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Nitrous Oxide Emissions in Irrigated Corn as Affected by Nitrification Inhibitors

K. F. Bronson, A. R. Mosier,* and S. R. Bishnoi

ABSTRACT

Nitrous oxide and N_2 are the major denitrification products in irrigated corn (*Zea mays* L.). In addition, N_2O is considered a gas that contributes to global warming and stratospheric O_3 depletion. Minimizing N_2O emissions in cropping systems is therefore an economic as well as an important environmental concern. In a 1989 field experiment, the nitrification inhibitor encapsulated calcium carbide (ECC) (0, 20, or 40 kg CaC_2 ha^{-1}) or nitrapyrin (0.5 L a.i. ha^{-1}) was banded with urea (218 kg N ha^{-1}) 7 wk after planting corn. Between 1 and 14 wk after fertilization in 1989, N_2O losses of 3226, 1109, 1017, and 1005 g N_2O–N ha^{-1} from urea alone, urea plus nitrapyrin, urea plus 20 kg ECC ha^{-1}, and urea plus 40 kg ECC ha^{-1}, respectively, were measured from vented chambers. Nitrous oxide fluxes were positively correlated with soil NO_3 levels, indicating that the nitrification inhibitors indirectly controlled N_2O emissions by preventing NO_3 from accumulating in the soil. Carbon dioxide emissions from the root zone were generally not affected by ECC or nitrapyrin. In 1990, losses of N_2O were less than in 1989 (1651 g N ha^{-1} with urea alone), probably because there were fewer irrigations. Nitrapyrin and ECC addition to urea resulted in 980 and 459 g N ha^{-1} N_2O being emitted the second year. Nitrification inhibitors appear to be a useful tool in mitigating N_2O emissions in agricultural systems.

PRODUCTION of N_2O and N_2 from denitrification are increased in N-fertilized systems (Rolston et al., 1976; Mosier et al., 1986). In addition, N_2O is a gas that is 300 times more radiatively active than CO_2 (Rodhe, 1990), while NO and NO_2 from N_2O oxidation catalytically destroy O_3 in the stratosphere (Crutzen, 1976). The amount of N_2O emitted from corn systems ranges from 1.3 (Mosier and Hutchinson, 1981) to 2% of applied N (Duxbury and McConnaughey, 1986). The total amount of N_2O emitted globally from fertilized soils is estimated to be 1.5 Tg N_2O–N yr^{-1} (Seiler and Conrad, 1987).

One strategy to limit N_2O emissions from fertilized fields is to use different N sources (Breitenbeck et al., 1980; Duxbury and McConnaughey, 1986). A few field studies have evaluated the use of nitrification inhibitors to reduce N_2O losses from soils (Aulakh et al., 1984; Magalhaes et al., 1984). Nitrification inhibitors can slow NH_4 oxidation to NO_3, and thereby limit loss of N_2O during nitrification and reduce N_2O emissions resulting from denitrification of NO_3 (Aulakh et al., 1984). Acetylene, which inhibits nitrification in soils at partial pressures of 0.1 to 10 Pa, is often introduced into soil in field studies at high concentrations (i.e., ≈1 kPa) to measure total denitrification by the acetylene-block method (blockage of the reduction of N_2O to N_2, Ryden et al., 1979; Rolston et al., 1982; Duxbury and McConnaughey, 1986). Encapsulated CaC_2 (Banerjee and Mosier, 1989) has been used as a slow-release source of C_2H_2 to inhibit nitrification and reduce N_2O and N_2 emissions in flooded rice (*Oryza sativa* L.) (Mohanty and Mosier, 1990; Banerjee et al., 1990; Bronson and Mosier, 1991). No studies have been conducted where low levels of C_2H_2 have been used to inhibit nitrification and thereby reduce gaseous N losses in upland crops such as corn. In a 2-yr field study, we evaluated the efficacy of the nitrification inhibitors ECC and nitrapyrin in reducing N_2O emissions from irrigated corn.

MATERIALS AND METHODS

The experimental site is on a Nunn clay loam (fine, montmorillonitic, mesic Aridic Argiustoll) at the Colorado State University experimental farm in Fort Collins. The top 30 cm of soil had the following chemical properties: 1:1 (soil/H_2O) pH of 7.2, 21 mg organic matter kg^{-1}, 16 mg NO_3–N kg^{-1}, electrical conductivity of 0.07 S m^{-1}, and medium to high levels of NH_4HCO_3–DTPA–extractable Ca, Mg, P, K, Zn, and Fe. The site had been planted with unfertilized corn the previous 2 yrs.

Corn hybrid DeKalb[1] 464 was planted 25 Apr. 1989 and 27 Apr. 1990 in 75-cm rows. Prior to planting, the soil was moldboard plowed and disked twice in 1989 and chisel plowed in 1990. Irrigation furrows were made with a ditcher 6 wk after planting in both years. Four furrow irrigations were applied to the corn field in 1989 and two in 1990.

Urea fertilizer and nitrification inhibitors were applied in the middle of the furrow at a depth of 15 cm and at 15-cm intervals on 19 June 1989 and 26 June 1990. Treatments consisted of ECC (0, 20, or 40 CaC_2 kg ha^{-1}), or nitrapyrin [2-chloro-6-(trichloromethyl)-pyridine] (0.5 L a.i. ha^{-1}) with urea (218 kg N ha^{-1}). Four replicate blocks contained the treatments in a completely randomized arrangement. Encapsulated CaC_2 consisted of 1 to 2-mm CaC_2 particles that were first coated with a layer of carnauba wax, then with a layer of beeswax, and finally with a layer of shellac. In 1989, ECC was 50% CaC_2 and 50% coating and, in 1990, 40% CaC_2 and 60% coating. Unfertilized blank plots were included as controls for a total of 20 plots in 1989. In 1990, additional blank plots (i.e., no fetilizer-N addition) were established that received 40 kg ECC ha^{-1}, making a total of 24 plots in 1990. In 1990, urea fertilizer labeled with 75 atom % ^{15}N was used in one 15-cm-diam. PVC ring in the border furrow of each of the 16 fertilized plots and placed at a 15-cm depth with the same rate of nitrapyrin or ECC.

Approximately three times a week, 1.2-L vented chambers (Hutchinson and Mosier, 1981) were placed in the furrows of each plot (two chambers per plot in 1989 and one chamber per plot in 1990) for 1 h in the morning. At 0, 30, and 60 min, 40-mL samples were taken from the chambers with 60-mL Monoject syringes (Monoject, Sherwood Medical, St. Louis, MO) fitted with stopcocks. Samples were analyzed for N_2O by GC (Mosier and Mack, 1980). Polyvinyl chloride (2.2-L) vented chambers were placed on the PVC rings in 1990 and left overnight for 14

Abbreviations: ECC, encapsulated calcium carbide; DTPA, diethylenetriamine pentaacetic acid; PVC, polyvinyl chloride; GC, gas chromatography; DAF, days after fertilization; CV, coefficient of variation.

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[1]Trade names and company names are included only as a convenience to the reader and do not constitute any preferential endorsement of these products.

to 16 h from 1 to 9 DAF, and for 3-h periods in the morning from 10 to 38 DAF. Dinitrogen and N_2O were determined on these samples by isotope ratio mass spectrometry (Mosier et al., 1986) on a VG -Micromass 903 (VG micromass Ltd., VG Isogas, Middlewich, England).

To determine if ECC or nitrapyrin adversely affect CO_2 emissions from soil and roots, in 1989 the headspace samples were also analyzed for CO_2 by GC (Bronson and Mosier, 1991). Acetylene produced by ECC in the soil was monitored by using two 3-mL gas samples taken from probes placed 15 cm deep in the plots that received 40 kg ECC ha^{-1} in 1989, and from all the ECC-treated plots in 1990. Acetylene concentration of soil gas was measured by GC (Bronson and Mosier, 1991).

At 2, 4, 6, and 9 wk after fertilization, soil samples were taken to a depth of 25 cm from two furrows of each plot. Fresh soils were extracted with 2 *M* KCl and the extracts were steam distilled with MgO and Devardas' alloy for NH_4 and NO_3 (Bremner, 1965). Soil moisture was determined gravimetrically on an oven-dry basis.

Fluxes of N_2O and CO_2 were calculated using the non-linear flux equation developed by Hutchinson and Mosier (1981). Calculation of flux of (N_2 + N_2O) was done with the linear equation of Rolston (1986).

Cumulative flux for the growing season was calculated for each plot by linearly interpolating data points and integrating the area by Simpson's Rule with the MathCad mathematics program (MathSoft, 1987). Gas-flux data were subject to analysis of variance for each date and for the end-of-season cumulative flux by using the General Linear Models procedure in the Statistical Analysis System framework (SAS Institute, 1985). Distributions were checked for normality ($P = 0.05$) using the Shapiro-Wilk statistic (Shapiro and Wilk, 1965). If the normality assumption was not met, then treatment means were separated using analysis of variance of the ranks of each treatment (ranked by replicate) ($P = 0.05$) (Conover, 1980).

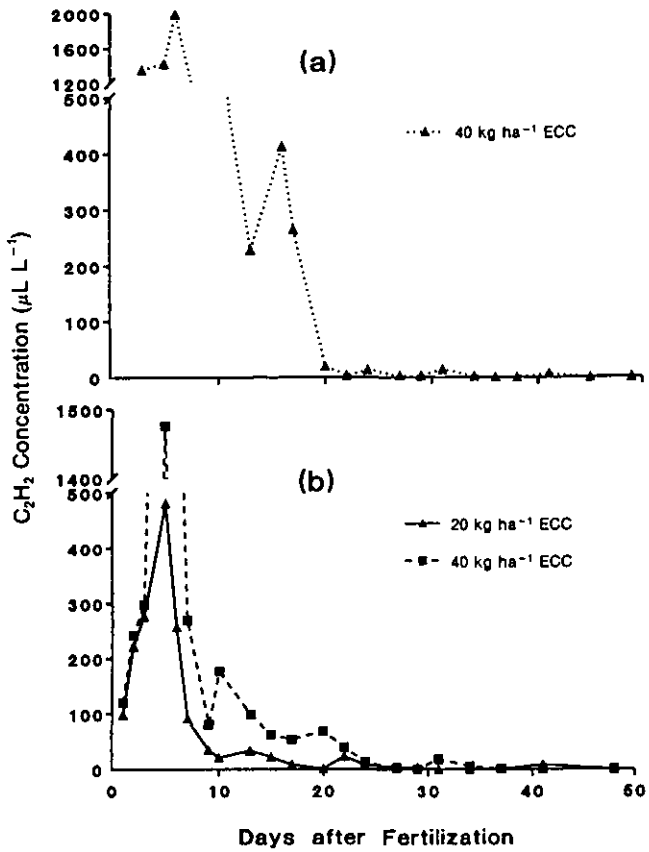

Fig. 1. Acetylene concentrations at 15-cm depth of soil as affected by encapsulated calcium carbide (ECC) application: (a) 40 kg ECC ha^{-1}, 1989 (CV = 197%); (b) 20 and 40 kg ha^{-1}, 1990 (CV = 148%).

RESULTS AND DISCUSSION

Year 1

Acetylene concentrations produced in the soil in Year 1 reached 1990 μL L^{-1} in the first 2 wk after fertilization (Fig. 1a). Acetylene was detected for 45 DAF at the 1 to 10 μL L^{-1} level. High levels of C_2H_2 at the onset were undesirable, which meant that the coatings on the ECC were not as effective as was required. Soil gas concentrations of C_2H_2 of 5 to 20 μL L^{-1} would be ideal for inhibiting nitrification (Berg et al. 1982). In laboratory incubations (data not shown), 45 and 80% inhibition of nitrification of 25 mg NH_4–N kg^{-1} was observed after 6 d in Nunn clay loam with a C_2H_2 concentration in the headspace of 5 and 20 μL L^{-1}, respectively.

Nitrous oxide fluxes reached a high rate of 356 g N ha^{-1} d^{-1} at 4 DAF in the ECC-treated plots (Fig. 2a; high rate of ECC plus urea is not shown because it was not different than low rate of ECC plus urea [$P > 0.05$]). Emissions of N_2O from the urea-alone and urea-plus-nitrapyrin treatments were small during the first 7 DAF. Denitrification of the native soil NO_3 (16 mg N kg^{-1}) occurred after the first irrigation (1 DAF). The high level of C_2H_2 produced in the ECC-treated plots apparently blocked the N_2O-to-N_2 reduction step of denitrification (Yoshinari et al., 1977), resulting in high rates of N_2O emission (i.e., N_2O was the only denitrification product). Laboratory studies (data not shown) indicate that, in Nunn clay loam, maximum blockage of N_2O reduction to N_2 occurs with a C_2H_2 concentration of 1000 μL L^{-1}. The difference between the N_2O flux in urea-plus-ECC treatments (where C_2H_2 blockage was occurring) and urea alone or urea plus nitrapyrin represents N_2 that was denitrified from the native soil NO_3 during the first 7 DAF.

Spatial variability of measured N_2O fluxes was large (average CV across dates = 80%), reflecting the heterogeneity of soil texture, soil structure, and soil NO_3 (Fig. 3, CV = 106%). Coefficients of variation of 80 to 200% have been commonly reported for field denitrification measurements (Mosier and Hutchinson, 1981; Duxbury and McConnaughey, 1986; Myrold, 1988). Distributions of the gas-flux data were nearly all normal, but the high CVs appeared to limit sensitivity in treatment-means separation only slightly.

At 10 DAF, N_2O emissions from urea plus ECC declined dramatically, and the N_2O flux from urea alone began to increase. Urea alone resulted in higher N_2O fluxes than either nitrification-inhibitor treatment between 10 and 60 d ($P < 0.01$). Nitrous oxide fluxes in urea alone usually increased rapidly and then decreased immediately after irrigation or rainfalls >2 cm. The wetting events probably resulted in limited O_2 diffusion in soil and enhanced denitrification (Mosier and Hutchinson, 1981).

Nitrate–N in the surface 25 cm of soil is shown in Fig. 3a. Nitrification of unamended urea resulted in

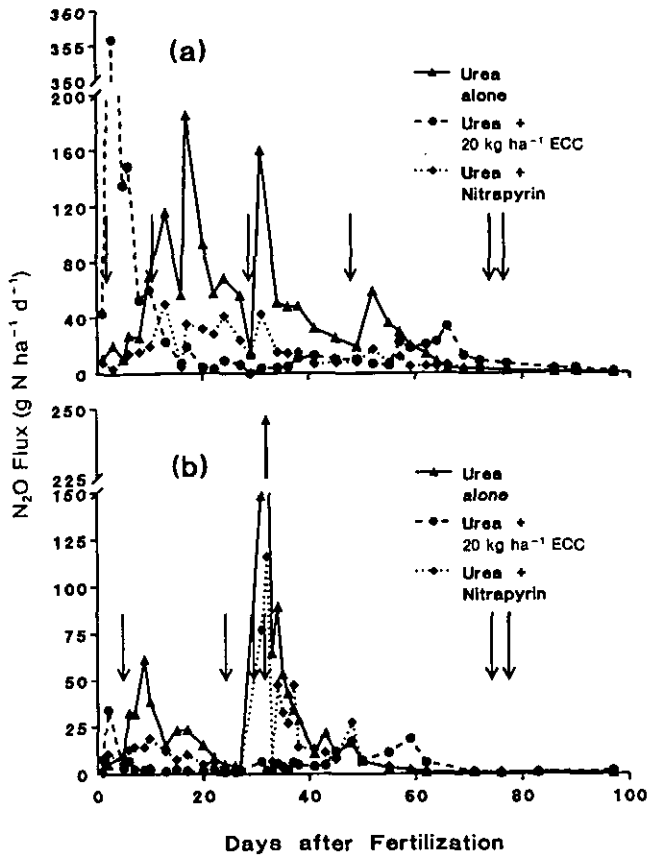

Fig. 2. Nitrous oxide emissions from irrigated corn as affected by urea with and without encapsulated calcium carbide (ECC) or nitrapyrin: (a) 1989 (CV = 80%); (b) 1990 (CV = 104%). Single arrows indicate an irrigation and double arrows indicate a rainfall >25 mm.

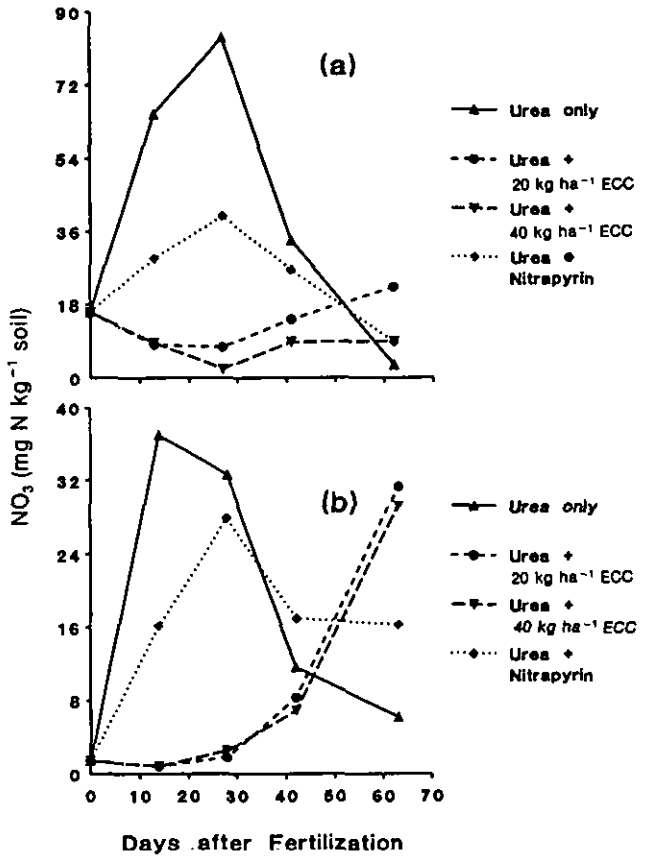

Fig. 3. Nitrate–N concentration in the 25-cm surface soil as affected by urea with and without encapsulated calcium carbide (ECC) or nitrapyrin: (a) 1989 (CV = 106%); (b) 1990 (CV = 61%).

high levels of NO_3–N (82 mg kg^{-1} at 28 DAF), but then concentrations declined, presumably due to plant uptake. Levels of NO_3 were low in the ECC treatments for the first 42 DAF, and then a small increase was observed, corresponding to an end in C_2H_2 production from ECC. Nitrapyrin addition to urea resulted in levels of NO_3 intermediate to that of the urea-alone and the urea-plus-ECC treatments. Nitrate–N was positively correlated with N_2O fluxes during the growing season ($r = 0.70$, $P < 0.01$, $n = 74$). By delaying and reducing NO_3 formation, the nitrification inhibitors indirectly reduced N_2O emissions from denitrification. A portion of the N_2O emitted from urea in the absence of nitrification inhibitors probably evolved during nitrification of NH_4 (Bremner and Blackmer, 1978; Breitenbeck et al., 1980). However, NH_4–N levels in soil (data not shown) were not as well correlated with N_2O fluxes ($r = 0.23$, $P < 0.05$, $n = 74$) as was NO_3–N. Nitrous oxide fluxes increased significantly ($P < 0.05$) in the ECC-treated plots after 60 DAF, the time when small amounts of NO_3 began to appear in these plots.

Carbon dioxide emissions from soil, which come from soil and corn root respiration, were higher ($P < 0.05$) from fertilized treatments than from the untreated control (data not shown). This is in contrast with Linn and Doran (1984), who reported that N-fertilizer addition did not affect CO_2 concentration in the 75-mm surface of plowed and no-till soils. There was generally no effect of ECC or nitrapyrin on CO_2 emissions. Comfort et al. (1990) also found no effect of C_2H_2 on CO_2 concentrations in soil, but they did report an enhancement of N_2O flux with nitrapyrin, as did Klemedtsson et al. (1988). Positive correlations between CO_2 and N_2O fluxes were observed ($P < 0.05$) on 12 out of the 35 d that gases were sampled. Yoshinari et al. (1977) reported that CO_2 is produced from the carbohydrates carrying the electrons that reduce NO_3 to N_2O in denitrification. On the other 23 d sampled, CO_2 from root respiration was probably more important than CO_2 from denitrification.

Year 2

Initial acetylene concentrations in soil were much lower than in Year 1 (Fig. 1b). The highest C_2H_2 levels in soil were reached on 5 DAF, with 480 and 1475 $\mu L\ L^{-1}$ measured in the 20 and 40 kg CaC_2 ha^{-1} plots, respectively. No C_2H_2 was detected after 48 DAF.

Blockage of N_2O reduction in the ECC treatments was observed again in the first 7 DAF in Year 2 (Fig. 2b; high rate of ECC plus urea is not shown because it was not different than low rate of ECC plus urea [$P > 0.05$]). The N_2O flux in the urea-plus-ECC plots,

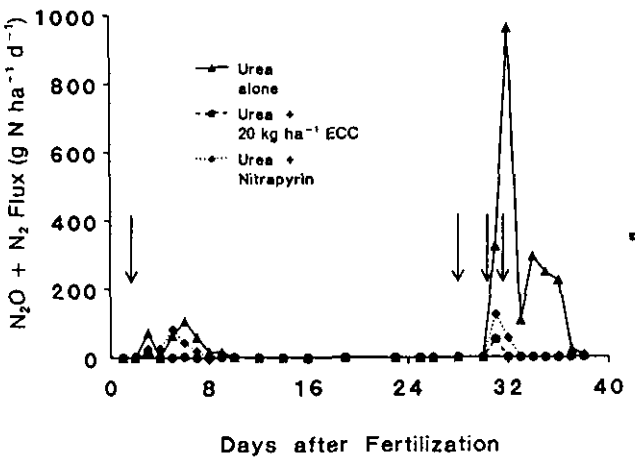

Fig. 4. Dinitrogen and nitrous oxide emissions from irrigated corn as affected by urea with and without encapsulated calcium carbide (ECC) or nitrapyrin, 1990 (CV = 176%). Single arrows indicate an irrigation and double arrows indicate a rainfall >25 mm.

however, was much less than the previous year, probably due to lower levels of C_2H_2 produced from ECC, and because concentration of NO_3 in the surface 0 to 25 cm of soil at the time of fertilization was lower (1 compared with 16 mg N kg^{-1}). Nitrous oxide flux with the high rate of ECC alone (data not shown) was not different from the high rate of ECC with urea during the first 6 DAF ($P > 0.05$). This indicates that N_2O emissions from the ECC-treated plots during the first 7 DAF (when C_2H_2 production was high) in both years was from residual soil NO_3 and not from fertilizer N. Urea alone resulted in the highest N_2O emissions for most of the growing season, similarly to Year 1; however, the magnitude of the fluxes were less than in Year 1.

Nitrous oxide fluxes were highest at 32 DAF, 2 d after the second irrigation. Urea alone resulted in a peak N_2O flux of 246 g N ha^{-1} d^{-1}, urea plus nitrapyrin emitted 116 g N ha^{-1} d^{-1}, and N_2O fluxes from the other plots were <3 g N ha^{-1} d^{-1} (the three groups are significantly different at $P = 0.01$). A hailstorm and 40 mm of rain fell on 32 DAF (anthesis), stripping most of the corn leaves. Since the soil was still at field moisture capacity when the storm hit, NO_3 leaching from the soil surface layer probably occurred. Nitrous oxide emissions declined after the hailstorm and, because no further irrigations were applied, N_2O fluxes became insignificant by 62 DAF.

Nitrous oxide fluxes were also correlated with NO_3–N in the surface 25 cm (Fig. 3b) during Year 2 ($r = 0.38$, $P < 0.01$, $n = 75$). Ammonium–N concentrations in soil (data not shown) were not correlated with N_2O fluxes in Year 2 ($r = -0.06$, $P > 0.05$, $n = 75$). Soil NO_3 levels were not as high as in Year 1 during the first half of the growing season, probably because the Year 2 site was not fertilized in 1989. Urea-only plots had a maximum of 37 mg NO_3–N kg^{-1} at 14 DAF, urea plus nitrapyrin had a maximum of 28 mg NO_3–N kg^{-1} at 28 DAF, and the urea-plus-ECC plots did not accumulate more than 8 mg NO_3–N kg^{-1} during the first 6 wk after fertilization. An additional 20 mg NO_3–N kg^{-1} accumulated in the ECC-treated plots between 42 and 62 DAF; the hail-damaged corn was not taking up much mineral N since NO_3 levels on urea-plus-nitrapyrin and urea-alone plots did not decline significantly during this time.

Table 1. Cumulative losses of N_2O–N in irrigated corn as affected by urea with and without encapsulated calcium carbide (ECC) or nitrapyrin.

Treatment	1989 0–97 DAF† Mean	SD‡	1989 7–97 DAF Mean	SD	1990 0–97 DAF Mean	SD
	g N ha^{-1}					
Urea alone	3362 a§	973	3226 a	965	1651 a	618
Urea + nitrapyrin	1174 bc	193	1109 b	188	980 b	593
Urea + 20 Kg ECC ha^{-1}	2255 ab	1223	1017 b	451	483 bc	128
Urea + 40 Kg ECC ha^{-1}	2270 ab	483	1005 b	171	434 bc	192
Blank	115 c	49	104 c	52	108 c	29

† DAF = days after fertilization.
‡ SD = standard deviation.
§ Means in a column followed by the same letter are not significantly different at $P = 0.05$ by Duncan's mean range test.

Dinitrogen plus N_2O emissions from the highly labeled ^{15}N microplots were observed in the first 9 DAF, and between 31 and 38 DAF (i.e., after the first and second irrigations) using the ^{15}N technique (Mosier et al., 1986) (Fig. 4; high rate of ECC plus urea is not shown since it was not different than low rate of ECC plus urea [$P > 0.05$]). Maximum ($N_2 + N_2O$) fluxes were measured on 32 DAF, with fluxes of 961 g N_2 ha^{-1} d^{-1} from urea alone and <60 g N_2 ha^{-1} d^{-1} in the other treatments (different at $P < 0.05$). The ratio of N_2 to ($N_2 + N_2O$) during peak emission periods ranged from 0.47 to 0.84 during the season. These ratios compare well with those reported by Mosier et al. (1986). A total of 2590 g ($N_2 + N_2O$-N) ha^{-1} was emitted from the urea-alone plots or 1.2% of the urea–N fertilizer applied. This compares with Mosier et al. (1986), who reported that 2.5% of N fertilizer applied was emitted as ($N_2 + N_2O$), and indicates that denitrification is not a major pathway for fertilizer N in irrigated corn.

Cumulative N_2O loss estimates for each year are presented in Table 1. The first column shows losses during the entire growing season in Year 1, and the second column represents the 1989 season minus the first week after fertilization, when high levels of C_2H_2 in the soil resulted in blockage of N_2O reduction to N_2. Nitrous oxide that evolved during the first 7 DAF was derived from native soil NO_3. Throughout the season, N_2O emitted from urea alone was 3362 g N ha^{-1} (1.5% of the urea–N applied), which was not significantly different ($P > 0.05$) from urea plus either rate of ECC (2255 or 2270 g N ha^{-1}). Nitrapyrin addition to urea resulted in significantly less ($P < 0.05$) cumulative N_2O emitted (1174 g N ha^{-1}). Losses of N_2O after the first week represent losses of fertilizer N_2O–N, and show that ECC and nitrapyrin controlled N_2O emissions equally well ($P > 0.05$).

In Year 2, the amount of N_2O emitted was less than in Year 1 (1651 g N_2O–N ha^{-1} from urea alone, or 0.7% applied fertilizer N), probably due to less frequent irrigations and lower soil NO_3 levels. Encapsulated CaC_2 or nitrapyrin addition controlled N_2O emissions again in Year 2 (980, 483, and 434 g N_2O–N ha^{-1}, for urea plus nitrapyrin, urea plus 20 kg ha^{-1}

ECC, and urea plus 40 kg ha^{-1} ECC, respectively; not different at $P = 0.05$). Comfort et al. (1990) reported that nitrapyrin addition to slurry did not consistently control N_2O emissions. Urea fertilizer resulted in 29 times more N_2O–N emissions than the unfertilized control in Year 1 and 15 times more in Year 2. Severalfold increases of N_2O flux with N-fertilizer application have been extensively reported (as summarized by Eichner, 1990).

SUMMARY

Nitrous oxide flux was positively correlated to NO_3–N concentration in the surface soil layer, and both soil NO_3 and N_2O fluxes were highest when no nitrification inhibitors were added with urea. Lower soil NO_3 concentrations and lower N_2O fluxes were observed when nitrification inhibitors were added with urea. Encapsulated CaC_2 controlled N_2O emissions from fertilizer as well as nitrapyrin in both years of the experiment. Carbon dioxide emissions in the first year were not consistently affected by ECC or nitrapyrin. This study shows that the concept of creating low levels of C_2H_2 in soil with ECC to inhibit nitrification shows promise, but that the coating process needs perfecting so that large, initial pulses of C_2H_2 are not produced.

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