AP42 Section:	9.2.1
Background Ch	4
Reference:	24
Title:	A. R. Mosier and G. L. Hutchinson, "Nitrous Oxide Emissions from Cropped Fields," *Journal of Environmental Quality*, 10(2):169-173, 1981.

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should be applied post emergence and P is more effective when accompanied by leaching.

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Nitrous Oxide Emissions From Cropped Fields[1]

A. R. MOSIER AND G. L. HUTCHINSON[2]

ABSTRACT

From mid-May to mid-September 1978, nitrous oxide (N_2O) emissions from an irrigated corn (*Zea mays* L.) field in northern Colorado totaled only 2.5 kg N ha^{-1}, and even smaller losses were measured from a nearby sugarbeet (*Beta vulgaris* L.) field. Fluxes measured by a simple soil cover method compared favorably with micrometeorological estimates of vertical N_2O flux density. About 30% of the N_2O lost from the corn field was emitted during the 2 weeks following fertilization while NH_3 was being rapidly nitrified, and 59% was evolved during the week following the field's first irrigation, when restricted oxygen diffusion favored denitrification. Other occurrences of irrigation or precipitation exceeding 0.7 cm were also followed by rapid, though much smaller, increases in N_2O emissions. The flux of N_2O was not significantly correlated with soil nitrate concentration but was strongly correlated with soil water content and N_2O concentration in the soil atmosphere, which always exceeded the ambient atmospheric concentration. We found no evidence that either site ever behaved as a sink for tropospheric N_2O. Total N_2O emissions from the corn field amounted to only 1.3% of the 200 kg NH_3-N ha^{-1} applied to the crop, a much smaller fraction than has been used in models predicting the effect of agricultural fertilizers upon stratospheric ozone depletion.

Additional Index Words: **denitrification, nitrification, nitrogen loss.**

Mosier, A. R., and G. L. Hutchinson. 1981. Nitrous oxide emissions from cropped fields. J. Environ. Qual. 10:169-173.

[1] Contribution of USDA-SEA-AR, P.O. Box E, Fort Collins, CO 80522, in cooperation with Colorado State Univ. Exp. Stn. Sci. J. Ser. no. 2476. Received 14 Oct. 1980.

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Nitrous oxide (N_2O) is important in the natural catalytic destruction of stratospheric ozone (Crutzen, 1970). Since ozone controls the intensity of biologically harmful ultraviolet radiation reaching the earth's surface, this discovery generated concern regarding the potential impact of man's activities on atmospheric N_2O concentrations. The Council for Agricultural Science and Technology (CAST) (1976), Crutzen and Ehhalt (1977), Hahn and Junge (1977), Liu et al. (1977), McElroy et al. (1976), and The National Research Council (1978) proposed models predicting that agriculture's increasing use of industrially and biologically fixed nitrogen (N) would increase atmospheric N_2O concentration, leading ultimately to lower ozone concentration in the stratosphere. Because of the scarcity of field data, these projections were necessarily based on the results of laboratory studies and mass balance estimates of global N_2O release. Differences between the mass balance estimates and very recent field estimates of N_2O emissions from agricultural soils (Hutchinson and Mosier, 1979; Rolston et al., 1978; and Ryden et al., 1979) are large, as discussed by Hutchinson and Mosier (1979). Additional field measurements from a variety of ecosystems around the world are needed to identify major N_2O sources and sinks and to determine the relative contribution of each to the atmospheric concentration and residence time of the gas. We report here measurements by two independent methods of N_2O emissions from N-fertilized, irrigated fields in a semiarid climate and relate these data to changes in the soil N status, soil water content,

and agricultural management practices used during the 1978 growing season.

MATERIALS AND METHODS

Two field sites were chosen for this study, based on their suitability for micrometeorological measurement of vertical N_2O flux density. At both sites the land was flat, and fetch across the crop in the direction of prevailing winds was about 500 m with no major obstructions for at least twice that distance. The primary site, a 120-ha field of corn (*Zea mays* L.) located about 4 km northeast of Berthoud, Colorado, was sampled periodically from mid-May through mid-September 1978, and a nearby 30-ha sugarbeet (*Beta vulgaris* L.) field was less intensively monitored. The principal soil type in the corn field was Nunn clay loam (fine, montmorillonitic, mesic Aridic Argiustolls) and in the sugarbeet field was the Wiley-Colby complex [Wiley, fine-silty, mixed, mesic Ustollic Haplargids; and Colby, fine-silty, mixed (calcareous), mesic Ustic Torriorthents]. Table 1 gives some properties of composite 0- to 20-cm samples from the two sites. The samples were taken in early June before application of 200 kg NH_4-N/ha to the corn field and 6 weeks following sugarbeet planting and fertilization with 75 kg NO_3-N/ha. The cooperating farmers used management practices typical of those used on furrow-irrigated farms in the area, and the presence of our instruments in the fields did not interfere with the practices.

N_2O Concentration Analysis

Air samples for measuring flux by the two methods to be described later were collected and transported to the laboratory in 60-ml polypropylene Monoject[1] disposable syringes fitted with vacuum-tight stock-cocks manufactored by Hamilton Company. In laboratory tests the N_2O concentration of samples (1.5 ppm v/v N_2O in air) stored in the syringes changed less than 1% in 24 hours, indicating that the syringes neither absorbed nor leaked N_2O at a significant rate. Air samples were analyzed for N_2O using a Tracor Inc. MT 150 gas chromatograph (GC) equipped with a linear ^{63}Ni electron capture (EC) detector and Valco Instruments pneumatically operated 10-port sampling and 4-port switching valves as described by Mosier and Mack (1980).

Flux Measurements

Soil Cover Method—Vertical N_2O flux density was estimated by monitoring accumulation of the gas beneath 1-liter glass bell jars placed over the soil for 1 hour. Quadruplicate measurements were made at new locations within a small uniform area of the field each sampling date, with two jars placed in the crop row and two in the irrigation furrow between rows. Each bell jar was inserted about 2 cm into the soil and then fitted with a styrofoam cover to minimize internal heating by solar radiation. The bell jars were vented to the atmosphere during insertion into the soil and during air sample withdrawal. After 0, 15, 30, and 60 minutes, 30-ml air samples were withdrawn from the jars and transported to our laboratory for same-day analysis by GC-EC. Nitrous oxide flux was computed from the concentration increase using the following equation (Hutchinson and Mosier, 1981), which corrects for the reduction in soil N_2O concentration gradient with time as the gas accumulates:

$$N_2O \text{ flux} = \frac{V(C_1 - C_0)^2}{A\,t_1\,(2C_1 - C_2 - C_0)} \ln \frac{(C_1 - C_1)}{(C_1 - C_0)}$$

where V is the volume of enclosed air, A is the area of soil covered, C_0 is the initial N_2O concentration in the bell jar, and C_1 and C_2 are the N_2O concentrations after time t, and t_2, where $t_2 = 2\,t_1$. Precautions that must be taken in acquiring and interpreting soil cover flux measurements are discussed by Hutchinson and Mosier (1981).

[1]Trade names and company names are included as a matter of convenience to the reader, and such inclusion does not constitute any preferential endorsement by the U.S. Department of Agriculture of products named over similar products available on the market.

Micrometeorological Method—Data obtained by the soil cover method were compared periodically with simultaneous measurements of vertical N_2O flux density determined by the micrometeorological techniques described by Thom (1975). Estimates of eddy diffusivity required by the method were obtained from a momentum balance. Vertical wind speed profiles were measured using C. W. Thornthwaite Associates cup anemometers, and temperature profiles were determined with Yellow Springs Instrument Co. linear thermistors mounted in radiation shields patterned after those described by Lourence and Pruitt (1969). Nitrous oxide concentration profiles were determined by using a modified Harvard Apparatus 975 constant rate syringe pump to simultaneously fill eight of the syringes described earlier, each with air from a different sampling height. Air samples accumulated over a 1-hour period were then returned to the laboratory for same-day analysis by GC-EC. Vertical profiles of wind, temperature, and N_2O were all determined in the first few meters of free airstream above the vegetation.

Other Measurements

Twelve 20-cm soil cores were taken on each sampling date, six each from the crop row and irrigation furrow. Cores from the row and furrow were combined separately, and duplicate subsamples of both composites were extracted with 2*N* KCl (3:1 vol/wt) and analyzed for NH_4^+ and NO_3^- by steam distillation (Bremner and Keeney, 1965) and for NO_2^- as described by Bremner (1965). Soil water content was determined gravimetrically. The data from row and furrow composites are averaged in Fig. 2.

Nitrous oxide concentration in the soil atmosphere was estimated by inserting hollow stainless steel probes (Fig. 1) into the soil and allowing the air within them to equilibrate with the soil atmosphere through vents located either 10 or 20 cm below the soil surface. During the time that each set of soil cover measurements was taken, duplicate 1-ml air samples were withdrawn through a chromatographic septum mounted atop each probe (three probes at each depth) and returned to the laboratory for same-day analysis by GC-EC.

RESULTS AND DISCUSSION

Vertical N_2O flux density; N_2O concentration in the soil atmosphere; soil NH_4^+-N, NO_2^--N, and NO_3^--N concentrations; and soil water content at the corn field site are plotted as functions of time in Fig. 2A, B, C, and D, respectively. Only the data for samples obtained during late morning hours are shown in Fig. 2A to minimize the possible effect of diurnal changes in N_2O flux. When measurements were taken more than once during the day, the flux appeared to vary with soil temperature, reaching in late afternoon or evening a maximum analogous to the diurnal variation of N_2O concentration observed by Matthias et al. (1979) and Denmead et al. (1979).

Table 1—Physical and chemical properties of field soils.

Soil property	Field site: Corn	Field site: Sugarbeets
pH	7.8	7.6
Organic matter, %	1.3	1.7
NO_3^- (ppm-N)	9.0	45.0
NH_4^+ (ppm-N)	4.0	3.0
Total N, %	0.088	0.122
Sand, %	29	37
Silt, %	27	27
Clay, %	44	36
Texture	Clay	Clay loam
Water potential, bars	% H_2O	
−15	12.5	11.4
−0.33	24.9	25.4
−0.10	34.4	35.4

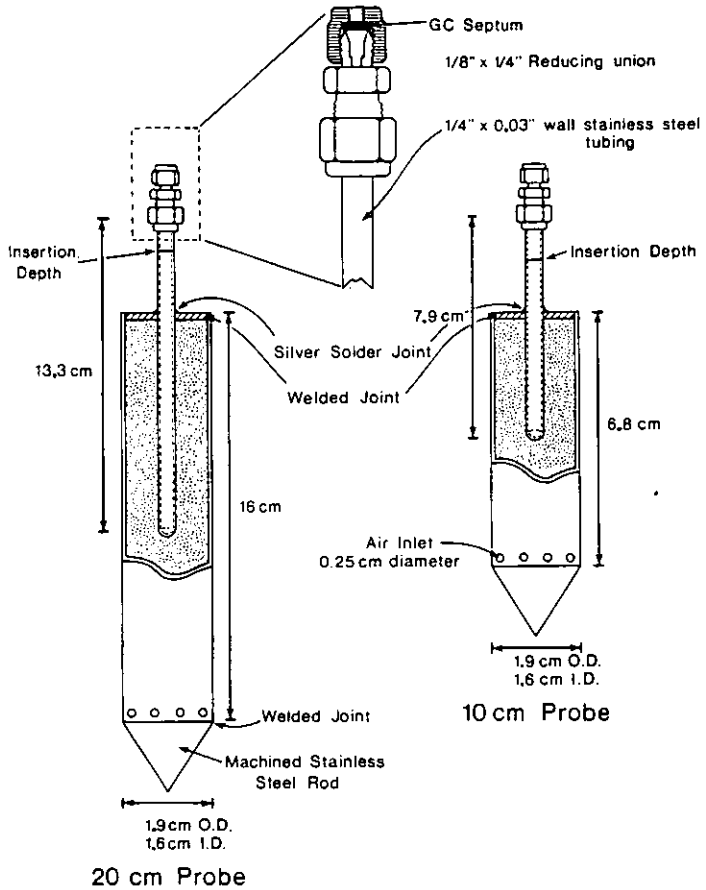

Fig. 1—Soil probes used for sampling soil nitrous oxide.

Temporal variability of the data in Fig. 2A was extremely high, with N_2O fluxes measured by the soil cover method ranging from a low of 0.3 g N ha^{-1} day^{-1} on 28 Aug. to a high of 550 g N ha^{-1} day^{-1} on 22 July. Most of this variability with time can be attributed to changes in the soil's N status and water content, as will be discussed later. Not shown in Fig. 2A is the spatial variability of our N_2O flux measurements. Points plotted in the figure represent the means of four individual determinations having coefficients of spatial variability averaging 77% over the 27 sampling dates. Since N_2O flux was controlled largely by soil N and soil water, much of this spatial variability was undoubtedly caused by the characteristically nonuniform distributions of these two parameters in furrow-irrigated fields fertilized by injection of anhydrous NH_3. The coefficients of spatial variability of soil NH_4^+-N and NO_3^--N were similar to those of N_2O flux, averaging 57 and 81%, respectively. Robbins et al.[4] found similar diversity in measurements of N_2O emissions from a wide range of Iowa soils; their coefficients of spatial variability averaged 70% even when replicate measurements were made "within small areas (usually 20 m by 30 m) of apparently uniform soil."

The high spatial variability of N_2O emissions from soil enhance the attractiveness of micrometeorological techniques for N_2O flux determination, since they provide a vertical flux estimate integrated over a large soil area. Unfortunately, however, micrometeorological techniques could be used only during periods of high N_2O flux, because only then were the differences in N_2O concentration between sampling heights greater than the minimum detectable difference of the analytical method. The N_2O flux density estimated by the micrometeorological method, squares in Fig. 2A, always fell within the range of the four individual flux estimates made by the soil cover method. We interpret this agreement as evidence that four soil cover determinations adequately sampled soil variability in N_2O emissions. Therefore, the soil covers used in this study furnished meaningful estimates of N_2O flux from the field site, when adequate precautions were taken to minimize disturbance of the energy and mass transfer processes normally operating at and above the soil surface (Hutchinson and Mosier, 1981).

Except for a 3-week period following fertilization on 23 June the data in Fig. 2A resemble results of the many laboratory studies that have shown denitrification in soil to be slow except during periods when oxygen diffusion is limited, usually by water (Broadbent and Clark, 1965). Nitrous oxide emissions from the corn field fluctuated within a range centered just under 2.7 g ha^{-1} day^{-1}, except immediately after additions of water. Each incidence of irrigation or of precipitation exceeding 0.7 cm was followed by a rapid increase in the vertical N_2O flux. The largest N_2O flux from the corn field was measured after a heavy irrigation (23 cm of water) on 19 July, followed by rainfall (2 cm) on 21 July, at a time when soil NH_4^+, NO_2^-, and NO_3^- levels were high (50, 20, and 100 μg N/g, respectively) as a result of fertilization about 4 weeks earlier. During the week of 19–25 July, N_2O emissions amounted to 59% of the total lost during the growing season before diminishing to low preirrigation levels. Peaks of N_2O flux following the second and third irrigations were of lower intensity and shorter duration, even though soil NO_3^--N concentrations remained above 10 μg/g and soil water potential of the upper 20 cm exceeded $-1/3$ bar on both occasions. Soil NH_4^+ concentration had declined to about 3 μg N/g by the time of the second irrigation, and NO_2^- was not detectable. Without simultaneous measurements of the N_2 flux from soil, we could not determine whether the smaller peaks resulted from lower total denitrification, from more complete denitrification in which the N_2/N_2O ratio was increased, or because substrate levels for N_2O-producing NH_4^+ oxidation and/or chemodenitrification reactions had diminished. However, recent data of Ryden et al. (1979) indicate that the former is more likely. Using acetylene to inhibit reduction of N_2O to N_2 in an irrigated field in California, they observed successively smaller emissions of N_2O associated with the second and subsequent irrigations after fertilizer application. As also suggested by Ryden et al. (1979), we believe the trend toward lower N_2O emissions rates as the growing season progressed was partly due to declining supplies of the C that the heterotrophic denitrifying organisms used as an energy source. Organic matter contents of the soils at both field sites were particularly low, and it seems reasonable to

[4] S. G. Robbins, A. M. Blackmer, and J. M. Bremner. 1979. Spatial and diurnal variability in emission of nitrous oxide from soils. Agron. Abstr. p. 37.

expect that much of the readily decomposable C was used early in the growing season.

During the period 23 June to 13 July, high N_2O emmissions, accounting for 30% of the growing season's total, coincided with the bacterial oxidation of applied NH_4^+ fertilizer to NO_2^- and NO_3^-. Unlike the other peaks in Fig. 2A, the N_2O flux during this period remained high for a comparatively long time and occurred while the soil apparently remained aerobic, as evidenced by rapid conversion of NH_4^+ to NO_3^- (Fig. 2C) and by low soil water content (Fig. 2D). We believe that some of this N_2O was produced as a product of NH_4^+ oxidation in soil, as has recently been demonstrated in laboratory studies by Bremner and Blackmer (1978) and Freney et al. (1979). Although we have no way of dividing N_2O emissions during this period between losses from oxidation of NH_4^+ and from denitrification of NO_3^-, the fact that the soil apparently was aerobic suggests that denitrification was probably slow.

Throughout the growing season, N_2O emissions were strongly correlated with N_2O concentrations in the soil atmosphere at both the 10- and 20-cm depths (r = 0.79 and 0.73, respectively). The soil gas concentrations ranged from near ambient to nearly 300 times ambient atmospheric N_2O concentration following the first irrigation (Fig. 2B). Peaks in N_2O concentration were short lived, with the concentration returning to near ambient levels in a few days. Soil gas N_2O concentrations always exceeded the ambient atmospheric level, indicating that the corn field always acted as an N_2O source. We found

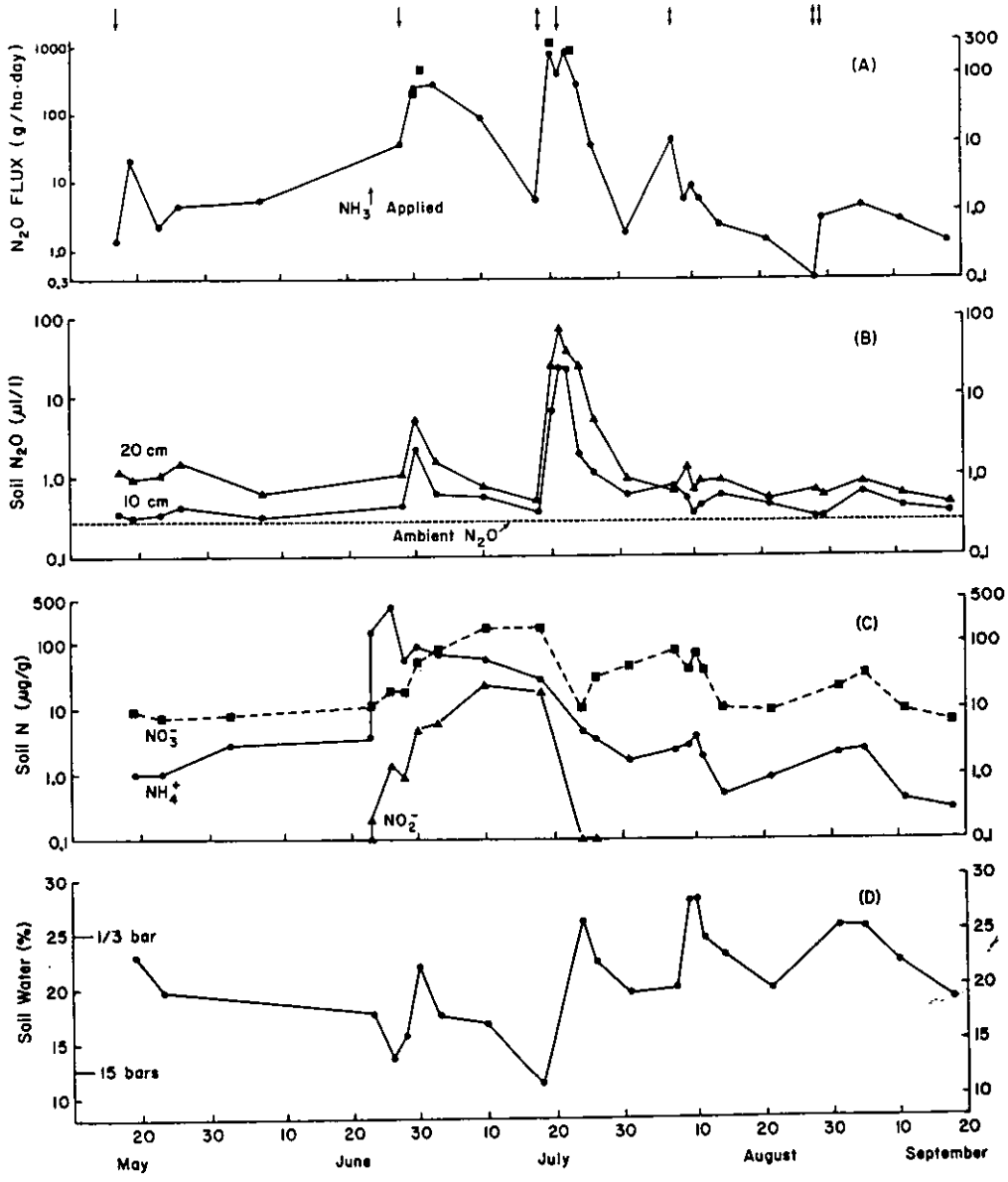

Fig. 2—(*A*) Nitrous oxide emission from corn field soil, (*B*) soil N_2O concentrations at 10- and 20-cm depths, (*C*) soil NH_4^+, NO_3^-, and NO_2^-, and (*D*) soil water content of corn field soil. Soil analyses were for 0- to 20-cm depth soil samples. Single arrows indicate precipitation >0.7 cm; double arrows indicate irrigation. Data points on *A* shown as ■ represent N_2O flux determined by a micrometerological method; other data points determined by soil cover method.

no evidence at either site that field soils behaved as a sink for tropospheric N_2O, even though some laboratory studies have shown that N_2O can be absorbed and reduced to N_2 in anaerobic soils (Blackmer and Bremner, 1976; Freney et al., 1978).

Despite the fact that denitrification was probably one of the sources of N_2O emitted from the corn field during much of the growing season, N_2O flux was not significantly correlated with soil NO_3^- concentration ($r = 0.22$). This correlation was poor because the high NO_3^- concentration alone was not sufficient to cause high denitrification. Limited soil aeration was also necessary, as evidenced by a significant correlation of N_2O flux with the water content of the top 20 cm of soil ($r = 0.53$, $P < 0.05$). Additional reasons for the poor correlation of N_2O flux with NO_3^- concentration were that processes other than denitrification produced some N_2O and that although the N_2O flux increased briefly immediately after irrigation, much of the soil NO_3^- was first leached below the 20-cm sampling depth and later carried upward again by water as the surface soil dried.

Periodic measurements taken at the sugarbeet field, although much less numerous, showed the same N_2O emission pattern as was observed at the corn field. Selected data are given in Table 2. Nitrous oxide flux was small early in the growing season, increased greatly following the first irrigation, and then returned to near preirrigation levels for the remainder of the growing season. No peaks in N_2O flux were detected following subsequent irrigations. While changes in N_2O emission rates in the two fields followed similar patterns, the magnitude of emissions from the sugarbeet field was much smaller. It is probably significant that conditions during the first irrigation of the sugarbeets were similar to those during the second irrigation of the corn field (i.e., high soil NO_3^- and water, but low NH_4^+, and NO_2^-), again suggesting the possible importance of N_2O losses during NH_4^+ oxidation and/or chemodenitrification.

Total N_2O emitted over the 1978 growing season was about 2.5 kg N_2O-N/ha from the corn field and a smaller amount from the sugarbeet field. The corn field total falls between CAST's estimates that 1 kg N_2O-N is liberated annually per hectare of harvested cropland on earth (CAST, 1976) and the estimate based on data of Ryden et al. (1979) that 7–9 kg N_2O-N/ha was lost from a heavily fertilized, frequently irrigated California vegetable crop. The losses we measured comprised only about 1–2% of the nitrogen applied to the crops, a much smaller fraction than the values of up to several tens of percent used by modelers (McElroy et al., 1976) to predict the effect of agricultural fertilizers upon stratospheric ozone depletion.

Table 2—Nitrous oxide emissions from corn and sugarbeet fields.

Sampling time	N_2O flux	
	Corn	Sugarbeet
	g N ha^{-1} day^{-1}	
Before first irrigation	3.8	0.30
1 day after first irrigation	520.	6.5
2 days after first irrigation	550.	8.2
12 days after first irrigation	1.3	0.60
1 day after second irrigation	30.	0.66

ACKNOWLEDGMENTS

We thank John Waggener, Mike Waggener, and Daryl Williams, owner-operators of the farms, for their cooperation and assistance. We also thank Charles Andre and Lynn Mack for their capable technical assistance.

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