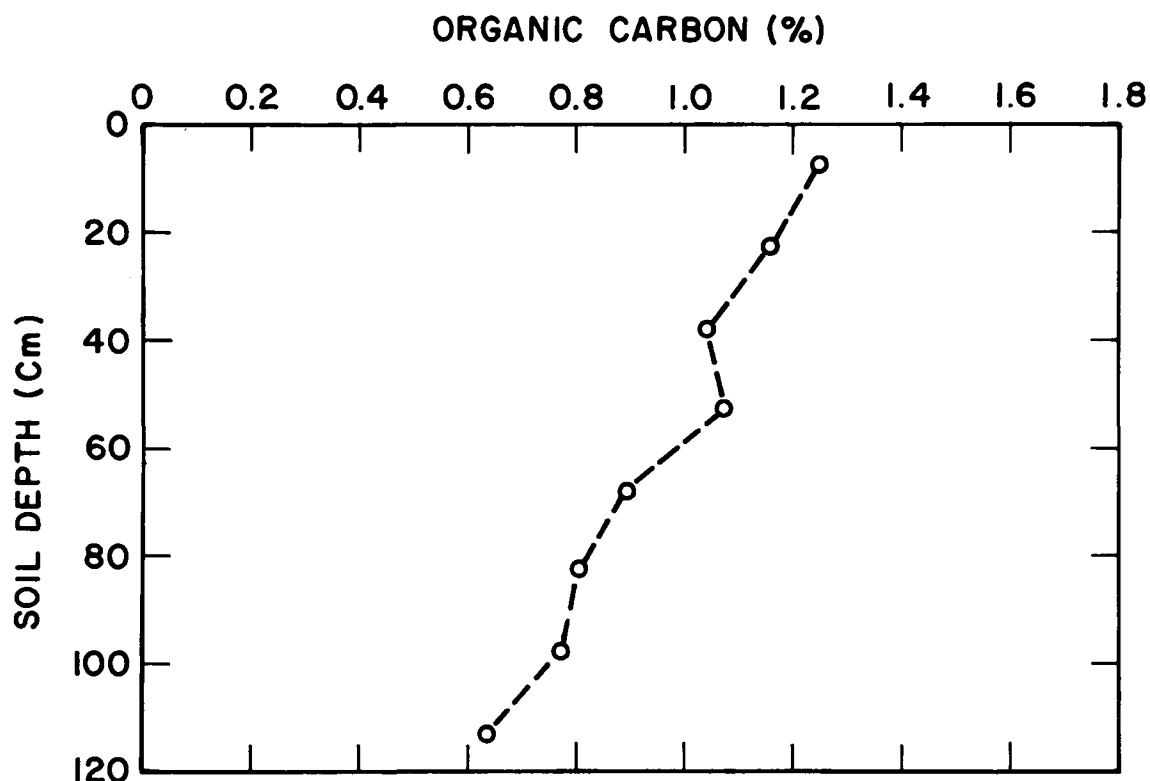


Figure 3. Mean percentage of organic C as a function of soil depth at the experimental site.

applying the fertilizer. Soil atmosphere samples were taken in 1-ml aliquots and  $N_2O$ ,  $O_2$ , and  $N_2$  analyzed by gas chromatography in the laboratory. Another 0.5 to 1 ml of gas was taken to determine  $^{15}N_2$  with the mass spectrometer. Gas samples from the profile and samples from beneath the cover were taken several times per day for a few days after irrigation and at less frequent intervals until the next irrigation cycle. The volume of the chambers placed over the plots are also given in Table 3. By using the volume of the chambers, the  $^{15}N$  enrichment of the applied fertilizer, the precision of measuring  $^{15}N_2$  by the mass spectrometer, and the time period that covers remained over the plots for each sampling period, a minimum detection limit for  $^{15}N_2$  of 0.1 to 0.2 kg N ha<sup>-1</sup> day<sup>-1</sup> was determined. Thus, for any flux smaller than this limit, it is uncertain whether those values are real or not. The minimum detection limit for  $N_2O$  was at least two orders of magnitude smaller than that for  $^{15}N_2$ .

For measurement of denitrification with the  $C_2H_2$  inhibition method, the three main plots (G, H, I) were divided into six sub-plots (0.05 m<sup>2</sup>) which were bounded by 25 cm deep, acrylic plastic barriers, protruding 10 cm above the soil surface. The sub-plots were separated by at least two meters. On three of the sub-plots  $C_2H_2$  flowed slowly (one liter hr<sup>-1</sup> for one hour) into the soil profile through six, 1-m long, perforated, acrylic plastic

TABLE 3. CHARACTERISTICS OF  $^{15}\text{N}$  PLOTS

Plot	Area ( $\text{m}^2$ )	Volume of Chamber ( $\text{m}^3$ )	Fertilizer (kg N/ha)	% $^{15}\text{N}$ excess of fertilizer	Starting date
A	1.0	0.0289	281	58.7	7/3/78
B	1.0	0.316	284	58.7	7/4/78
C	1.0	0.276	282	58.7	7/10/78
D	1.0	0.0265	288	59.8	8/28/78
E	1.0	0.0269	288	59.8	8/29/78
F	1.0	0.0349	287	55.9	9/4/78

tubes. The chambers for measuring  $\text{N}_2\text{O}$  flux were placed over the soil one hour after the  $\text{C}_2\text{H}_2$  flow had stopped. The six sub-plots, three with and three without  $\text{C}_2\text{H}_2$ , were subjected to the same three irrigation frequencies as those plots to which  $^{15}\text{N}$  was applied. (Table 1 and Figure 1.)

After two complete irrigation cycles,  $\text{KNO}_3$  solution equivalent to  $300 \text{ kg N ha}^{-1}$  were uniformly applied as for the  $^{15}\text{N}$  method, to a  $1\text{-m}^2$  area, enclosing each plot. Consequently,  $\text{NO}_3$  fertilizer was also applied to the surrounding border area. Six hours after applying the fertilizer solution, an airtight cover was placed over the plots and the enclosed air space ( $7.5$  liters) above the soil was slowly but continuously swept by drawing air through the chamber at a flow rate of  $25 \text{ liters hr}^{-1}$  for three hours. The gas swept from the cover was passed through dehydrite and ascarite to remove  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , respectively, and finally through a  $5 \text{ \AA}$  molecular sieve trap which quantitatively adsorbed  $\text{N}_2\text{O}$  (Hahn, 1972; Ryden *et al.*, 1979). A schematic diagram of the apparatus for measuring  $\text{N}_2\text{O}$  evolved using the  $\text{C}_2\text{H}_2$  inhibition method is given by Figure 4. The recovery of  $\text{N}_2\text{O}$  from the  $5 \text{ \AA}$  molecular sieve was carried out as described by Ryden *et al.* (1979). The minimum detectable flux of  $\text{N}_2\text{O}$  using the molecular sieve trap was approximately  $0.005 \text{ kg N ha}^{-1} \text{ day}^{-1}$ .

Soil solution samples were taken at two times during the experiment. The grass of the plots was cut periodically and the total clippings were dried for analyses. Soil samples were taken midway through the experimental period and at the end of the experimental period for Plots A, B, and C. Soil samples were taken only at the end of the experimental period for Plots D, E, and F. Soil samples were taken in  $15\text{-cm}$  increments down to  $120 \text{ cm}$ . The samples consisted of ten separate holes taken with a Veihmeyer tube within the  $1\text{-m}^2$  plots. The samples were combined to give two samples at each depth for analyses.

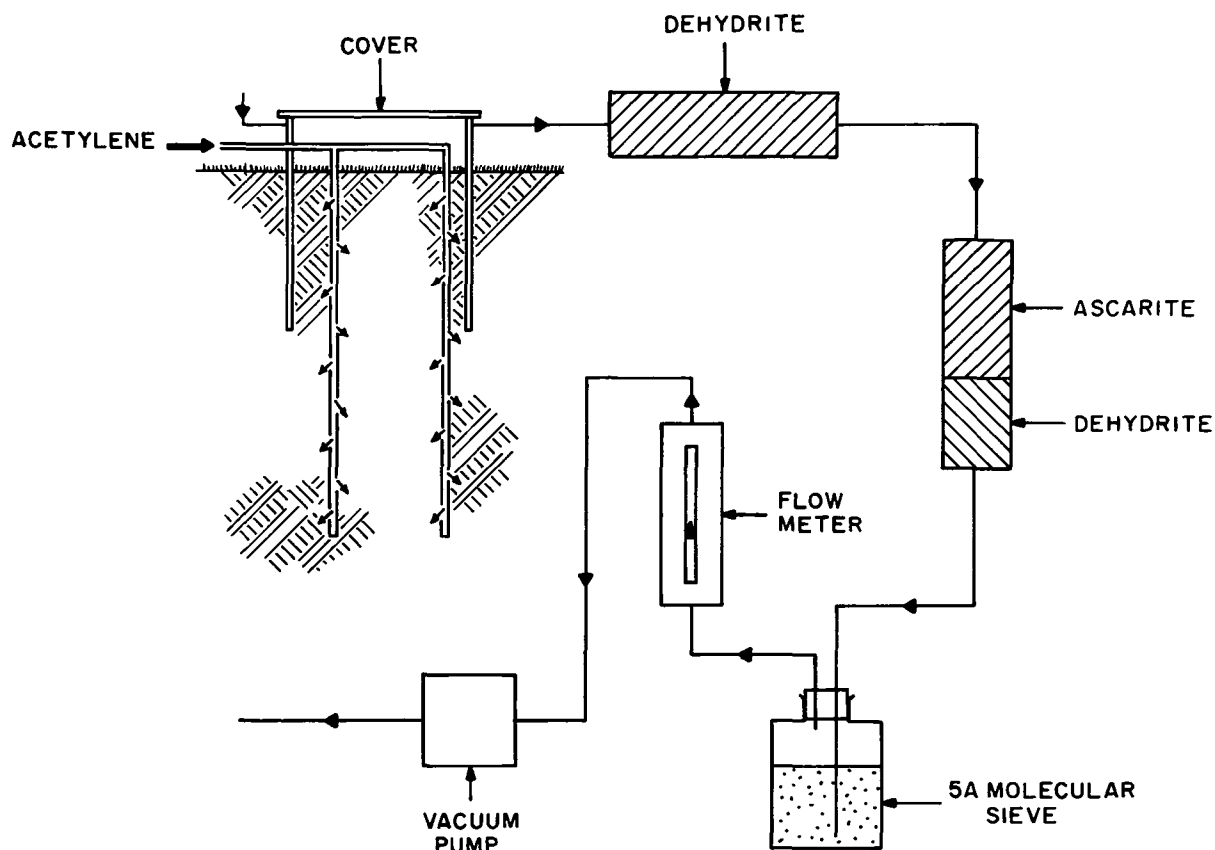


Figure 4. Schematic diagram of the apparatus for measuring  $\text{N}_2\text{O}$  evolved using the  $\text{C}_2\text{H}_2$  inhibition method.

#### ANALYTICAL TECHNIQUES

Oxygen,  $\text{N}_2$ , and  $\text{C}_2\text{H}_2$  were analyzed by gas chromatography with a thermal conductivity detector. The concentration of  $\text{N}_2\text{O}$  in the gas samples was determined by chromatography using a hot  $^{63}\text{Ni}$  electron capture detector as described by Rasmussen *et al.* (1976). The isotopic composition of N in gas samples was determined on samples scrubbed for  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  vapor and directly injected into the mass spectrometer. Details for determining isotopic composition of N by mass spectrometry is given by Rittenberg (1948).

Soil samples were analyzed for extractable (inorganic) and digestible (organic) N and soil solution samples were analyzed for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$ . A soil sample was extracted with 1.0 N KCl and the solution analyzed by the magnesium oxide-devarda alloy reduction technique. The extraction procedure removed solution  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and exchangeable  $\text{NH}_4^+$ . The  $\text{NH}_4^+$  and  $\text{NO}_2^-$  concentrations in all soil and soil solution samples were negligible. The Kjeldahl method was used to determine the total digestible N in soil and plant samples. Two-gram samples of soil were digested with 36 N  $\text{H}_2\text{SO}_4$  and salts ( $\text{K}_2\text{SO}_4$ ,  $\text{CuSO}_4$ , and selenium) for approximately 17 hours to convert the N to  $\text{NH}_4^+$ . The same procedure was used for the plant digests except that 0.25

g of plant material were used and the digestion time was 6 hours. The N in the digest was determined by titration of the  $\text{NH}_4^+$  liberated by distillation of the digest with 40% NaOH. Detailed procedures for determination of N in soil, plant, and soil solution samples were given by Bremner (1965).

The soil for organic C determination was ground to pass a 2mm sieve or finer. A subsample was then thoroughly ground with a pica mill to pass a 60 mesh sieve. Approximately 0.2 grams of the soil sample were placed in a crucible to which a small amount of iron and tin accelerator was added. The sample was covered with a single hole lid and placed into an induction furnace. The  $\text{CO}_2$  produced was collected in a Nesbit tower containing ascarite. The tower was weighed before and after the burn to determine the amount of  $\text{CO}_2$  trapped. Detailed procedures for determination of organic C in soil were given by Allison (1965). There was no difference in the % C between a soil sample that had been extracted with KCl and a sample that had not been extracted.

#### ANALYTICAL QUALITY CONTROL

To insure accuracy of the results all analytical methods were checked periodically with standard samples. For gas chromatography and mass spectrometer analyses, samples of standard gas were analyzed at least every twenty samples. Chemical techniques for determining inorganic and organic N in soil and soil solution samples and plant N were tested by evaluating standard samples at least every 30 samples. In addition, duplicate soil, soil solution, and plant samples were always used. If one duplicate varied by more than 5% from the other, samples were rerun. Also, blanks (deionized water) were run every 15 samples to check for contamination.

## SECTION 5

### RESULTS AND DISCUSSION

#### PLOT CHARACTERISTICS

Temperatures at the 5-cm soil depth as a function of time during the experimental period are given by Figure 5. The arrows indicate the time that fertilizer was applied to particular plots. Plots G, H, and I were conducted at the same time as Plots A, B, and C. Soil temperature remained relatively constant during most of the measurements on Plots A, B, C, G, H, and I. However, on Plots D, E, and F, the soil temperature tended to decrease with time later in the summer.

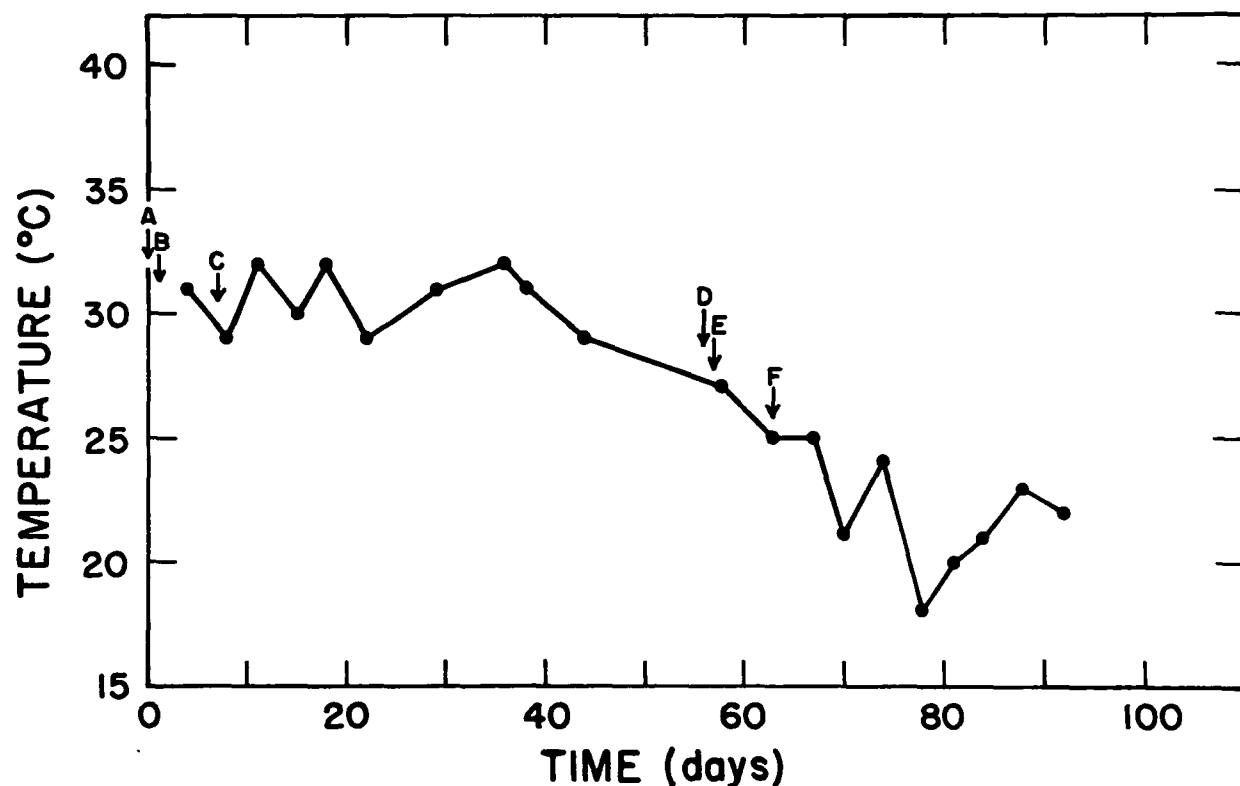


Figure 5. Mean soil temperature at the 5-cm soil depth as a function of time during the experimental period. The arrows and symbols on the graph indicate the time that fertilizer was applied to the various plots.

The  $O_2$  concentration as a function of soil depth for two or three sampling times for the six  $^{15}N$  plots, are given in Figure 6. These data represent typical measurements after irrigation. It can be seen that for

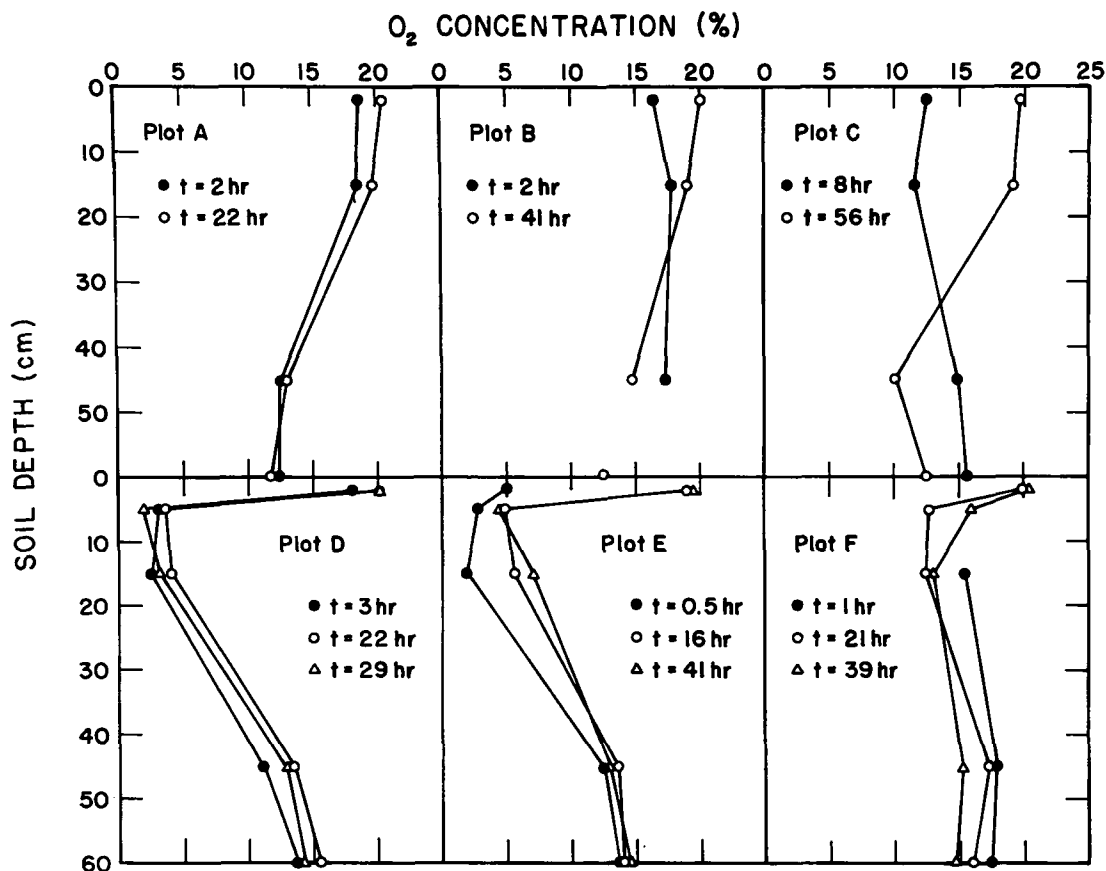


Figure 6.  $O_2$  concentration as a function of soil depth for two to three sampling times after irrigation for each of the six plots.

Plots A, B, and C (no C additions) that  $O_2$  concentrations were relatively high, even within a few hours after irrigation. Oxygen concentrations did not decrease below 10% at any depth within the profile. The effect of the straw addition is demonstrated by the low  $O_2$  concentrations near the soil surface for Plots D, E, and F. The lowest  $O_2$  concentrations tended to occur immediately after irrigation. There was a slight increase in  $O_2$  concentration as the soil profile drained and water was used by the crop. The concentrations of  $O_2$  in Plot F did not drop below 10%. The small decrease in  $O_2$  was probably due to the fact that irrigation was made only every two weeks. Therefore, the water infiltration and redistribution in the dry profile was relatively rapid with little opportunity for depletion of  $O_2$  within the soil profile. Although  $O_2$  concentration within the soil profiles is not a good indication of denitrification due to the fact that the samples are taken primarily from large pore sequences, these data indicate that one should



expect more denitrification in Plots D, E, and F than in Plots A, B, and C due to the low  $O_2$  concentrations for those plots to which straw had been added.

Table 4 gives the amount of irrigation water applied and the estimated ET for 10 or 11 day periods during the experiment. The ET was estimated from pan evaporation data taken from a grassed area near the experimental plots. The crop ET was estimated from the pan evaporation data and a crop coefficient factor which was determined over many years of experiments relating pan evaporation to ET of grass using lysimeters near the experimental site. For most time periods during the experiment, the amount of irrigation water applied was greater than the estimated ET. The objective was to apply approximately 15% more water by irrigation than was evapotranspired.

TABLE 4. AMOUNT OF IRRIGATION WATER APPLIED AND ESTIMATED EVAPOTRANSPIRATION FOR 10- OR 11-DAY PERIODS DURING THE EXPERIMENTAL PERIOD

Dates	Irrigation water applied (cm)	Estimated evapotranspiration (cm)
7/1 - 7/10	5.7	5.0
7/11 - 7/20	5.7	4.8
7/21 - 7/31	6.0	4.9
8/1 - 8/10	6.0	5.3
8/11 - 8/20	6.0	5.6
8/21 - 8/31	5.2	4.1
9/1 - 9/10	4.6	3.3
9/11 - 9/20	4.0	5.2
9/21 - 9/30	4.0	3.2
10/1 - 10/10	4.0	3.0
Total	51.2	44.4

The soil-water content,  $\theta$  ( $\text{cm}^3\text{cm}^{-3}$ ), for the 15- and 60-cm depths of the six  $^{15}\text{N}$  plots are given as a function of time in Figures 7, 8, 9, and 10. Zero time is initiation of irrigation. The water content data for Plots A and B, Plot C, Plots D and E, and Plot F are given by Figures 7, 8, 9, and 10, respectively. The arrows on each figure indicate the time of irrigation

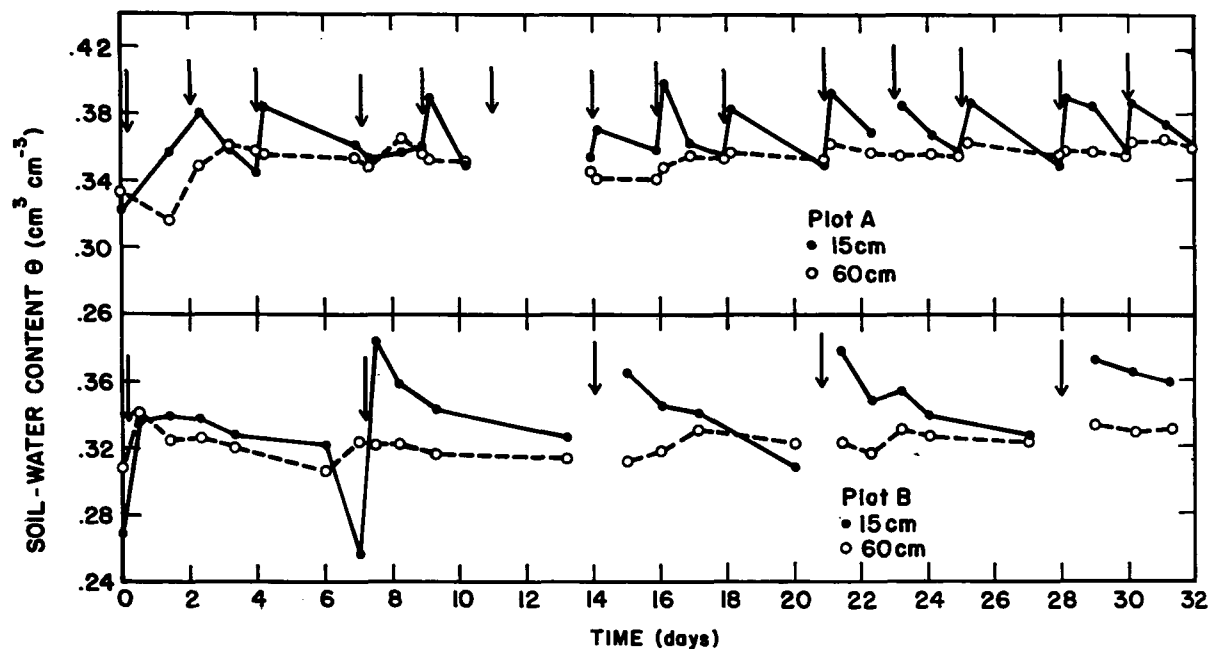


Figure 7. Soil-water content for the 15- and 60-cm soil depths as a function of time for Plots A and B. The data points represent values determined from neutron moisture meter data. The arrows on the figures indicate the times of irrigation.

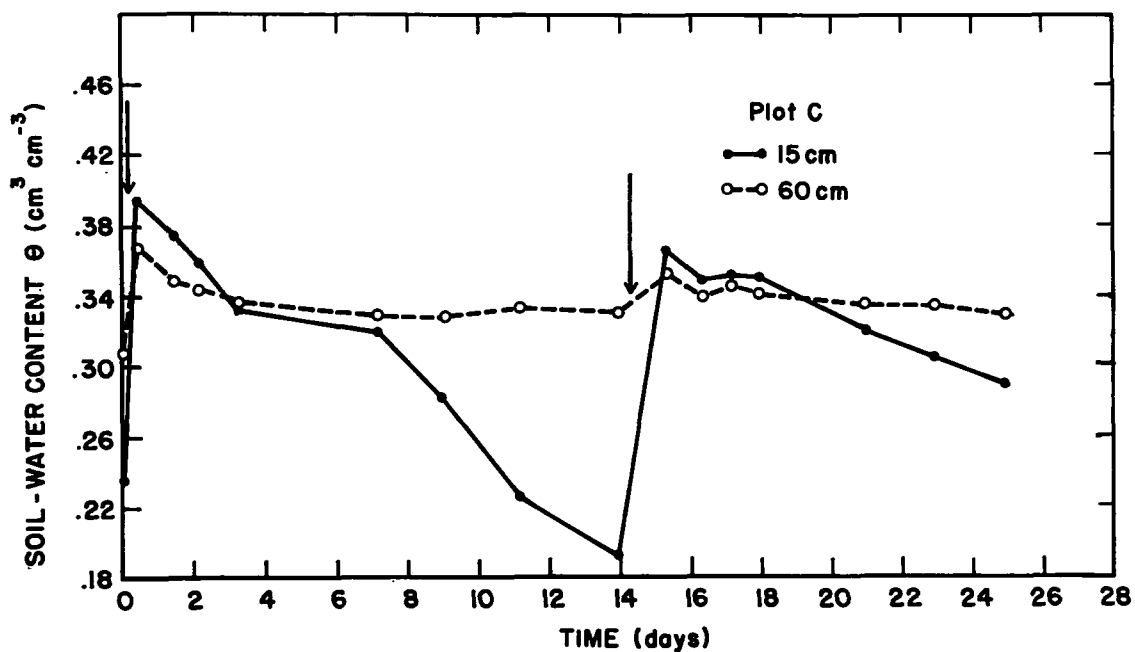


Figure 8. Soil-water content for the 15- and 60-cm soil depths as a function of time for Plot C. The data points represent values determined from neutron moisture meter data. The arrows on the figures indicate the times of irrigation.

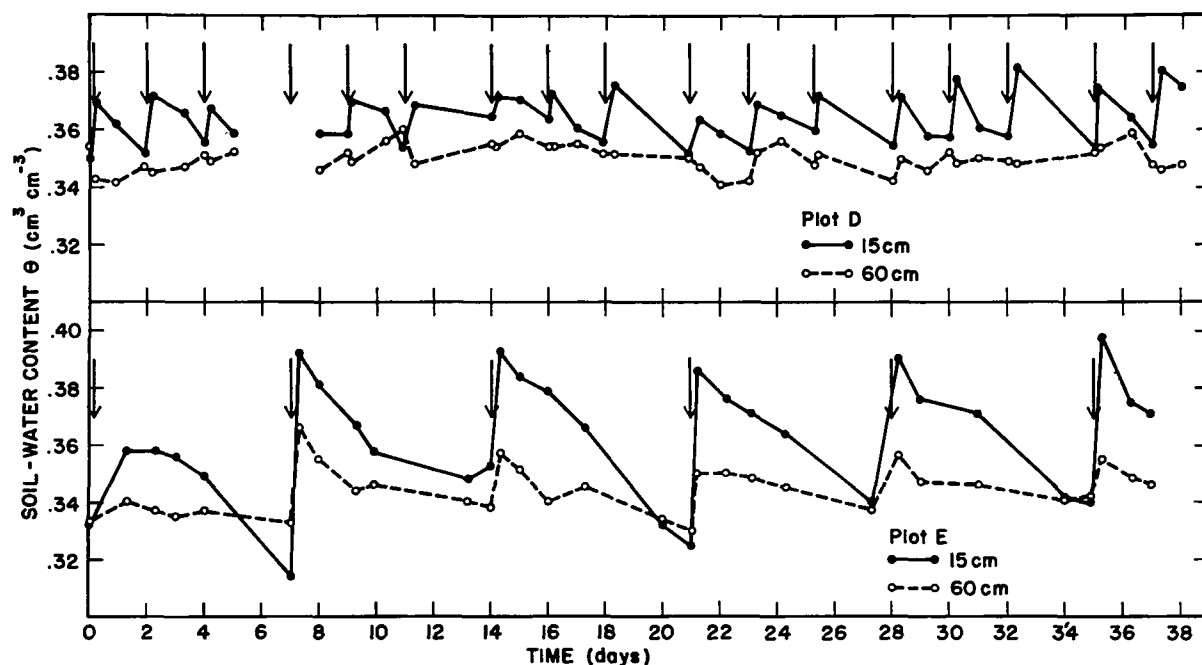


Figure 9. Soil-water content for the 15- and 60-cm soil depths as a function of time for Plots D and E. The data points represent values determined from neutron moisture meter data. The arrows on the figures indicate the times of irrigation.

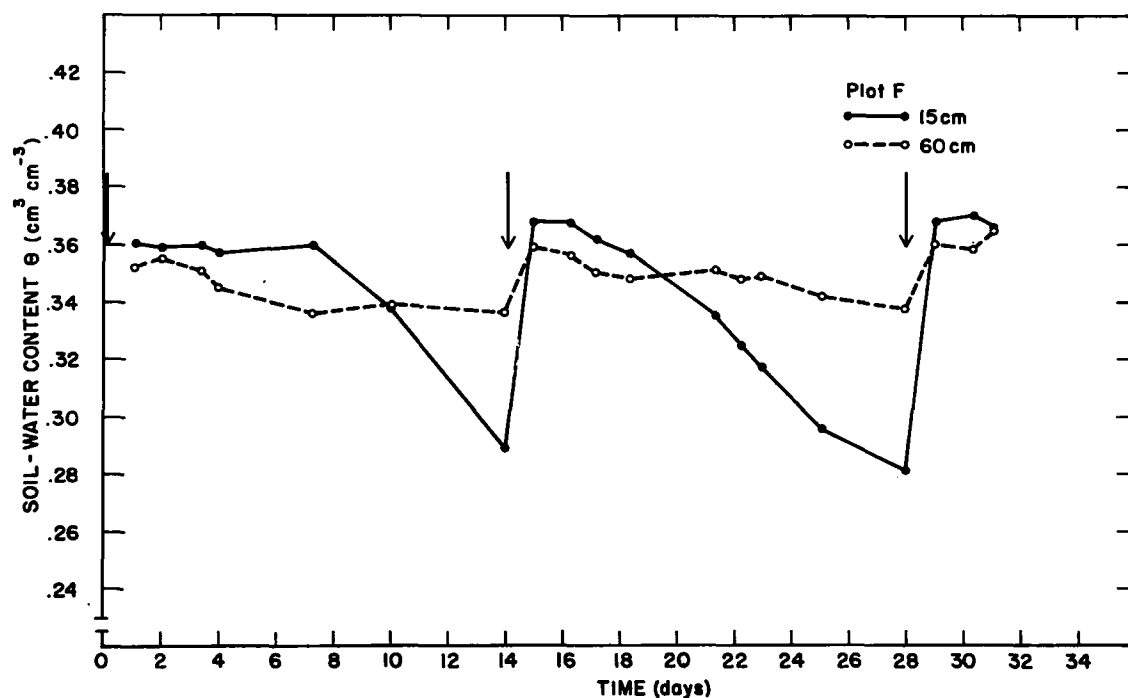


Figure 10. Soil-water content for the 15- and 60-cm soil depths as a function of time for Plot F. The data points represent values determined from neutron moisture meter data. The arrows on the figures indicate the times of irrigation.

for each treatment. As expected, the water content at the 15-cm depth was greatly dependent upon rate of drainage, ET, and irrigation application. The water content at the 15-cm depth increases immediately after irrigation to nearly the saturated water content value and then slowly decreases due to drainage and crop use until the next irrigation. As expected, the water content of the 60-cm depth was less variable and remained fairly constant with slight increases in water content after each irrigation. The magnitude and rate of change of  $\theta$  at the 15-cm depth was strongly dependent upon irrigation frequency as shown in the figures.

The soil-water pressure head,  $h$  (cm of water), at the 30- and 60-cm depths as a function of time are given for Plots A and B, Plot C, and Plots D, E, and F, by Figures 11, 12, and 13, respectively. The arrows on each figure indicate the time of irrigation. The 30- and the 60-cm tensiometers

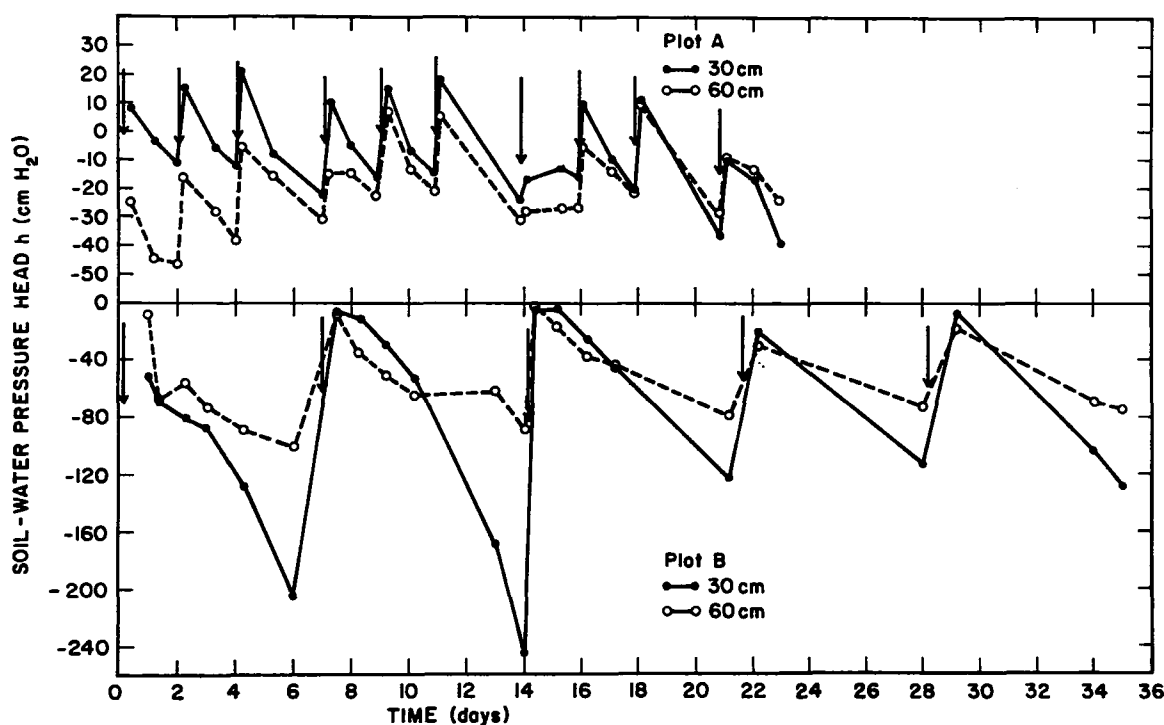


Figure 11. Soil-water pressure head at the 30- and 60-cm soil depths as a function of time for Plots A and B. Each data point represents the mean from triplicate tensiometers at each depth. Arrows give the times of irrigation.

responded fairly quickly to each irrigation for Plot A (irrigated three times per week). The 30-cm depth tensiometer did not decrease below  $h = -40$  cm during the measurement period. For Plots B and C, however, the 30-cm tensiometers dropped down to  $h = -240$  cm and  $h = -600$  cm, respectively. Plots D, E, and F did not show as great a decrease in soil-water pressure head due most likely to decreasing ambient temperatures resulting in less

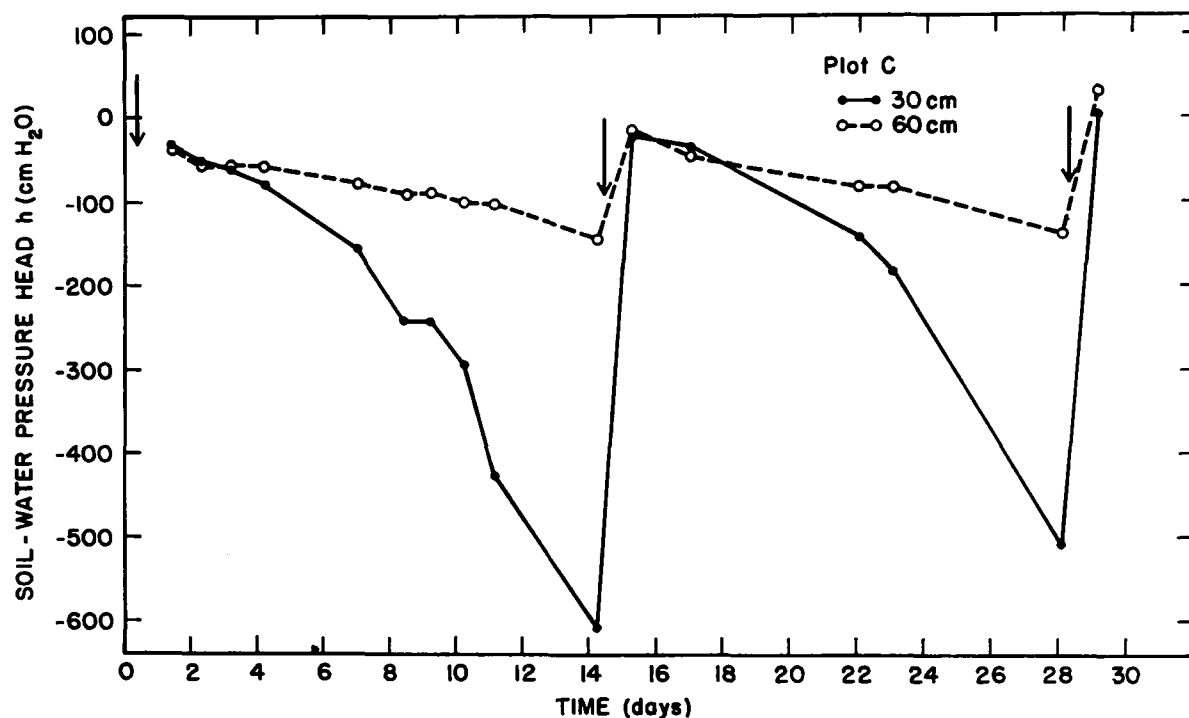


Figure 12. Soil-water pressure head at the 30- and 60-cm soil depths as a function of time for Plot C. Each data point represents the mean from triplicate tensiometers at each depth. Arrows give the times of irrigation.

ET than that anticipated. The experiments described by Rolston *et al.* (1978, 1979) demonstrated for Yolo loam soil, that denitrification became very small after soil-water pressure heads became less than -70 cm of water. Thus, one would expect from the data in Figures 11, 12, and 13 for  $h$  vs. time for all six plots, that denitrification would generally occur for only one or two days after irrigation when  $h$  was greater than -70 cm. The soil water re-distributes rather rapidly in this well-drained, alluvial soil resulting in decreases in  $h$  within a few days after irrigation. Thus, one would expect that the amount of time available for denitrification is relatively small compared to the entire cropping season as long as restrictive layers do not result in a buildup of water at some depth. There is a limited amount of  $h$  data for Plot F because all tensiometers were switched over to soil solution extractors in order to get a sample of the soil solution before the end of the experimental period.

#### N<sub>2</sub> AND N<sub>2</sub>O SURFACE FLUXES

The N<sub>2</sub>O and N<sub>2</sub> fluxes at the soil surface as measured by the accumulation of gases beneath the covers are given as a function of time for the six <sup>15</sup>N plots in Figures 14, 15, 16, 17, 18, and 19. The N<sub>2</sub> flux is given by the open circles and broken lines, whereas the N<sub>2</sub>O flux is given by the solid circles and solid lines. It is apparent that many of the data points for N<sub>2</sub>

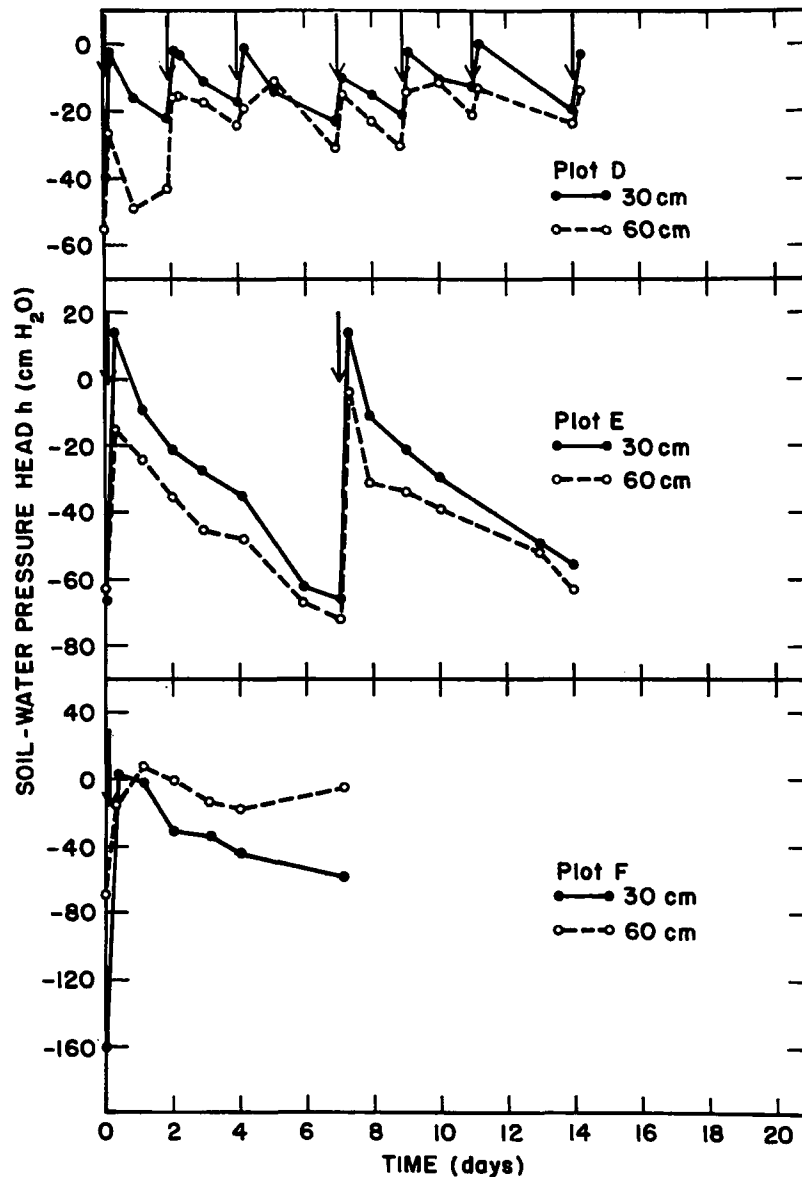


Figure 13. Soil-water pressure head at the 30- and 60-cm soil depths as a function of time for Plots D, E, and F. Each data point represents the mean from triplicate tensiometers at each depth. Arrows give the times of irrigation.

flux fall below the minimum detection limit of 0.1 to 0.2 kg N ha<sup>-1</sup> day<sup>-1</sup> for Figures 14, 15, and 16. Thus, the N<sub>2</sub> flux is highly uncertain for the three plots (A, B, C) which did not receive C additions. Due to an unfortunate accident with Plot A, within one day after fertilizer application, the cover over the plots was left unshaded and high temperatures built up beneath the cover with considerable damage to the grass. ET and water movement for Plot A was thus expected to be much different from that of the other plots.

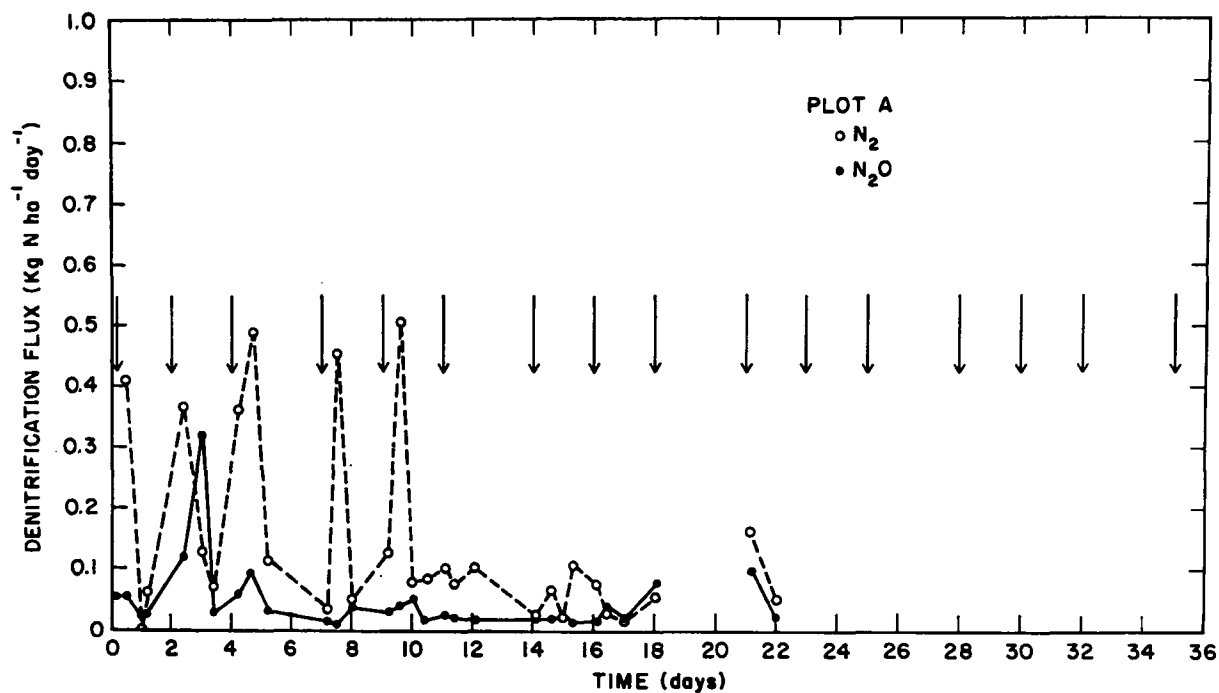


Figure 14. The  $N_2O$  and  $N_2$  flux at the soil surface as measured by the accumulation of gases beneath covers as a function of time for Plot A. The open circles are for  $N_2$  and the closed circles are for  $N_2O$ . The arrows give the times of irrigation.

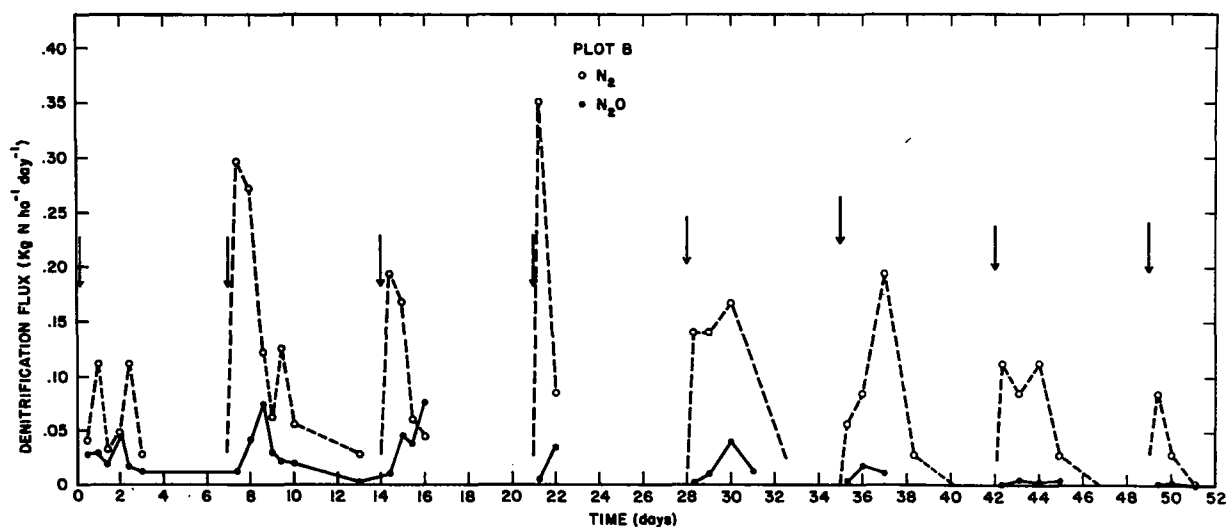


Figure 15. The  $N_2O$  and  $N_2$  flux at the soil surface as measured by the accumulation of gases beneath covers as a function of time for Plot B. The open circles are for  $N_2$  and the closed circles are for  $N_2O$ . The arrows give the times of irrigation.

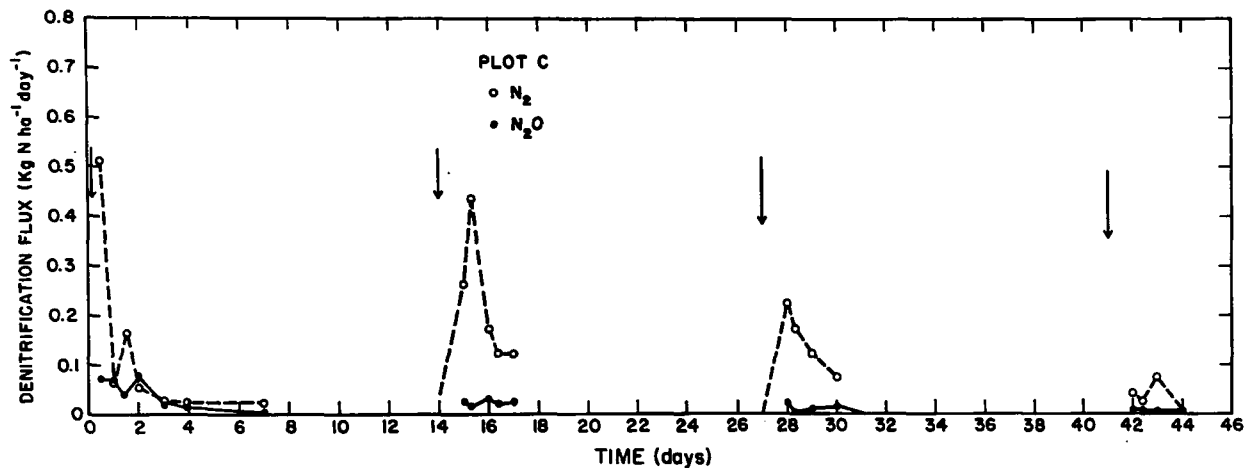


Figure 16. The  $N_2O$  and  $N_2$  flux at the soil surface as measured by the accumulation of gases beneath covers as a function of time for Plot C. The open circles are for  $N_2$  and the closed circles are for  $N_2O$ . The arrows give the times of irrigation.

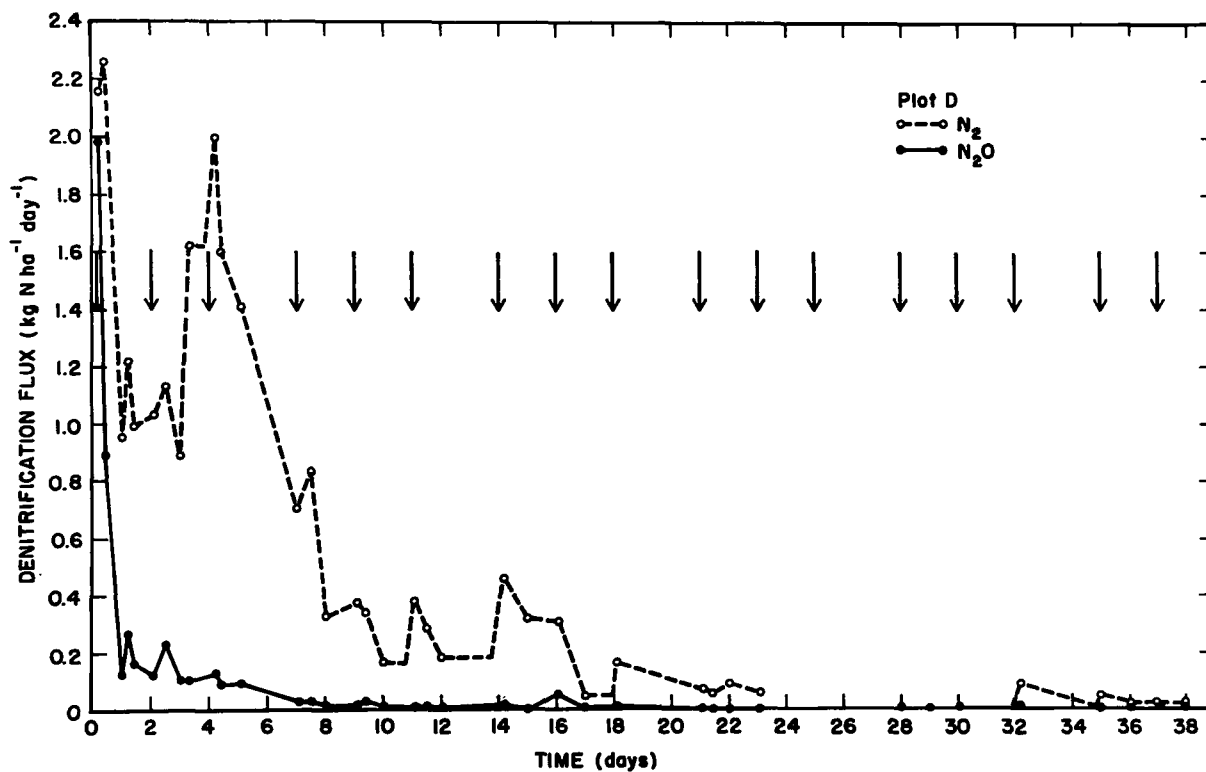


Figure 17. The  $N_2O$  and  $N_2$  flux at the soil surface as measured by the accumulation of gases beneath covers as a function of time for Plot D. The open circles are for  $N_2$  and the closed circles are for  $N_2O$ . The arrows give the times of irrigation.



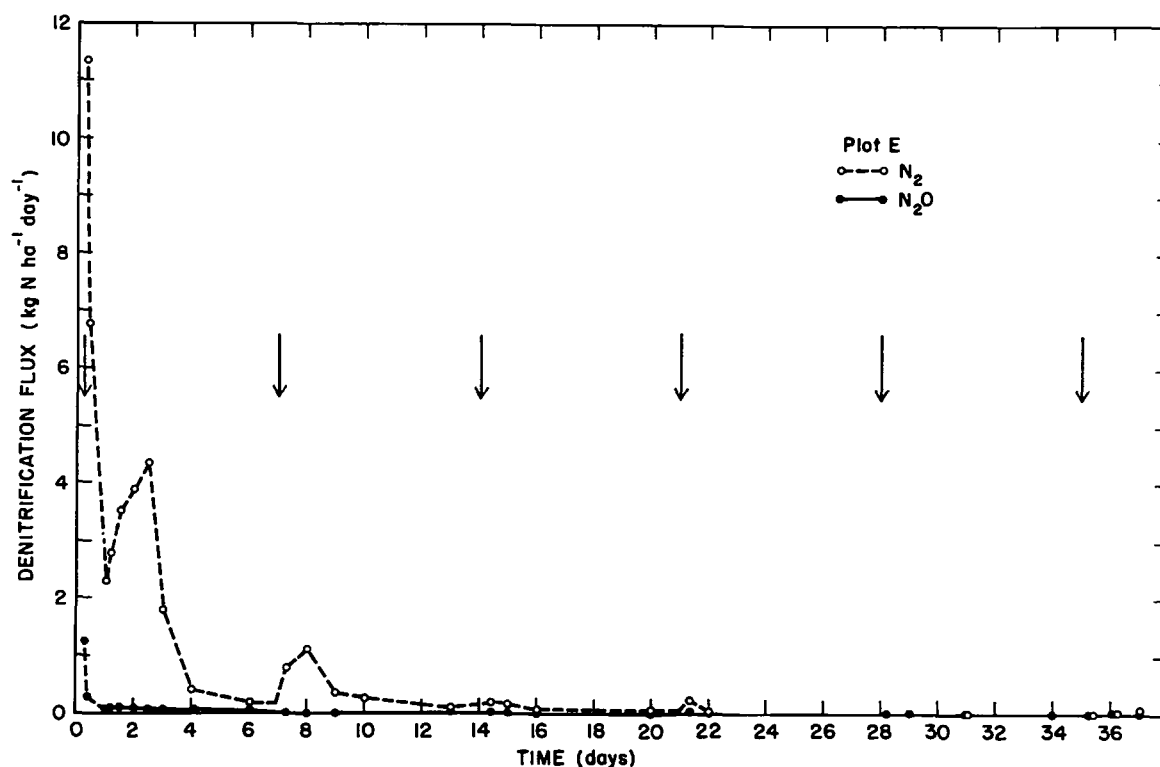


Figure 18. The  $N_2O$  and  $N_2$  flux at the soil surface as measured by the accumulation of gases beneath covers as a function of time for Plot E. The open circles are for  $N_2$  and the closed circles are for  $N_2O$ . The arrows give the times of irrigation.

$NO_3^-$  was apparently leached from the top part of Plot A by 22 days (Figure 14) with the result that denitrification essentially ceased by Day 22. For Plots B and C, however, small amounts of denitrification were measured up to between 40 and 50 days after fertilizer application, although rates were very small as irrigation progressed. In general, the flux of  $N_2$  was much greater than the flux of  $N_2O$ .

The  $N_2$  and  $N_2O$  flux for Plots D, E, and F was greatly increased over that of Plots A, B, and C due to the addition of barley straw. There was a tendency for denitrification to approach zero much sooner for Plots D, E, and F than that for the plots which did not receive C. This may be due to differences in the amount of water movement through the soil profile with leaching of  $NO_3^-$  from the upper part of the soil profile where low  $O_2$  and high C values were maintained. Even with the addition of a relatively large amount of crop residue into the soil profile, the denitrification rates were relatively small compared to rates observed by Rolston *et al.* (1978) for plots maintained uniformly wet for long time periods.

A comparison of the total denitrification gas flux as a function of time measured by the  $^{15}N$  and  $C_2H_2$  methods is given by Figure 20. The total

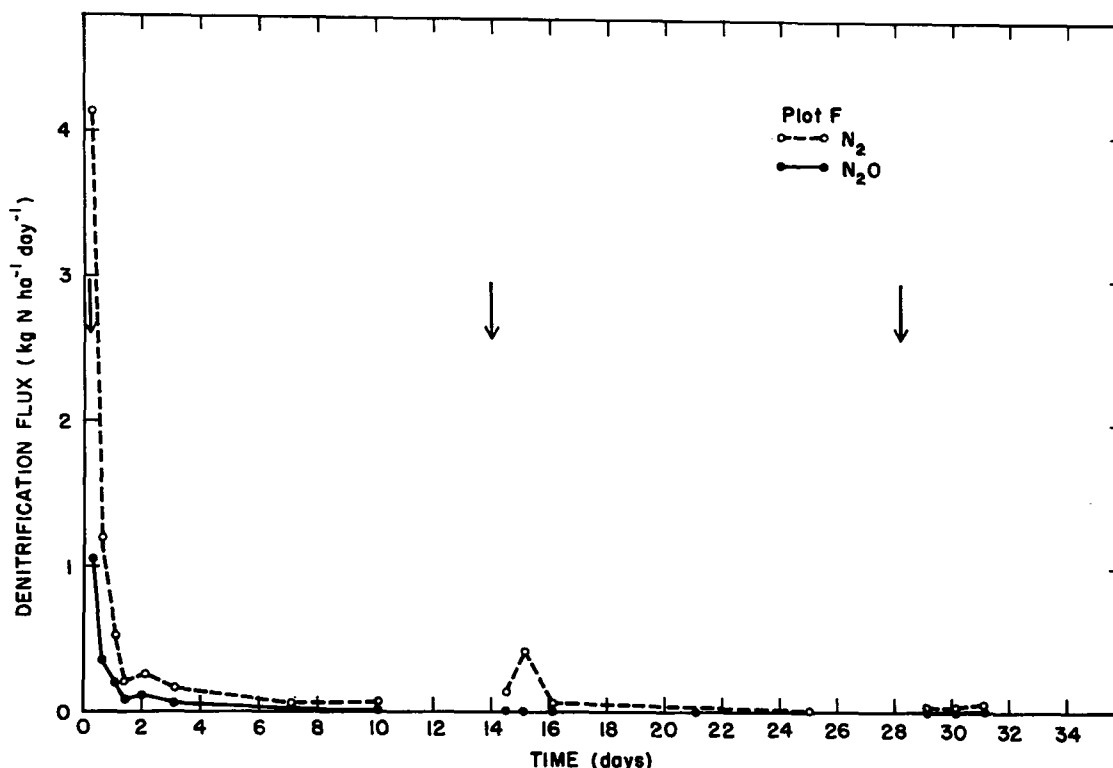


Figure 19. The  $N_2O$  and  $N_2$  flux at the soil surface as measured by the accumulation of gases beneath covers as a function of time for Plot F. The open circles are for  $N_2$  and the closed circles are for  $N_2O$ . The arrows give the times of irrigation.

denitrification gas flux for the  $^{15}N$  method is the sum of  $^{15}N_2$  and  $N_2O$  gas fluxes. The total denitrification gas flux for the  $C_2H_2$  method is only  $N_2O$  flux since reduction of  $N_2O$  to  $N_2$  was inhibited. The denitrification flux plotted in Figure 20 is the total of  $N_2$  and  $N_2O$  for Plots A, B, C, G, H, and I at any sampling time. The pattern of gas flux produced during denitrification was similar for both methods with peak flux occurring shortly after application of water. It was observed, however, that denitrification at any one time during the repeated irrigation cycles was not equal for both methods. For Plots B and H the flux of gas produced during denitrification as measured by the  $C_2H_2$  method was initially greater than that measured by the  $^{15}N$  method. For example, 0.42, 0.66, and 0.46  $kg\ N\ ha^{-1}$  of denitrification gas was evolved in the presence of  $C_2H_2$  and 0.26, 0.52, and 0.27  $kg\ N\ ha^{-1}$  of denitrification gases were evolved in the absence of  $C_2H_2$  using the  $^{15}N$  method during the first three days after irrigation for the first three applications, respectively. Following this, however, the opposite was true when only 0.1 and 0.06  $kg\ N\ ha^{-1}$  of denitrification gases were evolved in the presence of  $C_2H_2$  and 0.28 and 0.19  $kg\ N\ ha^{-1}$  of denitrification gases were evolved in the absence of  $C_2H_2$  by the  $^{15}N$  method in the first two days after the fifth and sixth irrigation applications, respectively. For Plots A and G, the amounts of denitrification gases evolved in the first two days after the initial

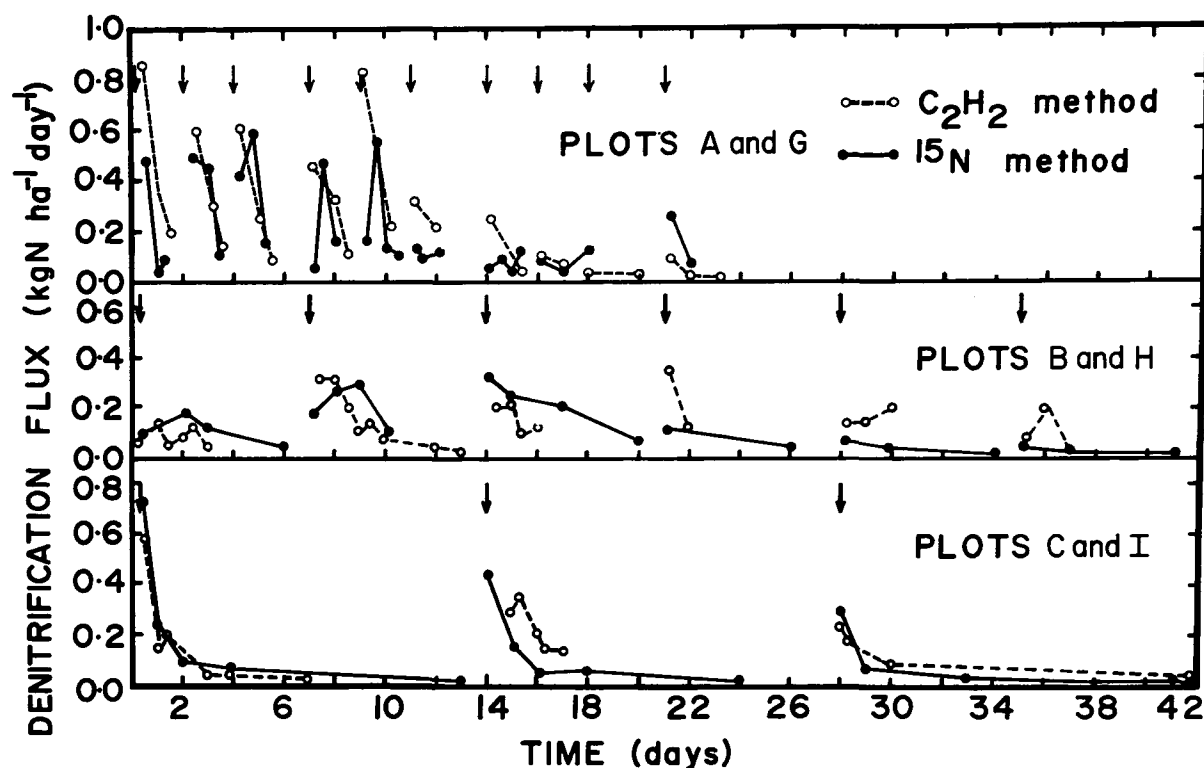


Figure 20. Comparison of the denitrification flux as a function of time as measured by the  $^{15}\text{N}$  and  $\text{C}_2\text{H}_2$  inhibition methods for Plots A, B, C, G, H, and I. The denitrification flux is the sum of  $\text{N}_2$  plus  $\text{N}_2\text{O}$ . The broken lines and open circles are for the  $\text{C}_2\text{H}_2$  method. The closed circles and solid line are for the  $^{15}\text{N}$  method. Arrows give the times of irrigation.

irrigation in the presence and absence of  $\text{C}_2\text{H}_2$  were  $0.93$  and  $0.72 \text{ kg N ha}^{-1}$ , respectively. In the same time period, after the tenth irrigation, the amounts of denitrification gases evolved in the presence and absence of  $\text{C}_2\text{H}_2$  were  $0.12$  and  $0.33 \text{ kg N ha}^{-1}$ , respectively. For Plots C and I, the amounts of denitrification gases evolved in the first two days after the initial irrigation in the presence and absence of  $\text{C}_2\text{H}_2$  were  $0.82$  and  $0.61 \text{ kg N ha}^{-1}$ , respectively. For a two day period after the third irrigation, the amounts of denitrification gases evolved in Plots C and I in the presence and absence of  $\text{C}_2\text{H}_2$  were  $0.35$  and  $0.43 \text{ kg N ha}^{-1}$ , respectively.

The data of Figure 20 suggest that the production of denitrification gases during the initial stages of denitrification can be increased by the presence of  $\text{C}_2\text{H}_2$ . This increase results from the fact that  $\text{N}_2\text{O}$  was converted to  $\text{N}_2$  in the absence of  $\text{C}_2\text{H}_2$  leading to a delay in evolution of  $\text{N}_2$  compared to  $\text{N}_2\text{O}$  from the field soil. Furthermore, after a certain period of time, the presence of  $\text{C}_2\text{H}_2$  can result in a decrease in production of  $\text{N}_2\text{O}$  compared to  $\text{N}_2\text{O}$  and  $^{15}\text{N}_2$  in the absence of  $\text{C}_2\text{H}_2$ . Part of the reason for this behavior may be that  $\text{O}_2$  concentrations were slightly reduced in the presence of  $\text{C}_2\text{H}_2$ . Also

Yeomans and Beauchamp (1978) using soil incubation studies, reported that  $C_2H_2$  is effective in inhibiting  $N_2O$  reduction for a limited time only in the continued presence of  $C_2H_2$  such that  $N_2O$  could eventually be converted to  $N_2$ . It is possible that several applications of  $C_2H_2$  at the same site in the field soil in order to measure variations in  $N_2O$  flux at frequent intervals could facilitate the growth of organisms capable of reducing  $N_2O$  in the presence of  $C_2H_2$ . The results of the present study indicate that such a population may have developed when  $N_2O$  flux in the presence of  $C_2H_2$  became lower than that of  $N_2O$  and  $N_2$  in the absence of  $C_2H_2$ . This occurred in Plots G, H, and I after 13, 15, and 17  $C_2H_2$  applications, respectively. The differences between treatments may have resulted from the increased variation in the soil moisture content as irrigation frequency decreased, with a subsequent decrease in soil microbial activity.

It is interesting to note for the denitrification flux comparisons of Figure 20 for Plots A and G that the fluxes were comparable at 22 days. However, it would be expected that fluxes would not be the same for the  $^{15}N$  and  $C_2H_2$  methods since the grass of Plot A was not transpiring, whereas in Plot G the grass was transpiring. One would possibly expect differences in water movement and differences in the residence time of  $NO_3^-$  in the active zone where denitrification was occurring for these two areas. However, gas fluxes were similar indicating that the differences in residence time may not have been that different with or without the grass.

The total amounts of gases produced during denitrification of applied fertilizer N as measured by the  $C_2H_2$  and  $^{15}N$  methods are presented in Table 5. Although denitrification flux at any single time as measured by the two methods was greatly different, only a slightly different total amount of denitrification gases was measured by the two methods. The denitrification of fertilizer in the presence of  $C_2H_2$  for the three treatments (1.4, 1.2, and 1.0% for Plots G, H, and I, respectively) was slightly greater than that using  $^{15}N$  (1.5, 1.1 and 0.7% for Plots A, B, and C, respectively).

The total denitrification as measured by the  $^{15}N$  method for Plots D, E, and F which had received straw are also given in Table 5. It is obvious from Table 5 that the addition of the straw greatly increased denitrification over that without straw addition. However, the total amount denitrified from the straw treatments was still not very large compared to the total amount of fertilizer N applied. This indicates that denitrification fluxes under normal irrigated conditions where the soil profile was not kept continuously wet, is rather small, at least for deep, well-drained alluvial soils such as Yolo. The data of Table 5 show that the least amount of denitrification occurred for the irrigation frequency of one irrigation every two weeks. This small amount of denitrification is due primarily to the fact that the soil is relatively dry for an extended time period and that when irrigation water is applied, infiltration and redistribution of the soil water occurs rapidly resulting in only a very short time period when the soil is anoxic enough for denitrification to occur. The effect of infrequent irrigation is also to move the fertilizer N into the lower part of the root zone, resulting in less  $NO_3^-$  in the upper part of the soil where high C and high water contents may occur simultaneously. For the other two irrigation frequencies, the  $^{15}N$  and  $C_2H_2$  methods show that the largest amount of denitrification occurred for the most

TABLE 5. AMOUNTS OF N<sub>2</sub>O AND N<sub>2</sub> PRODUCED DURING DENITRIFICATION OF ADDED FERTILIZER N AS MEASURED BY THE C<sub>2</sub>H<sub>2</sub> AND <sup>15</sup>N METHODS

Plot	Denitrification (kgN ha <sup>-1</sup> )			$\frac{\text{N}_2\text{O}}{(\text{N}_2\text{O} + \text{N}_2)}$	Loss of fert. N as total denit. (%)
	N <sub>2</sub> O	N <sub>2</sub>	Total		
<sup>15</sup> N Method					
A	1.1	3.0	4.1	0.27	1.5
B	0.6	2.6	3.2	0.19	1.1
C	0.3	1.6	1.9	0.16	0.7
D	1.8	13.1	14.9	0.12	5.2
E	0.8	17.6	18.4	0.04	6.4
F	1.0	4.0	5.1	0.22	1.8
C <sub>2</sub> H <sub>2</sub> Method.					
G	1.0	3.5	4.3	0.23	1.4
H	0.8	2.6	3.4	0.24	1.2
I	0.7	2.0	2.7	0.26	1.0

frequently irrigated plot of three irrigations per week. The soil was kept fairly wet for long time periods and by adding small, frequent amounts of water, the NO<sub>3</sub> tended to remain in the upper portion of the soil profile for longer time periods resulting in more denitrification. For Plots D and E, the irrigation frequency of one irrigation per week (Plot E) gave the greatest amount of denitrification. However, the differences between Plots D and E are small and there is some indication from the water content data (Figure 9) that an impeding layer or a hardpan existed in Plot E which tended to keep water contents higher in the profile for longer time periods creating more anoxic conditions. These results indicate that very frequent irrigations tend to result in the largest amount of denitrification, whereas infrequent irrigations result in the least amount of denitrification.

#### N<sub>2</sub>O MOLE FRACTION

The various proportions of N<sub>2</sub>O and N<sub>2</sub> produced during denitrification is of great interest due to the potential that N<sub>2</sub>O may be contributing to the depletion of the ozone layer of the lower stratosphere. Figures 21 through 26 give N<sub>2</sub>O mole fraction as a function of time for the nine plots of this experiment. Figures 21, 22, and 23 give the N<sub>2</sub>O mole fraction from both the

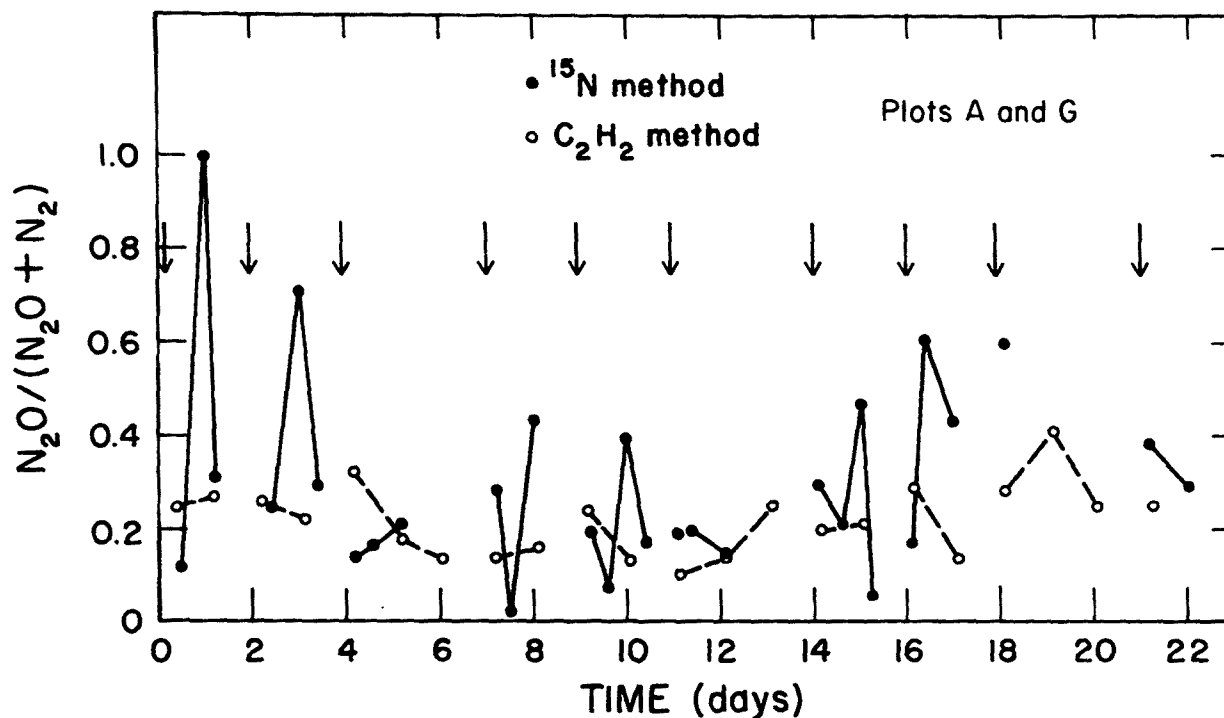


Figure 21. The  $\text{N}_2\text{O}$  mole fraction as a function of time for Plots A and G. The solid lines give the  $\text{N}_2\text{O}$  mole fraction using the  $^{15}\text{N}$  method, and the broken lines give the  $\text{N}_2\text{O}$  mole fraction using the  $\text{C}_2\text{H}_2$  method.

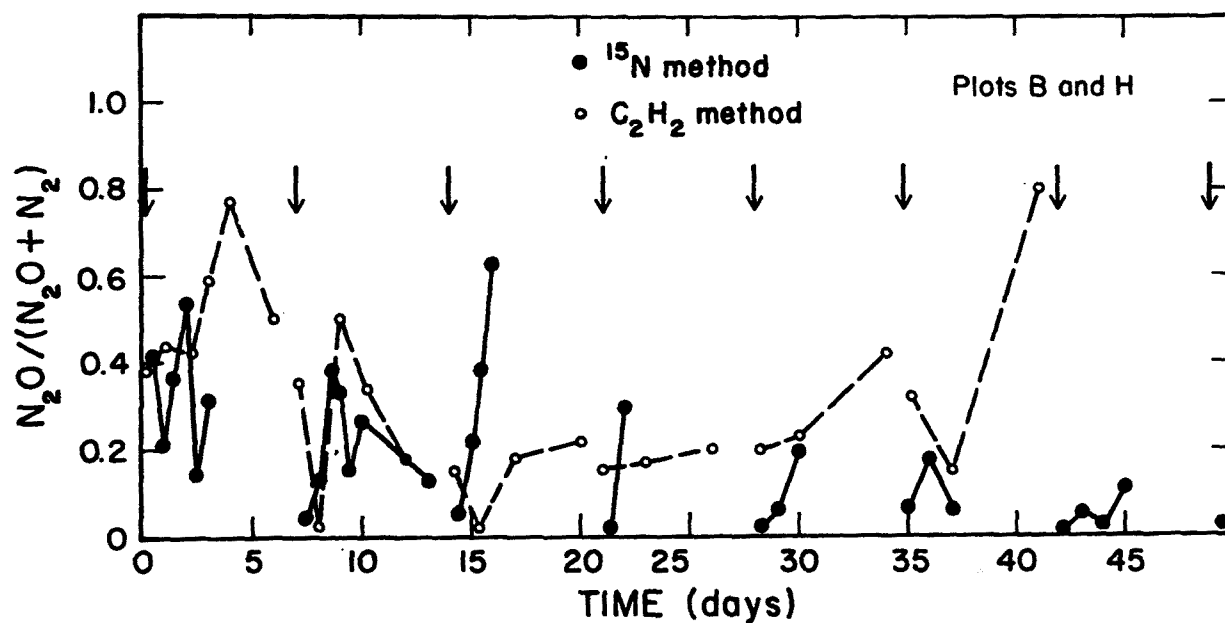


Figure 22. The  $\text{N}_2\text{O}$  mole fraction as a function of time for Plots B and H. The solid lines give the  $\text{N}_2\text{O}$  mole fraction using the  $^{15}\text{N}$  method, and the broken lines give the  $\text{N}_2\text{O}$  mole fraction using the  $\text{C}_2\text{H}_2$  method.

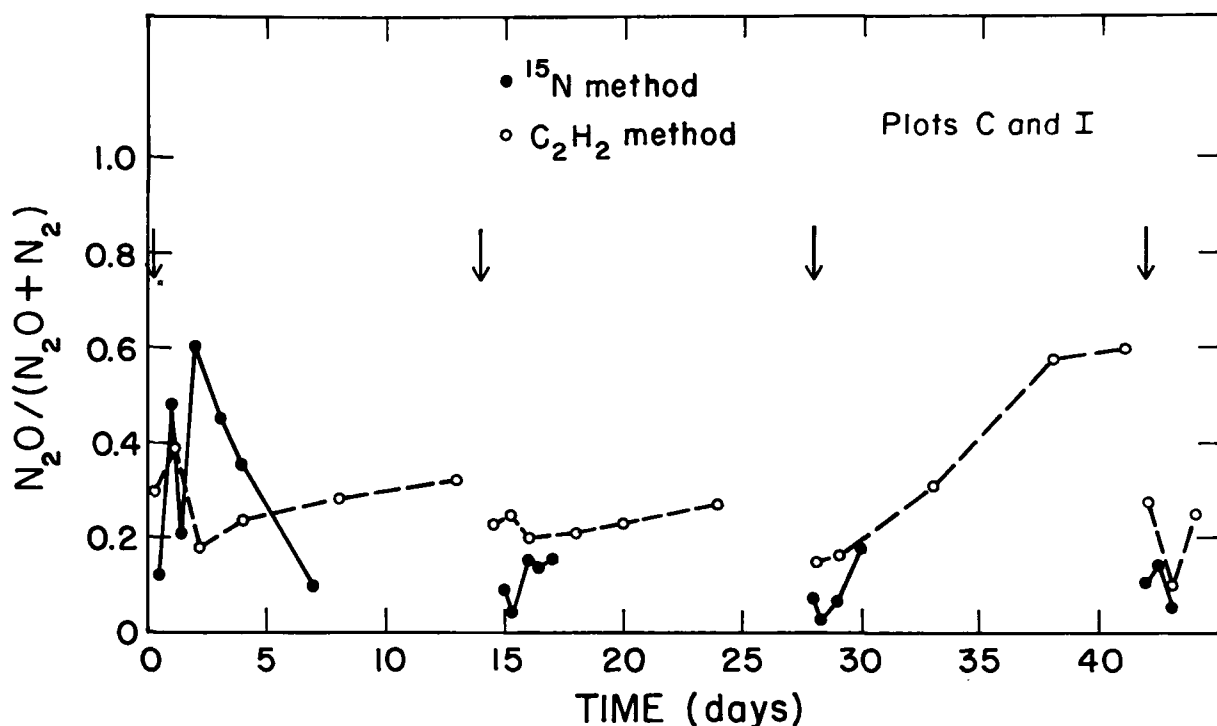


Figure 23. The  $N_2O$  mole fraction as a function of time for Plots C and I. The solid lines give the  $N_2O$  mole fraction using the  $^{15}N$  method, and the broken lines give the  $N_2O$  mole fraction using the  $C_2H_2$  method.

$^{15}N_2$  and the  $C_2H_2$  methods. For the frequently irrigated plots (Plots A and G), the  $N_2O$  mole fraction was quite dynamic due to the frequent irrigation applications. The  $N_2O$  mole fraction varied from nearly zero to one during different irrigation cycles. The mole fraction as measured by the two different methods compared reasonably well. For Plots B and H (Figure 22) there was a general tendency for a decrease in the  $N_2O$  mole fraction with increasing time. This may be due to the effects of high  $NO_3$  concentration initially which tends to inhibit  $N_2O$  reduction, and therefore, would result in high  $N_2O$  mole fractions shortly after fertilizer application. The  $C_2H_2$  method compared reasonably well with the  $^{15}N$  method except toward the end of the sampling. After the first two irrigation cycles, both sets of data indicate that the mole fraction tended to be relatively small immediately after irrigation and then increased as the soil profile dried or became less anoxic. This would be expected since under less anoxic conditions there is a decreased potential for  $N_2O$  reduction to  $N_2$ .

Similar behavior is demonstrated by the  $N_2O$  mole fraction for Plots C and I (Figure 23) demonstrating that the  $N_2O$  mole fraction tended to increase from the low value immediately after irrigation to higher values as the profile dried.

For Plots D, E, and F (Figures 24, 25, and 26), which were the plots to which C was added as chopped barley straw, the  $N_2O$  mole fractions tended to

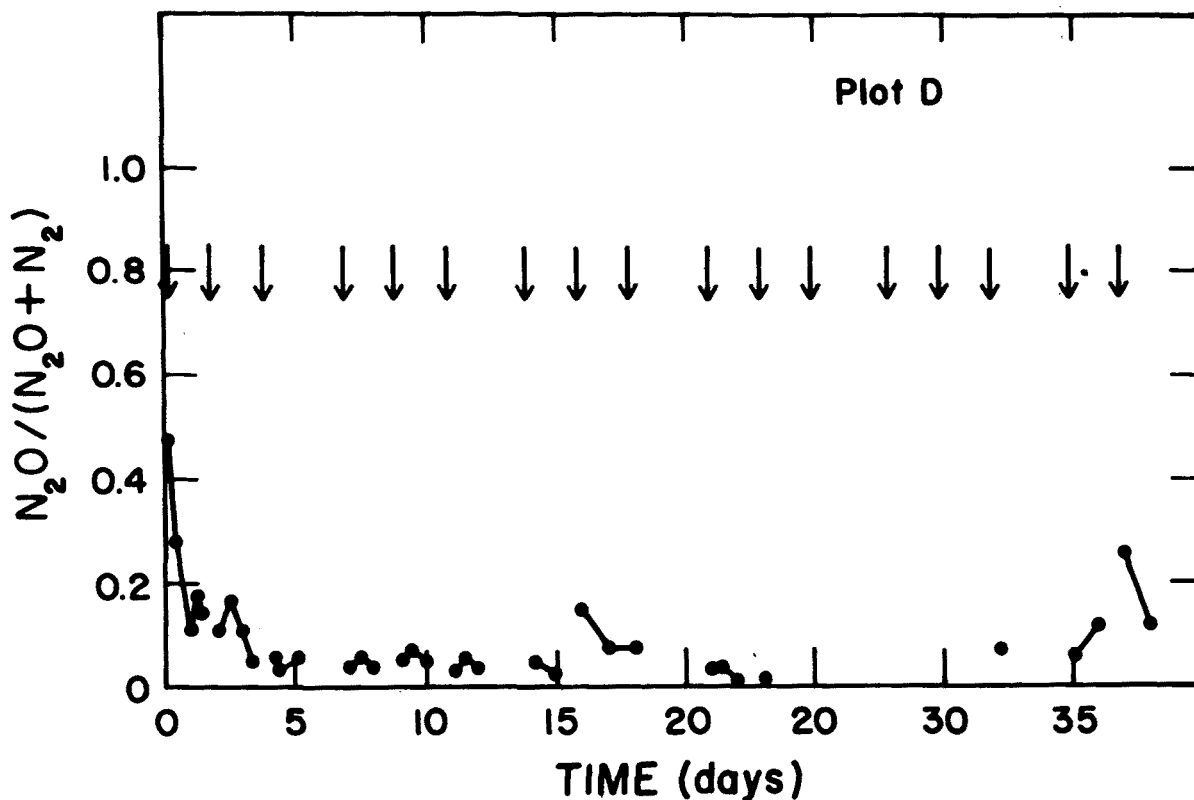


Figure 24. The  $\text{N}_2\text{O}$  mole fraction as a function of time using the  $^{15}\text{N}$  method for Plot D. The arrows give the times of irrigation.

be much lower than those measured for the plots without C addition. This again would be expected since much more anoxic conditions developed in plots to which straw was added than those without straw resulting in better conditions for  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$ . There does seem to be a general decrease in  $\text{N}_2\text{O}$  mole fraction with time for Plots D and F. Plot E did not show that behavior. The data for Plot E, however, definitely showed the increase in  $\text{N}_2\text{O}$  mole fraction within each irrigation cycle. In fact, there is essentially no  $\text{N}_2\text{O}$  produced very shortly after irrigation to result in mole fractions near zero.

The data on  $\text{N}_2\text{O}$  mole fraction demonstrate that the proportion of  $\text{N}_2\text{O}$  produced during denitrification was a very dynamic and variable property. Mole fractions varied all the way from zero to one for treatments without C additions and varied from nearly zero to 0.4 or 0.5 for plots with C additions. A time-averaged  $\text{N}_2\text{O}$  mole fraction would be about 0.2 or 0.3 for those plots without C additions and approximately 0.1 for those plots with C additions. The overall  $\text{N}_2\text{O}$  mole fraction calculated from the data in Table 5 varied from 0.04 for Plot E to 0.27 for Plot A.



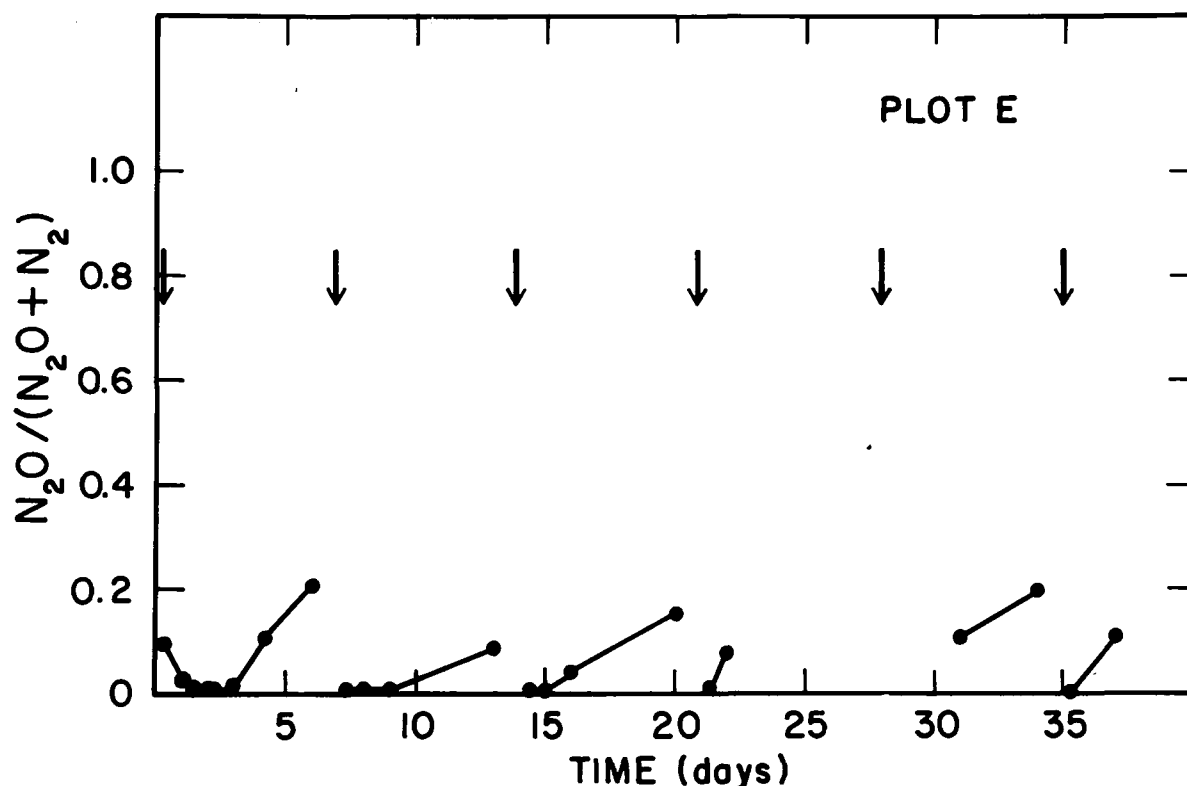


Figure 25. The  $N_2O$  mole fraction as a function of time using the  $^{15}N$  method for Plot E. The arrows give the times of irrigation.

#### PLANT UPTAKE

Figure 27 gives the plant uptake of fertilizer N as a function of time after fertilizer addition for Plots B, C, D, E, and F (no uptake for A). Plots B and C for the experiments without C addition compared reasonably well in total uptake versus time. In a similar fashion, Plots D, E, and F showed similar N uptake. The cooler temperatures later in the summer appeared to have an effect on Plots D, E, and F with less uptake than that of Plots B and C. Plot D took up more N than the other two plots, most likely due to much better water conditions from frequent small irrigations.

#### SOIL SOLUTION N

The soil solution fertilizer N within the six  $^{15}N$  plots for two sampling times are given by Figures 28 and 29. Figure 28 gives the data for Plots A, B, and C for a sampling time midway through the experimental period and for a sampling time shortly before termination of the experiment. Data for Plots D, E, and F are given by Figure 29 for a sampling time midway through the period and near the end of the experimental period. Data points given here are the mean soil solution  $NO_3^-$  concentrations derived from the fertilizer from triplicate solution extractors at each depth for each plot. Both figures show that the two plots which received irrigation once per week and once every two weeks had similar soil solution  $NO_3^-$  concentrations. The two

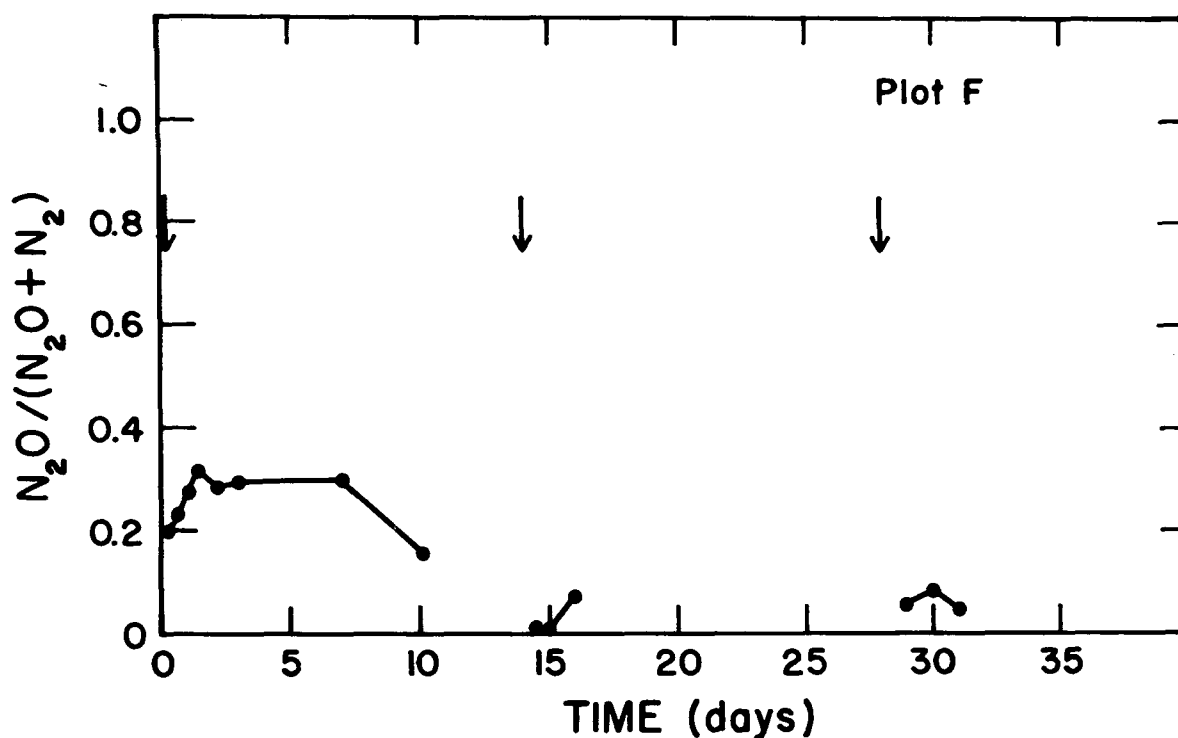


Figure 26. The  $N_2O$  mole fraction as a function of time using the  $^{15}N$  method for Plot E. The arrows give the times of irrigation.

plots which received irrigation water three times per week, however, behaved very differently with much higher concentrations of fertilizer remaining in the upper part of the profile especially for the sampling midway through the experimental period (the top part of both figures). This demonstrates that the frequent, small irrigations tended to keep the  $NO_3^-$  in the upper part of the soil profile whereas the infrequent, large irrigations tended to move the  $NO_3^-$  deeper into the soil. Part of this was due to the fact that the initial distribution of the fertilizer was somewhat different due to the fact that the fertilizer was applied uniformly during the first irrigation. Therefore, all the fertilizer was applied in a very small pulse for Plots A and D, whereas for Plots C and F, all the fertilizer was applied in one large irrigation which would tend to distribute the fertilizer over a deeper depth. These figures also show that, even for the sampling period midway through the experiment, that fertilizer  $NO_3^-$  concentrations at the 90-cm depth were already quite high for Plots B, C, E, and F, indicating that probably large amounts of fertilizer N would be leached below the grass root system for these plots. By the last sampling time near the end of the experiment, the fertilizer  $NO_3^-$  in the soil solution for Plot D began to decrease at the 30-cm depth due to denitrification and continual leaching to deeper soil depths.

As demonstrated by Rolston et al. (1979), the variability in the  $NO_3^-$  concentration of the triplicate samples at any particular soil depth was quite high. Standard deviations were sometimes as great as 150% of the mean, with 60% of the mean being fairly common.

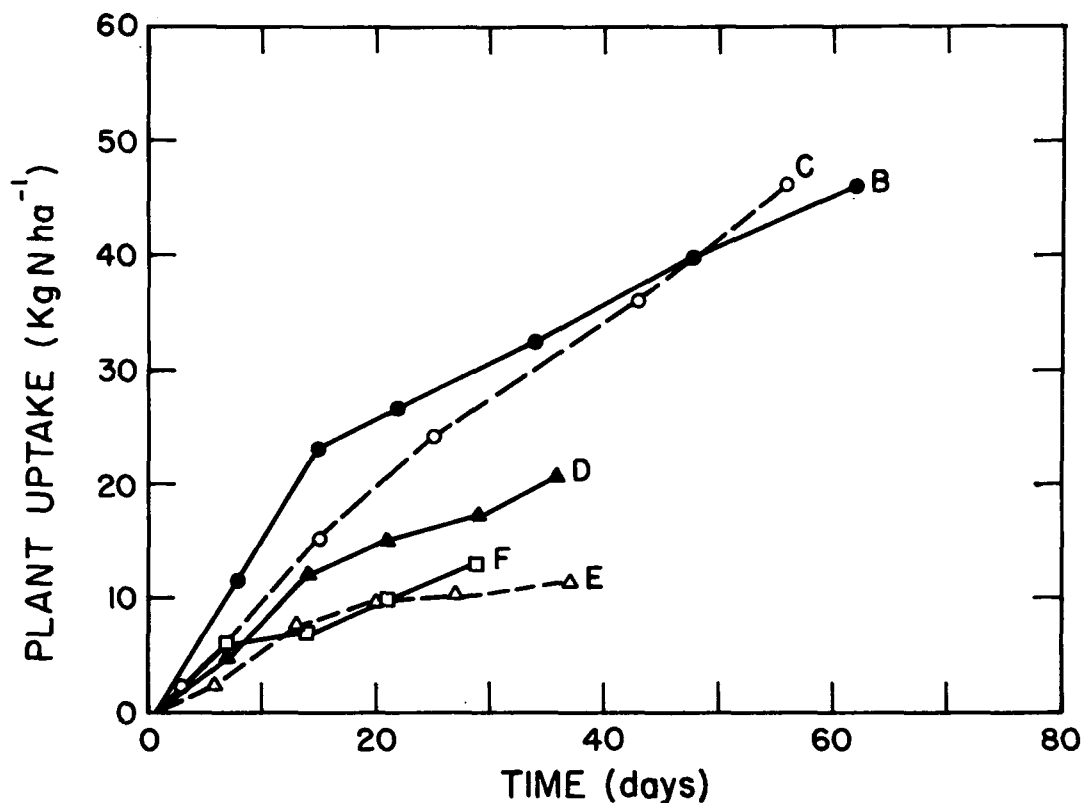


Figure 27. Plant uptake of fertilizer N as a function of time after fertilizer addition for all six plots, except for Plot A for which no grass was harvested.

#### SOIL RESIDUAL N

The labeled inorganic N (fertilizer derived N) for the six plots at the end of the sampling period are given by Figures 30 and 31. Each data point represents the mean from ten individual soil samples at each depth combined to two samples for analyses. The labeled inorganic N represents primarily  $\text{NO}_3\text{-N}$  whereas the labeled organic N is simply organic N which had been immobilized by microorganisms or by live or dead plant roots. The effect of the three different irrigation frequencies are also demonstrated here on the leaching of  $\text{NO}_3$  through the soil profile. In Plot A, a relatively high  $\text{NO}_3$  peak occurred between 60 and 75 cm after approximately 60 days. Plot A received small frequent irrigations. For Plots B and C which received irrigations less frequently, the high peak did not occur and the  $\text{NO}_3$  concentrations were relatively uniform with depth. Relatively high concentrations still existed at the 120-cm soil depth, indicating that substantial  $\text{NO}_3$  was potentially leached below 120 cm. The labeled organic N within the soil profile was predominantly due to live or dead plant material. The result of extreme damage to the grass of Plot A was very low labeled organic N in the upper part of the profile, whereas Plots B and C had high organic N in the top 30 cm of soil. However, the organic N values continued to be measurable

down to 120 cm in this profile, indicating that roots extended fairly deep or that there was some immobilization of added N by microorganisms.

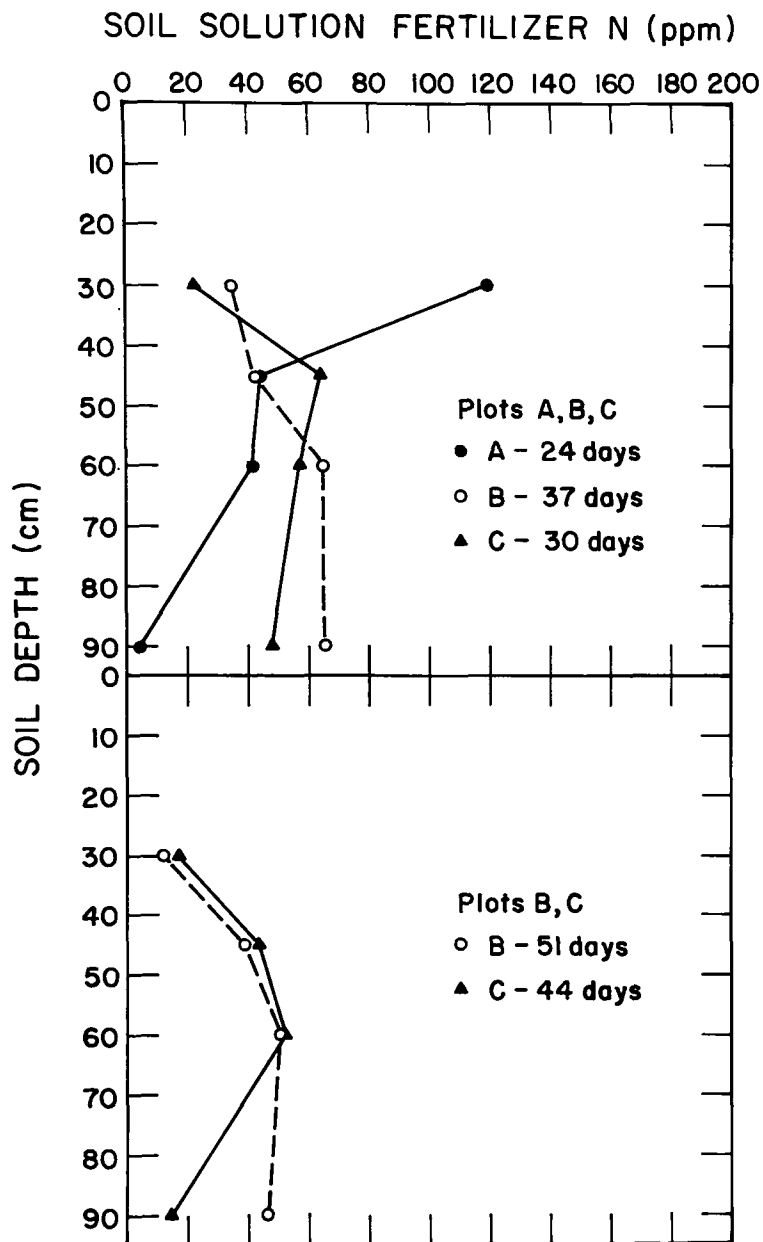


Figure 28. Soil solution fertilizer N as a function of depth for Plots A, B, and C for a sampling time midway through the experimental period (upper part of figure) and at the end of the experimental period (lower part of figure). Plot A was not sampled at the end of the period. The data points represent the mean concentration from triplicate soil solution samplers.

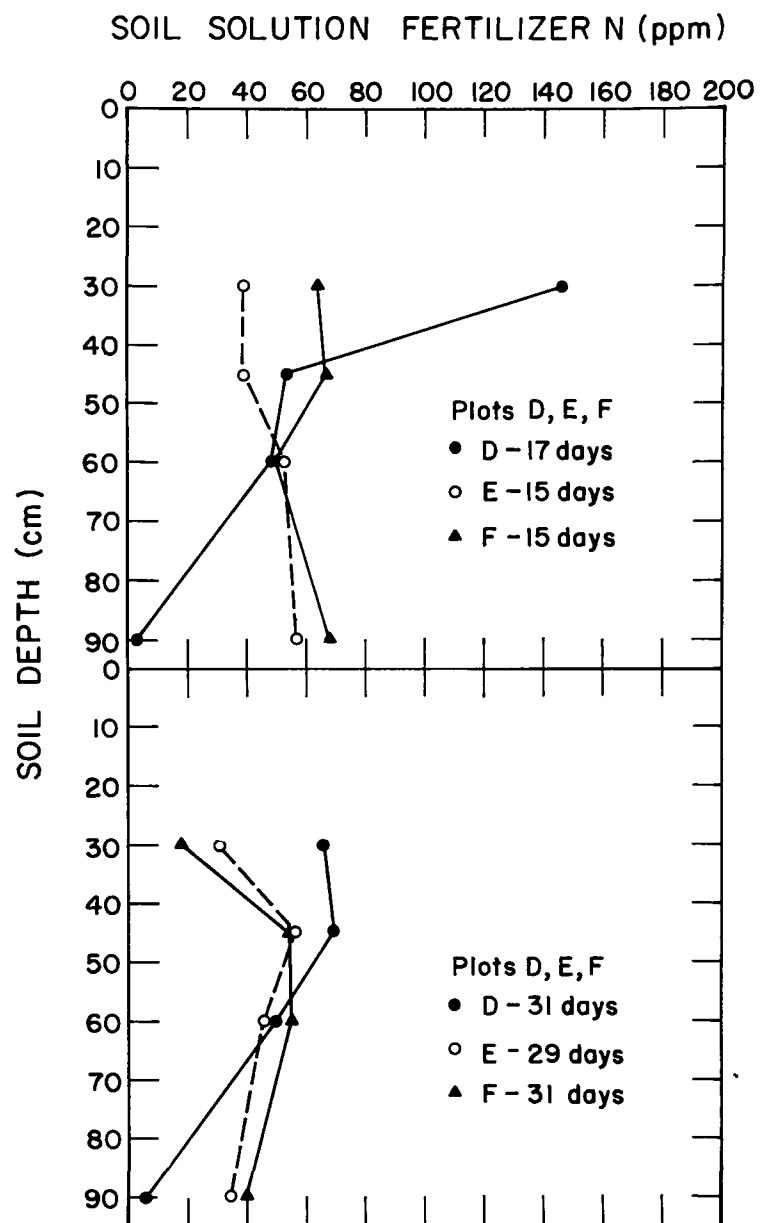


Figure 29. Soil solution fertilizer N as a function of depth for Plots D, E, and F for a sampling time midway through the experimental period (upper part of figure) and at the end of the experimental period (lower part of figure). The data points represent the mean concentration from triplicate soil solution samplers.

A similar behavior of organic and inorganic N is demonstrated by Figure 31 for the plots receiving straw additions. As for Plot A, the plot receiving frequent, small irrigations (Plot D) demonstrated a peak in  $\text{NO}_3^-$  concentration between 30 and 45 cm, indicating less leaching of the applied

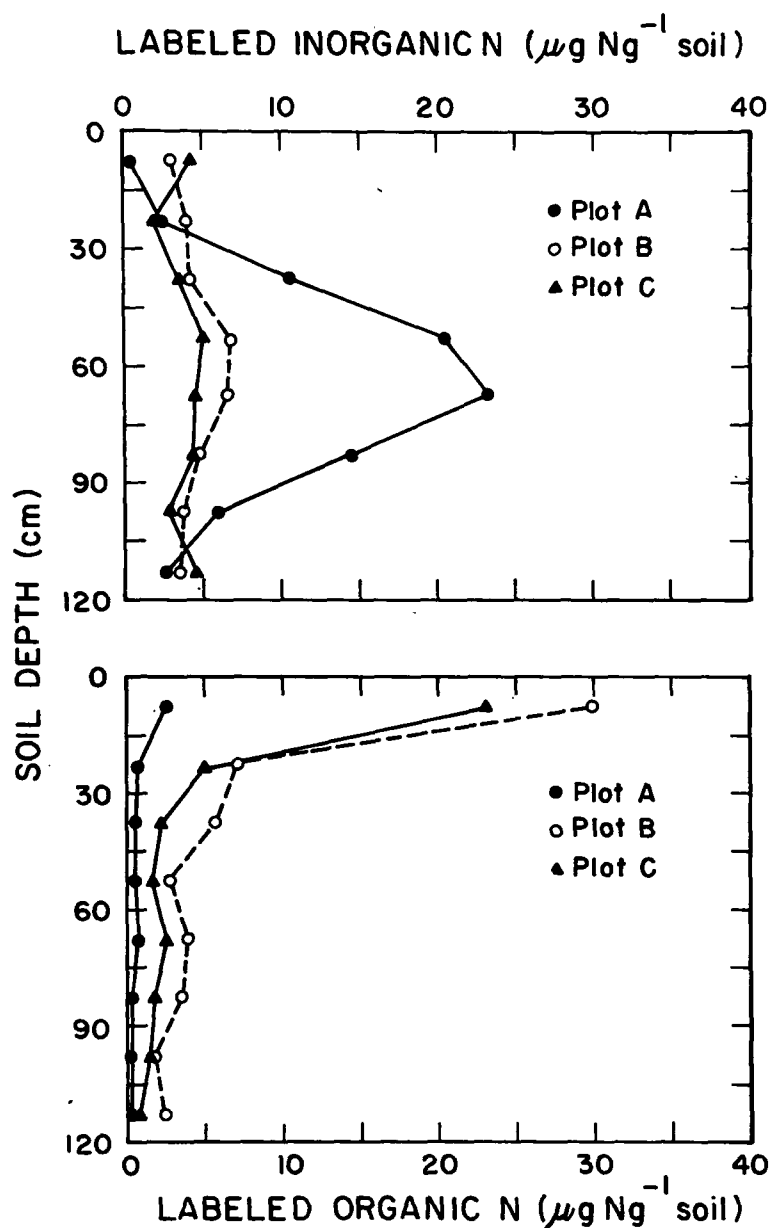


Figure 30. Labeled inorganic and organic N for Plots A, B, and C as a function of soil depth at the end (63 days for B and C, 49 days for A) of the experimental period.

fertilizer through the profile than for the other plots. Although a definite  $\text{NO}_3$  peak occurred for both Plots A and D, the magnitude of the peak was greater in A than in D due to no plant uptake of N in A and very little denitrification in A. As was the case for Plots B and C, Plots E and F showed very little difference in  $\text{NO}_3$  due to irrigation treatment. The labeled organic N was similar for all three plots, with high, labeled organic N in the top 15 cm and a rapid decrease to fairly low levels deeper in the profile.

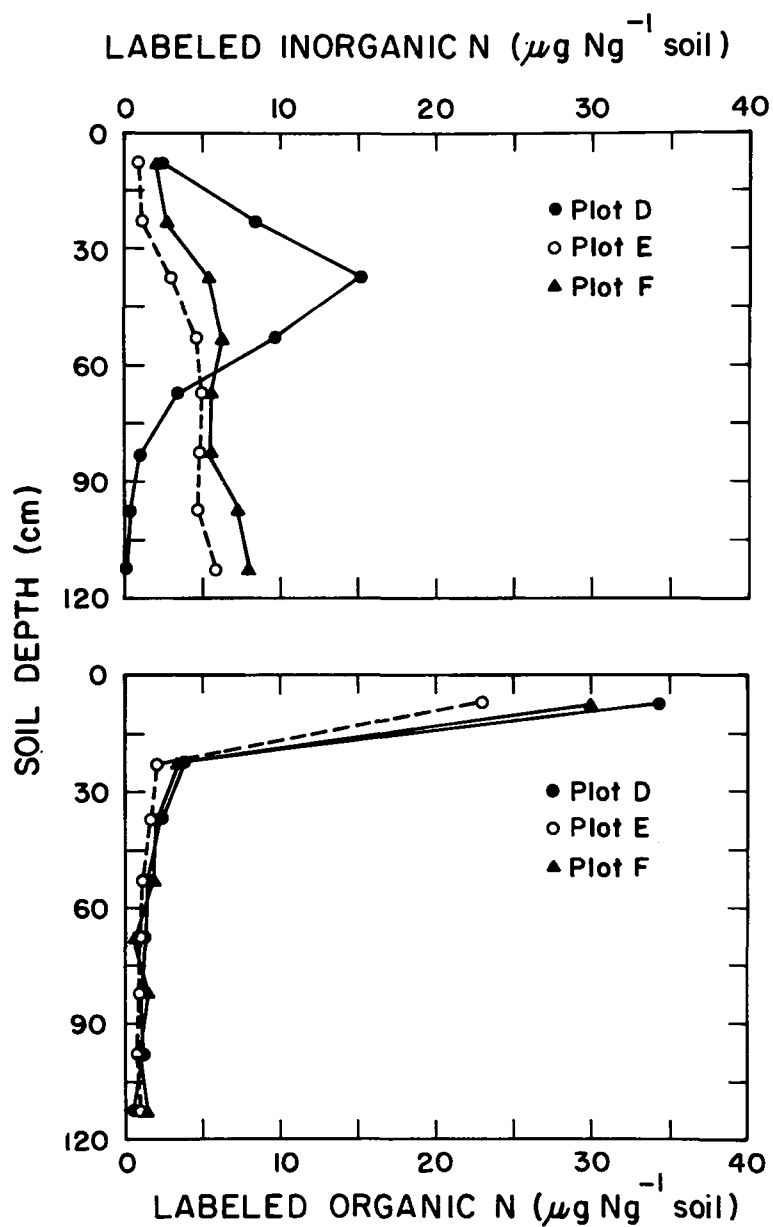


Figure 31. Labeled inorganic and organic N for Plots D, E, and F as a function of soil depth at the end (36 days) of the experimental period.

The labeled inorganic N values demonstrate that leaching of  $\text{NO}_3^-$  was decreased by small, frequent irrigations. However, as shown under the section on gas fluxes, the frequent, small irrigation treatments resulted in the greatest amount of denitrification loss. Thus, although  $\text{NO}_3^-$  leaching may be less, frequent irrigations would result in more denitrification. A balance would have to be drawn between denitrification losses and leaching

losses. These data show that over the time period of this experiment that although denitrification was increased on the frequently irrigated plots, the increased denitrification was not as great as the leaching that occurred in the infrequently irrigated plots. Thus, frequent small irrigations would result in maintaining high  $\text{NO}_3$  in the upper part of the soil profile, and would, thus, be more accessible for plant uptake.

#### MASS BALANCE OF N

Table 6 gives the amounts of fertilizer N for the various components of the N cycle. The amount of fertilizer, the amount remaining in the soil, the

TABLE 6. MASS BALANCE OF FERTILIZER IN THE VARIOUS COMPONENTS OF THE N CYCLE FOR EACH OF THE SIX  $^{15}\text{N}$  PLOTS. LEACHING WAS DETERMINED BY DIFFERENCE FROM THE OTHER COMPONENTS

Component	Plots					
	A	B	C	D	E	E
	kg N ha <sup>-1</sup>					
Fert. applied	281.0	284.0	282.0	288.0	288.0	287.0
Soil digests	10.8	114.9	77.7	95.3	65.7	82.9
Soil extracts	149.8	68.8	60.7	82.3	54.4	77.9
Plant uptake	--	45.8	46.7	21.0	11.9	13.0
Denitrification	4.1	3.2	1.9	14.9	18.4	5.1
Leaching (by difference)	116.3	51.3	95.0	74.5	137.6	108.1

amount taken up by the plant, and denitrification were measured directly. Due to the difficulties in estimating the leaching component even in small plots such as those used by Rolston *et al.* (1979), leaching was estimated by difference from the other measured components. The residual soil N in the upper 120 cm of soil was determined with reasonable accuracy. There could be some question about the accuracy or the ability to measure all of the denitrification gases produced. However, the  $\text{C}_2\text{H}_2$  and  $^{15}\text{N}$  methods gave nearly the same total denitrification indicating that the flux of denitrification gases below the borders of the  $^{15}\text{N}$  plots was insignificant. Thus, it seems that although some errors in denitrification fluxes could easily have been made, it appears that the numbers given for denitrification are reasonable.

The determination of leaching by difference in Table 6 shows that considerable N was lost below the 120-cm depth for these experiments. These data are somewhat confusing for Plot A since the calculation gives greater leaching for Plot A than for Plots B or C. However, the soil solution  $\text{NO}_3$



values and the residual soil  $\text{NO}_3^-$  values showed considerable  $\text{NO}_3^-$  remaining in the soil profile for Plot A, whereas Plots B and C had much less  $\text{NO}_3^-$  remaining in the upper 120 cm of soil. Plant uptake was zero and very little N remained in the soil as labeled organic N for Plot A. Thus, the N not taken up by the plant and not immobilized as organic N was apparently available for leaching, resulting in 116 kg leached out of 281 kg applied. For Plots D, E, and F, however, Plot D, which was the frequent, small irrigations, resulted in the least amount of leaching. For Plot D, substantial  $\text{NO}_3^-$  remained in the upper 120 cm of the profile, considerable N was immobilized in the organic fraction, and plant uptake of applied N was high. Nearly one-half of the applied N was leached from the plot with an irrigation frequency of one irrigation per week, and something less than one-half was leached from the plot with an irrigation frequency of once every two weeks.

This amount of leaching seems excessive if the amount of irrigation was no greater than 15% of the ET. Evidence exists from the denitrification modeling section that the amount of irrigation water applied was greater than 115% of actual ET. The plots may have been using less water than the estimated ET due to frequent cuttings of the grass and the effect of placing covers over the plots for two to four hours per day on each sampling day. This effect of more leaching than anticipated will be discussed further in the section on the denitrification simulation model.

#### DENITRIFICATION SIMULATION MODEL

The mathematical equations used to describe the transient behavior of water and N in soils are similar to those presented by Davidson et al. (1978). The numerical procedures used to solve these equations, however, were different in that plate theory rather than finite difference techniques were employed. The numerical scheme used in this report and verification of the model are also presented by Rao et al. (1980). A flow diagram giving the order of calculations in the simulation model is given by Figure 32.

To verify the denitrification portion of the N simulation model described by Rao et al. (1980), the experimental results of Rolston et al. (1978) and those of this report were used. The field experiments used  $^{15}\text{N}$  tagged  $\text{NO}_3^-$  fertilizer to measure  $\text{N}_2$  and  $\text{N}_2\text{O}$  gas emission from the soil surface during denitrification. To simulate denitrification, a first-order reaction with respect to  $\text{NO}_3^-$  and C concentration was assumed. It was also assumed that the time required for the  $\text{N}_2$  and  $\text{N}_2\text{O}$  gases to diffuse from the site of production to the soil surface was small relative to the time scale of the experiments. Thus, the model contained no gaseous diffusion component. The effect of soil temperature on denitrification was accounted for by using a  $Q_{10}$  (temperature coefficient) value of 2. The effect of anoxic conditions on denitrification was accounted for through a water function which was based upon degree of soil-water saturation. The rate of denitrification was calculated from:

$$\rho \frac{dG}{dt} = k_1 \theta f_W f_T C_W C_N \quad [1]$$

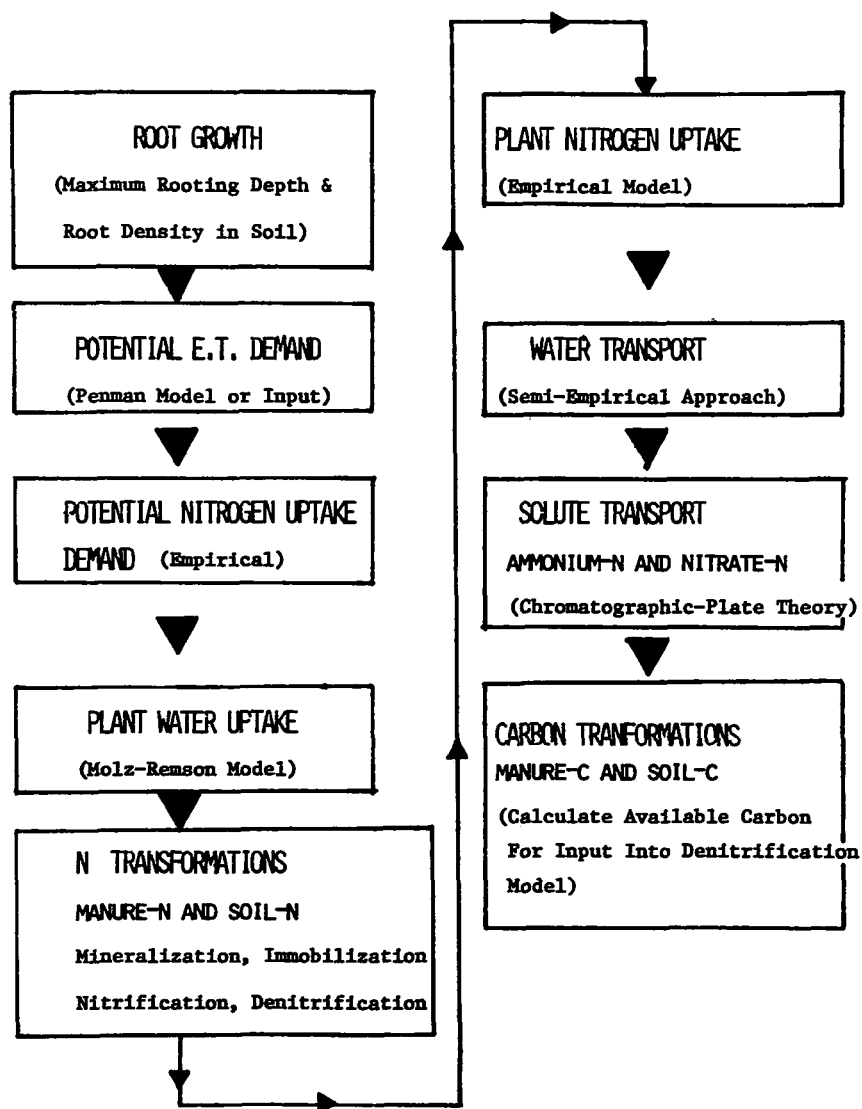


Figure 32. Flow diagram giving the order of calculations in the simulation model.

where  $G$  is sum of denitrification gases ( $N_2 + N_2O$ ),  $C_N$  is the concentration of  $NO_3^-$ ,  $C_W$  is the concentration of water-soluble carbon,  $f_W$  is the water function,  $f_T$  is the temperature function,  $\rho$  is the soil bulk density,  $\theta$  is the volumetric soil-water content, and  $k_1$  is the first order denitrification rate constant.

The water-soluble carbon,  $C_W$ , in Eq. [1] has been shown by Burford and Bremner (1975) to correlate significantly with denitrification. For soil organic matter, the water extractable C was calculated from the following relationship (Burford and Bremner, 1976; Reddy *et al.*, 1979):

$$C_W = 24.5 + 0.0031 C_S \quad [2]$$

where  $C_W$  is water extractable C concentration and  $C_S$  is total soil organic C concentration. The total soil organic C decomposition rate was assumed to be a first-order reaction:

$$-\frac{d C_S}{dt} = k_S f_T g_W C_S \quad [3]$$

where  $t$  is time,  $k_S$  is the first-order constant for C decomposition, and  $g_W$  is a function describing relative respiration as a function of relative soil-water content:

$$g_W = 1.67 (\theta/\theta_S) \text{ for } 0.1 \leq (\theta/\theta_S) \leq 0.6 \quad [4a]$$

$$g_W = 1.75 - 1.25 (\theta/\theta_S) \text{ for } 0.6 \leq (\theta/\theta_S) \leq 1.0 \quad [4b]$$

adapted from Reddy *et al.* (1979) where  $\theta_S$  is the saturated soil-water content ( $cm^3 cm^{-3}$ ). Equations [4a] and [4b] are specific for the Yolo soil but may be reasonable for other fine textured soils. This function gives a maximum decomposition ( $g_W = 1$ ) at a soil-water potential of 0.33 bar ( $\theta/\theta_S = 0.6$ ).

Relationships between water extractable C (or C available for denitrification) and total organic C in manure or plant residue are not readily available. Thus, it was assumed for this study that the C in the manure or plant residues could be divided into a portion which was readily decomposed (Fraction I) and totally available for denitrification and a portion which was slowly decomposed (Fraction II) and only partially available. The latter portion was assumed to follow the same relationship as that for soil organic C (Eq. [2]). The percentages of C in Fractions I and II and the rate constants for various manures and plant residues are presented by Reddy *et al.* (1979). The decomposition of manure or plant residues can be described by:

$$-\frac{d C_i}{dt} = k_i g_W f_T C_i \quad [5]$$

where the subscript  $i$  refers to Fraction I or II. The value of  $C_i$  for Fraction I enters directly into the denitrification equation (Eq. [1]). The

value of  $C_1$  for Fraction II is considered to be the same as soil C and is substituted for  $C_S$  into Eq. [2]. Thus, the total "soil" C for cases where manure or plant residues are added to soil is the sum of Fraction II C from the manure or residue and the soil C. The decomposition of manure C of Fraction I can be more adequately described by two subfractions, each having different rate constants (Reddy et al., 1979).

#### MODEL INPUT DATA

The input data for the denitrification model were obtained from Rolston et al. (1978), and the data of this report on Yolo loam soil at Davis, California. Rate constants for the decomposition of C in soils are presented by Reddy et al. (1979).

The field experiment of Rolston et al. (1978) consisted of six, 1-m<sup>2</sup> field plots maintained at two soil-water contents near water saturation and at three C levels established by applying manure ( $3.4 \times 10^4$  kg ha<sup>-1</sup> in the top 10 cm of soil) to some plots, cropping some plots with perennial ryegrass, and leaving some plots uncropped. These experiments were conducted during the summer and the winter to obtain two temperature levels. Steady state soil-water contents were maintained in the soil profile during the denitrification process by small but frequent irrigations each day. These field experiments by Rolston et al. (1978) will subsequently be referred to as "constant water" plots throughout this report. The constant water plots were used to develop the empirical water function,  $f_w$ , in Eq. [1] by forcing the calculated denitrification to be the same as that measured for the two plots at different soil-water contents. The water function is further described in the "Comparison of Calculated and Measured Denitrification" section of this report. After the water function was developed and the denitrification rate constant for the two plots determined, the same water function and rate constant  $k_1$  were used to calculate denitrification for the other ten constant water experiments. The effect of the crop root system through the additional C it added and O<sub>2</sub> depletion which resulted also increased denitrification. The rate constant required for cropped plots was approximately four times greater than that for the uncropped plots.

The water function and the denitrification rate constant determined from the constant water plots were subsequently used to calculate denitrification for field experiments described in this report. These plots will subsequently be referred to as the "irrigation frequency" plots in this report.

Denitrification in the constant water plots and irrigation frequency plots was determined by measuring the flux of N<sub>2</sub>O and N<sub>2</sub> gases at the soil surface after the addition of <sup>15</sup>NO<sub>3</sub> fertilizer. The uptake of <sup>15</sup>N by the grass as a function of time was used as input data in the denitrification and N transport model.

Soil-water content and pressure head were measured at frequent intervals in all plots and these data were used to check the calculated soil-water contents predicted by the model, especially in the irrigation frequency plots. For the irrigation frequency plots, it became immediately apparent that the predicted soil-water contents versus time after each irrigation

were smaller than those measured values. For four plots, it was necessary to decrease the estimated ET by 50 to 85% in order to attain a reasonable comparison of calculated and measured water contents within the soil profile. The ET may have been underestimated due to placement of covers over the plots for up to eight hours on some days and to decreased transpiration from short, clipped grass.

Soil-water characteristic curves at various depths for the Yolo soil were taken from Rolston and Broadbent (1977) and LaRue *et al.* (1968). The relationship between hydraulic conductivity and soil-water content was taken from LaRue *et al.* (1968) for a Yolo loam field site within 100 m of the plots used for direct measurement of denitrification.

#### COMPARISON OF CALCULATED AND MEASURED DENITRIFICATION

Comparisons of the measured and calculated denitrification flux as a function of time for two constant water plots with manure during the summer (23°C) are given by Figure 33. The solid circles are measured values of

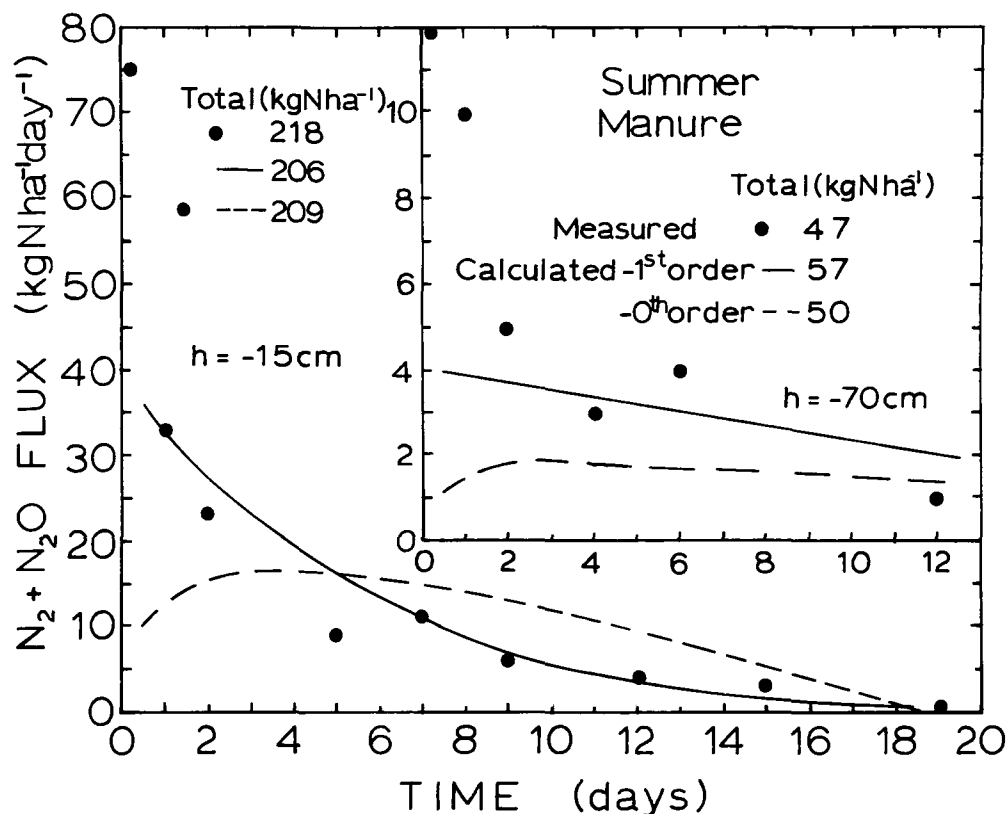


Figure 33. Measured and calculated surface fluxes of denitrification products ( $N_2 + N_2O$ ) as a function of time for two manure-amended plots maintained at two different values of soil-water pressure head,  $h$ .

the  $N_2$  and  $N_2O$  flux, and the solid line is the calculated denitrification flux assuming first-order kinetics as derived by Eq. [1]. The rate coefficient,  $k_1$ , used for the calculations in Figure 33, was  $1.68 \times 10^{-4}$  g soil  $day^{-1}$  ( $\mu g C$ ) $^{-1}$ . Since  $NO_3^-$  concentrations within the soil profile were generally large in all plots, it might be assumed that denitrification followed zero-order kinetics with respect to  $NO_3^-$  concentration rather than first-order kinetics as given by Eq. [1]. For zero-order kinetics, the denitrification rate is given by:

$$\frac{dG}{dt} = k_0 f_w f_T C_w \quad [6]$$

Where  $k_0$  is the zero-order denitrification constant and the other functions and coefficients are the same as in Eq. [1]. The broken line in Figure 33 is the calculated denitrification rate assuming zero-order kinetics (Eq. [6]). The zero-order rate coefficient,  $k_0$ , used for the calculations in Figure 33 was  $0.046 \mu g N day^{-1}$  ( $\mu g C$ ) $^{-1}$ . The zero-order model does not predict the large denitrification rate that occurred immediately after the  $NO_3^-$  was applied. The first-order equation describes these large initial rates better than does the zero order case.

The calculated denitrification rates given in Figure 33 were developed using the water function,  $f_w$ , in Figure 34. The water function was developed by forcing the calculated amounts of denitrification for the indicated period in the two plots shown in Figure 33 to be approximately equal to the measured values. The water function in Figure 34 is an empirical relationship which explicitly implies a relative degree of anoxic development for these field plots. The water function provides a simple way of accounting for the change in  $O_2$  diffusion and storage in the soil as the soil-water content changes. Denitrification becomes essentially zero below 80% of the saturated water content value. The maximum potential for denitrification would occur at saturation where all pores are completely filled with water, and the diffusion of  $O_2$  is limited to diffusion through water.

Total denitrification, as determined by integrating the flux versus time data, is also given in Figure 33. Comparisons of total denitrification for all 12 of the constant water plots are given in Table 7. The same water function presented in Figure 34 was used to calculate denitrification for all plots. Also, the same denitrification rate constant was used for all plots except those cropped with grass. The constant required to describe denitrification from plots cropped with grass was approximately 3.6 times greater than that for the other plots due to the effect of the root system in consuming  $O_2$  and in adding soluble C to the soil.

The denitrification rate constant ( $6 \times 10^{-4}$  g soil  $day^{-1}$  ( $\mu g C$ ) $^{-1}$ ), determined for the cropped plots of the constant water experiments and the water function of Figure 34, were subsequently used in calculating denitrification for the six irrigation frequency plots of this report. Figure 35 gives the surface flux of  $N_2O$  plus  $N_2$  for the plots receiving three irrigations per week (1.15 ET). The arrows at the top of the figure indicate when the irrigation was made. The top and bottom sections of Figure 35 are for plots without and with added straw, respectively. Note that the scales of

TABLE 7. COMPARISON OF MEASURED AND CALCULATED DENITRIFICATION FROM CONSTANT WATER PLOTS ON YOLO LOAM SOIL. A VALUE OF  $k_1$  OF  $1.68 \times 10^{-4}$  g SOIL DAY<sup>-1</sup> (μgC)<sup>-1</sup> WAS USED FOR THE MANURE AND UNCROPPED CALCULATIONS. A VALUE OF  $k_1$  OF  $6 \times 10^{-4}$  g SOIL DAY<sup>-1</sup> (μgC)<sup>-1</sup> WAS USED FOR THE CROPPED CALCULATIONS

CROPPED CALCULATIONS			
Temperature °C	Treatment	Denitrification	
		Measured	Calculated
		kg N ha <sup>-1</sup>	
23	Manure, h = -15 cm	218	206
23	Manure, h = -70 cm	47	57
23	Cropped, h = -15 cm	40	47
23	Cropped, h = -70 cm	9	8
23	Uncropped, h = -15 cm	10	15
23	Uncropped, h = -70 cm	4	2
8	Manure, h = -8 cm	33	52
8	Manure, h = -50 cm	30	0
8	Uncropped, h = -8 cm	0.4	3
8	Uncropped, h = -50 cm	0.4	0
8	Cropped, h = -8 cm	19	21
8	Cropped, h = -50 cm	2	1

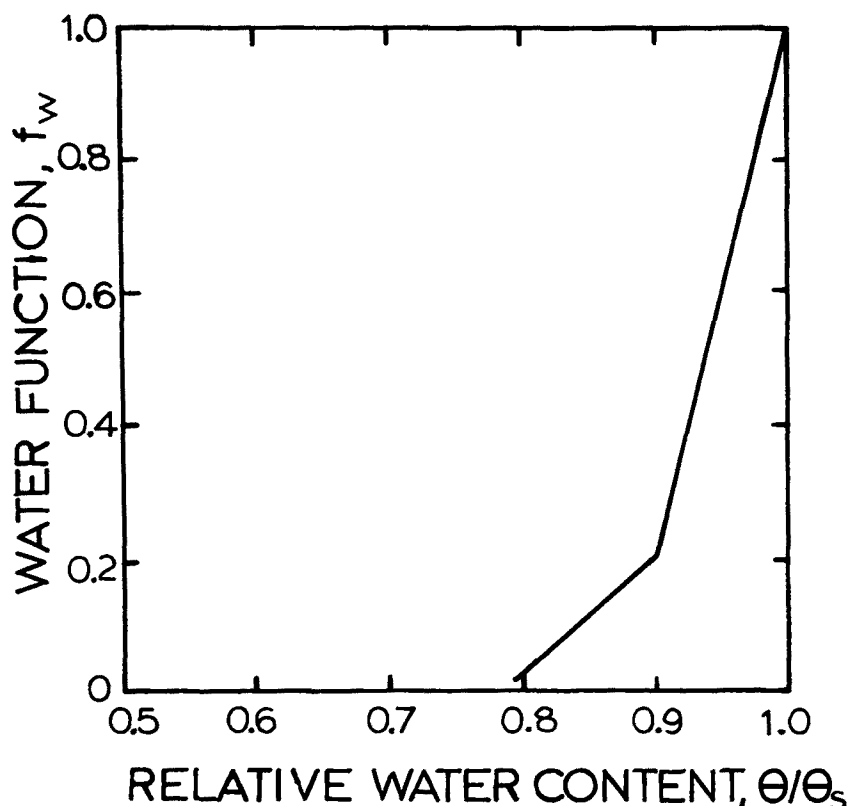


Figure 34. The dependence of the empirical water function,  $f_w$ , (Eq. [1]) on relative soil-water content (water content/saturated water content).

the ordinate are greatly different for the top and bottom sections of the figure (Figures 36 and 37 also). It is also important to recall that the minimum detection limit for  $N_2$  flux was in the neighborhood of 0.1 to 0.2 kg  $N\ ha^{-1}\ day^{-1}$ . Thus, many of the data points for the top section of each figure are highly uncertain. The data points are the measured denitrification flux and the solid lines are calculated denitrification rates using the simulation model assuming first-order kinetics. The total measured and calculated denitrification are also given in each section for each plot. The data in Figure 35 illustrate that both denitrification rate and total denitrification were described reasonably well using the model.

Figures 36 and 37 give the denitrification flux as a function of time for the plots irrigated once per week and once every two weeks, respectively. Again, the data in Figures 36 and 37 illustrate that the calculated denitrification compares reasonably well with measured rates and total amounts of denitrification.



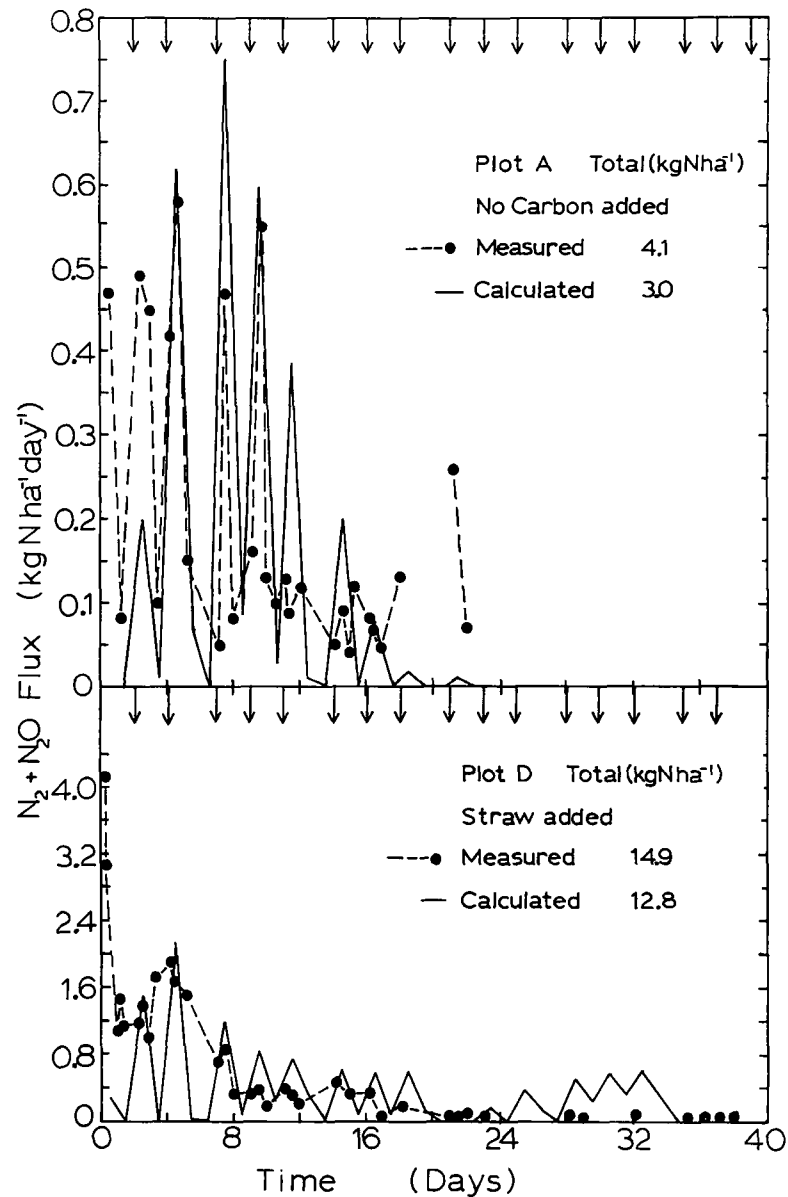


Figure 35. Measured and calculated surface fluxes of denitrification products ( $N_2 + N_2O$ ) as a function of time for plots with and without straw incorporation at an irrigation frequency of three irrigations per week. The solid lines are simulations based on Eq. [1]. The broken lines simply connect measured data points. Arrows indicate time of irrigation. Note that the scales of the ordinate are greatly different for the "no straw" and "straw" plots.

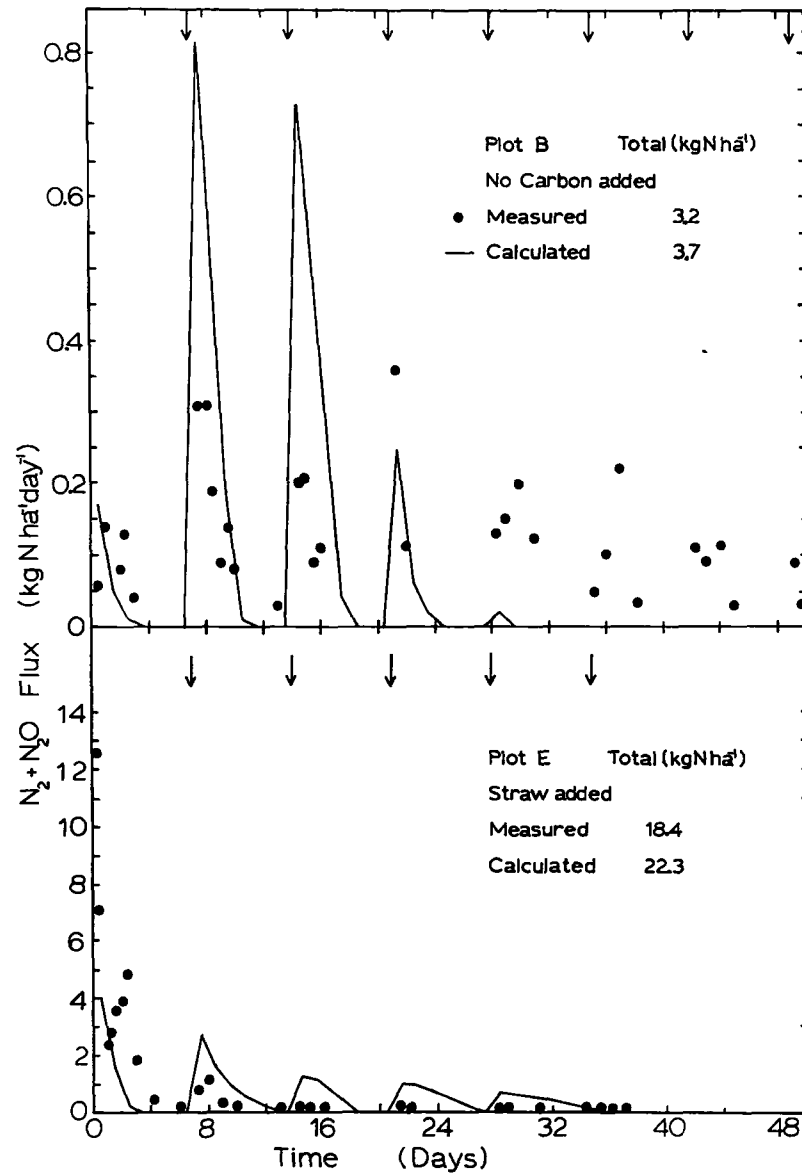


Figure 36. Measured and calculated surface fluxes of denitrification products ( $N_2 + N_2O$ ) as a function of time for plots with and without straw incorporation for an irrigation frequency of one irrigation per week. The calculated lines are simulations based on Eq. [1]. Arrows indicate time of irrigation. Note that the scales of the ordinate are greatly different for the "no straw" and "straw" plots.

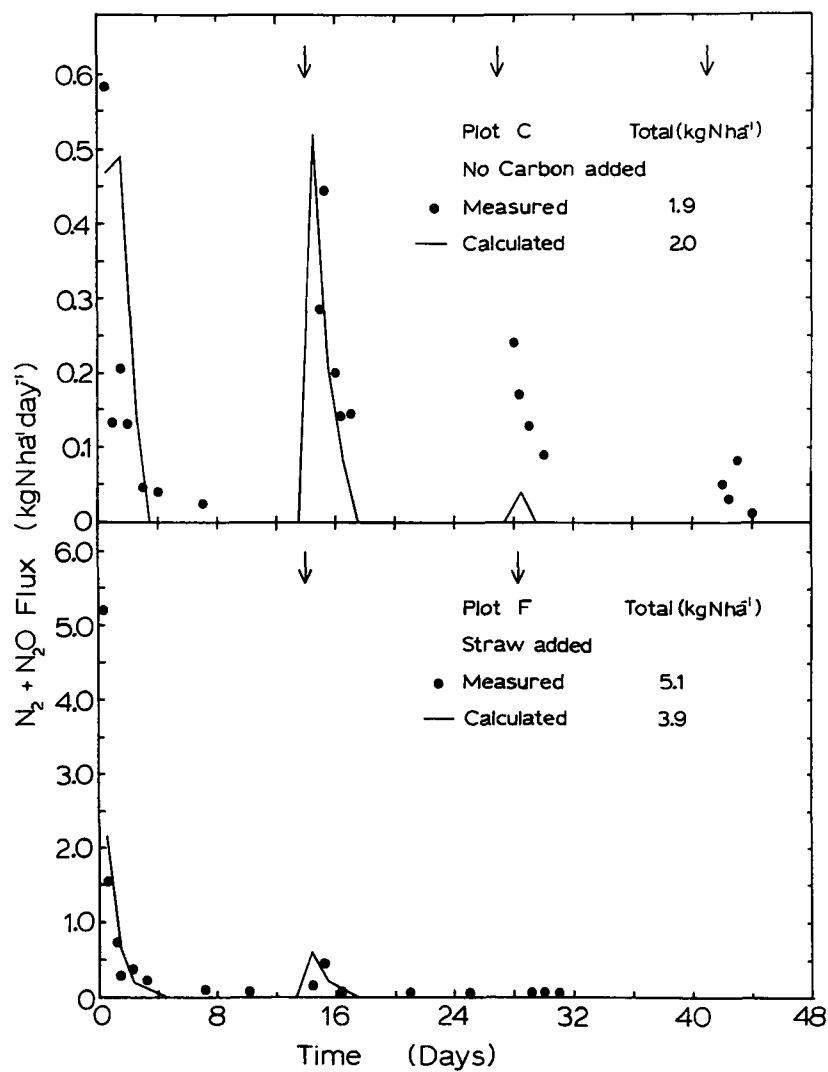


Figure 37. Measured and calculated surface fluxes of denitrification products ( $N_2 + N_2O$ ) as a function of time for plots with and without straw incorporation for an irrigation frequency of one irrigation every two weeks. The calculated lines are simulations based on Eq. [1]. Arrows indicate time of irrigation. Note that the scales of the ordinate are greatly different for the "no straw" and "straw" plots.

Simulations of denitrification were sensitive to the empirical water function in Figure 34. Figure 38 gives three hypothetical water content (15 cm depth) versus time curves for the one irrigation per week irrigation frequency plot with straw added. Line B in Figure 38 is the soil-water content calculated by the model for Plot E (Figure 36). Lines A and C are  $0.01 \text{ cm}^3 \text{ cm}^{-3}$  larger or smaller, respectively, than the soil-water content represented by curve B. For differences in soil-water content of  $0.01 \text{ cm}^3 \text{ cm}^{-3}$  (Figure 38), the calculated denitrification was different by approximately a factor of two.

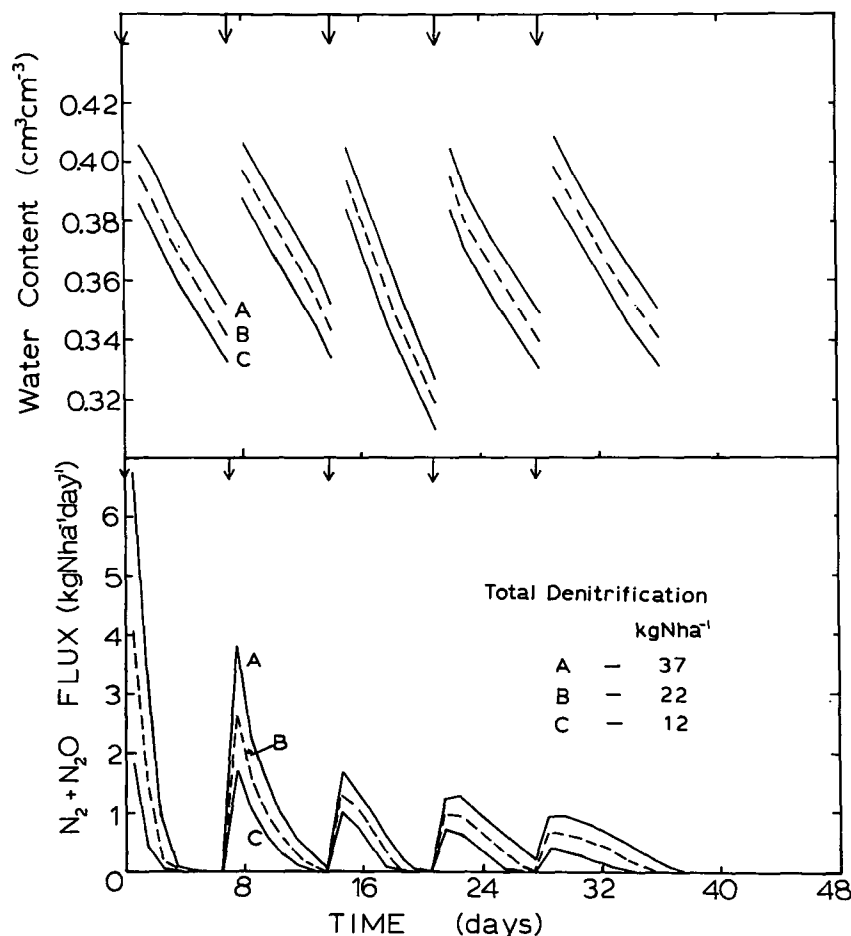


Figure 38. Three hypothetical soil-water content versus time curves for an irrigation frequency of one irrigation per week for plots with straw incorporation.

The sensitivity of denitrification to the soil-water function makes it difficult to accurately simulate denitrification for field situations. Measured water contents in the field frequently vary by as much or more than the  $\pm 0.01 \text{ cm}^3 \text{ cm}^{-3}$  considered in Figure 38. For a site adjacent to the plots of Rolston *et al.* (1978) and those of this report, Simmons *et al.*

(1989) measured standard deviations of  $\pm 0.02-0.03 \text{ cm}^3 \text{ cm}^{-3}$  for 16 soil-water content measurements (at one depth) from a 1 ha field. Thus, it would be desirable to have a function which accounted for the degree of anoxic development in the soil which was not as sensitive as the empirical water function given in Figure 34. On the other hand, a function which accounted for diffusion of  $\text{O}_2$  in the macropores and diffusion of  $\text{O}_2$  through water films or into aggregates could be equally sensitive to the diffusion rate of  $\text{O}_2$  in the water, the size of the microsites, and the consumption of  $\text{O}_2$  by microorganisms and roots. It is probable that the sensitivity demonstrated in this model due to the empirical water function is indeed real. Therefore, one would expect that denitrification would vary substantially from spot to spot in a field. In fact, the concept of microsites as sites of denitrification requires that denitrification be sensitive to the amount of soil water and the diffusion of  $\text{O}_2$  to zones of high microbial activity. It is not known whether the water function developed for these Yolo loam soil field sites can be extrapolated to other soils. Considerably more research is needed on other soil types to determine whether soil-water content or  $\text{O}_2$  diffusion is the most sensitive and which procedure could be more easily extrapolated to other situations.

#### MANAGEMENT SIMULATIONS

The simulation model described and used in this manuscript can be used to calculate potential denitrification losses for various soil-water, soil, and crop management situations. For example, total denitrification for six hypothetical cases involving the possibilities of applying  $\text{NO}_3^-$  fertilizer with irrigation water are given in Table 8. All input data for the simulations

TABLE 8. TOTAL DENITRIFICATION ( $\text{kg N ha}^{-1}$ ) CALCULATED FOR VARIOUS WAYS OF APPLYING  $\text{NO}_3^-$  FERTILIZER DURING ONE IRRIGATION CYCLE OF CROPPED SOIL TO WHICH STRAW WAS APPLIED 43 DAYS PRIOR TO FERTILIZATION. SIMULATIONS WERE MADE FOR APPROXIMATELY 40 DAYS AFTER FERTILIZATION

Irrigation frequency	Fertilizer timing		
	Applied uniformly during entire irrigation	Applied during 1st 1/3 of irrigation	Applied during last 1/3 of irrigation
3 Irrigations per week	10.7	13.8	14.3
1 Irrigation per two weeks	4.6	2.8	5.4

are the same as those used in Figures 35 and 37 (straw addition) with the exception of when the  $\text{NO}_3$  fertilizer was applied. Simulations of denitrification were made for applying  $\text{NO}_3$  fertilizer uniformly during the entire first irrigation, during the first one-third of the first irrigation, and during the last one-third of the first irrigation. For each of these three timings of fertilizer application during irrigation, two irrigation frequencies of three irrigations per week and one irrigation every two weeks were used. The calculations given in Table 8 demonstrate that the fertilizer application time did not affect denitrification significantly for the frequent irrigation system. This was due primarily to the fact that only small amounts of water were applied at any one time and the  $\text{NO}_3$  resided at about the same position in the soil profile regardless of whether it was applied during the first one-third or the last one-third of the irrigation cycle. Denitrification was calculated to be slightly greater by applying fertilizer during one-third of the cycle than for the case where the fertilizer was applied uniformly throughout the first irrigation period (Table 8). This is primarily due to the increased  $\text{NO}_3$  concentration in the narrow band when the same quantity of fertilizer is applied in one third the water.

The computed values in Table 8 suggest, however, that the timing of fertilizer application may be more important for the infrequent irrigation system. If the fertilizer were applied during the first one-third of the first irrigation for an infrequent irrigation program, the  $\text{NO}_3$  will be pushed deeper into the soil profile during successive irrigations and less denitrification occurs than that calculated for a uniform application during the irrigation. If the fertilizer were applied during the last one-third of the first irrigation, the  $\text{NO}_3$  remains in the upper part of the soil profile and is susceptible to denitrification. The calculated denitrification for this case was only slightly greater than that for the case where the fertilizer was applied uniformly during the irrigation process.

Other management simulations demonstrate that increasing the soil organic C level by three or four times would result in only a 10 to 20% increase in denitrification. This is due to the fact that only a small part of the soil organic C is water soluble or available for denitrification.

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## PUBLICATIONS

The following manuscripts have to date resulted from this research:

- Rolston, D.E., and S. Cervelli. 1978. Denitrification as affected by irrigation frequency and applied herbicides. Combined FAO/IAEA Advisory Group and Research Coordination Meeting on Isotopic Tracer-Aided Studies of Agrochemical Residue-Biota Interactions in Soil and Water, Vienna, Austria.
- Sharpley, A.N., and D.E. Rolston. 1980. Comparison of the acetylene inhibition and  $^{15}\text{N}$  methods for the direct field measurement of denitrification loss from soils. Soil Sci. Soc. Am. J. (submitted)

<b>TECHNICAL REPORT DATA</b> <i>(Please read Instructions on the reverse before completing)</i>		
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16. ABSTRACT <p>The influence of irrigation frequency on denitrification was studied on a Yolo loam field profile at Davis, California. Two carbon treatments were also established by using plots with and without incorporated crop residues. Irrigation frequencies of three irrigations per week, one irrigation per week, and one irrigation every two weeks were established on areas cropped with grass. Fertilizer was applied as <math>\text{KNO}_3</math> enriched with <math>^{15}\text{N}</math> to 1-m<sup>2</sup> plots. The flux of volatile gases at the soil surface was measured from the accumulation of <math>\text{N}_2\text{O}</math> and <math>^{15}\text{N}_2</math> beneath airtight covers placed over the soil surface for 1 to 4 hours at several times after irrigation. For plots with and without addition of crop residue, the largest denitrification was only 6.5 and 1.5% of the applied fertilizer (300 kg N ha<sup>-1</sup>), respectively. Denitrification from the least frequently irrigated treatments was less than that in the most frequently irrigated treatments. The <math>\text{N}_2\text{O}</math> flux at the soil surface varied between 5 and 27% of the total denitrification over a 40 to 50 day period. Denitrification of <math>\text{NO}_3</math> fertilizer was simulated using a mathematical model that included transport and plant uptake of water and nitrogen in soil. Reasonable agreement was found between measured rates and total amounts of denitrification with those calculated from the model.</p>		
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