Fertilizer and Irrigation Management Effects on Nitrous Oxide Emissions and Nitrate Leaching

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ABSTRACT

Irrigation and N fertilizer management are important factors affecting crop yield, N fertilizer recovery efficiency, and N losses as nitrous oxide (N_2O) and nitrate (NO_3^-). Split application of conventional urea (split-U) and/or one-time application of products designed to perform as enhanced-efficiency N fertilizers may mitigate N losses. The objective of this study was to compare the effects of controlled-release polymer-coated urea (PCU), stabilized urea with urease and nitrification inhibitors (IU) and split-U on direct soil-to-atmosphere N_2O emissions, NO_3^- leaching, and yield for fully irrigated and minimum-irrigated corn in loamy sand. Indirect N_2O emissions due to NO_3^- leaching were estimated using published emission factors (EF_5). Split-U increased yield and N uptake compared with preplant-applied PCU or IU and decreased NO_3^- leaching compared with PCU. Direct N_2O emissions were significantly less with IU or split-U than with PCU, and there was a trend for greater emissions with split-U than with IU ($P = 0.08$). Irrigation significantly increased NO_3^- leaching during the growing season but had no significant effect on direct N_2O emissions. After accounting for significantly increased yields with irrigation, however, N losses expressed on a yield basis did not differ and in some cases decreased with irrigation. Post-harvest soil N and soil-water NO_3^- in spring showed the potential for greater N leaching in minimum-irrigated than fully irrigated plots. Indirect emissions due to NO_3^- leaching were estimated to be 79 to 117% of direct emissions using the default value of EF_5, thus signifying the potential importance of indirect emissions in evaluating management effects on N_2O emissions.

Nitrous oxide is a major greenhouse gas and also the single most important ozone-depleting emission (Ravishankara et al., 2009). Its exponential buildup in the atmosphere during the past 300 yr is of increasing concern, and agricultural land is its primary anthropogenic source (Denman et al., 2007). Increasing N_2O emissions from agriculture are linked to soil management and application of N fertilizers. About 46% of all N fertilizers used in United States in 2010 were applied to corn (*Zea mays* L.) (Economic Research Service, 2012). Hence, management of corn production can potentially play a role in N_2O mitigation efforts.

The use of PCU or IU has the potential to mitigate N_2O emissions. These products are designed to release N more gradually over the course of the season compared with conventional urea to minimize N loss and improve synchrony between soil N availability and crop N demand. Some field studies have shown the effectiveness of these products in improving plant N use efficiency (NUE) (Shoji et al., 2001; Freney et al., 1992) and reducing N_2O emissions (Halvorson et al., 2010, 2011, 2013; Hyatt et al., 2010; Bronson et al., 1992) while others have shown limited or no effectiveness (Sistani et al., 2011; Venterea et al., 2011b; Parkin and Hatfield, 2010). These products, if effective, may also eliminate the need for multiple split applications of N, which are recommended to reduce NO_3^- leaching (Rosen and Bierman, 2008) especially in irrigated sandy soils.

In 2008, 16% of the total corn hectares in the United States were under irrigation (National Agricultural Statistics Service, 2008). Irrigation is a major factor that influences the leaching of NO_3^-, which is a groundwater contaminant. Nitrogen lost from fertilized fields through NO_3^- leaching can also contribute to the so-called "indirect" N_2O emissions by conversion of NO_3^- to N_2O in a receiving aquatic ecosystem. Apart from direct soil-to-atmosphere N_2O emissions occurring in the field, indirect emission of N_2O downstream may be significant, especially in cases of sandy soils under irrigation. There is only one study, to our knowledge, that compares the effects of irrigation vs. no irrigation on direct N_2O emissions (Horvath et al., 2010) and there have been no studies as far as we know that have reported direct N_2O emissions and indirect N_2O emissions due to NO_3^- leaching simultaneously for corn production.

In evaluating management impacts on N_2O emissions, alterations in crop yield resulting from a shift in N and irrigation management also need to be considered (Venterea et al., 2011b; Van Groenigen et al., 2010). Corn is very sensitive to water stress (El-Hendawy and Schmidhalter, 2010; NeSmith and Ritchie, 1992), and timely water input by irrigation has been shown to

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Abbreviations: DCD, dicyandiamide; DI, direct plus indirect nitrous oxide emissions due to nitrate leaching; DRY, minimum-irrigated system; EF_5, emission factor to estimate amount of leached nitrate that would convert to nitrous oxide downstream; FIEF, fertilizer-induced emission factor; FILF, fertilizer-induced leaching factor; IRG, fully irrigated system; IU, stabilized urea containing urease and nitrification inhibitors; split-U, split application of conventional urea; NFRE, nitrogen fertilizer recovery efficiency; PCU, polymer-coated urea; WFPS, water-filled pore space.

increase yield (Stone et al., 2010); however, loss of N through leaching, which can be significant in some irrigated systems, can negatively affect NUE (Errebhi et al., 1998) and yield. Irrigation can also increase direct N_2O emissions compared with water-stressed systems (Horvath et al., 2010). Split application of N can increase grain yield compared with a single application (Sitthaphanit et al., 2009). Hence, expressing N_2O emissions per unit yield can be a useful metric to compare the impacts of different fertilizer and irrigation management practices on N_2O emissions.

The main objective of this study was to compare area- and yield-based direct N_2O emissions, NO_3^- leaching, and N fertilizer recovery efficiency (NFRE) in fully irrigated, non-water-stressed (IRG) or minimally irrigated, water-stressed (DRY) corn plots, each of which received split applications of urea and a onetime application of urea–NH_4NO_3 for the IRG plots to simulate fertigation (split-U) or single preplant applications of either PCU or IU over two consecutive growing seasons. Split-U is considered a best management practice in sandy soils in the region (Rehm et al., 2008), and thus the objective of the study was to compare alternative best management practices. We also estimated direct plus indirect (DI) N_2O emissions by adding direct soil-to-atmosphere emissions to indirect N_2O emissions due to NO_3^- leaching estimated using published emission factors (De Klein et al., 2006).

MATERIALS AND METHODS

Site Description and Experimental Design

The site is located at the University of Minnesota's Sand Plain Research Farm in Becker, MN (45°23′ N, 93°53′ W), where the soil is a Hubbard loamy sand (a sandy, mixed, frigid Entic Hapludoll) containing 820 g kg^{-1} sand, 100 g kg^{-1} silt, and 80 g kg^{-1} clay in the upper 0.15 m. Soil organic matter (SOM) determined by loss-on-ignition was 25 g kg^{-1} in samples from the 0- to 0.1-m depth and 17 g kg^{-1} in samples from the 0.1- to 0.2-m depth. The 30-yr average precipitation and daily temperature during April through October are 531 mm and 16.0°C, respectively (Minnesota Climatology Working Group, http://climate.umn.edu/).

The experiment was conducted during the course of two consecutive growing seasons (2009 and 2010), using adjacent sections of the farm each year. The fields were planted to unirrigated, unfertilized rye (*Secale cereal* L.) for 3 yr before the experiment. Rye grain was harvested in summer followed by a rye winter cover crop each year. In spring, the rye residue was incorporated using chisel plowing followed by shallow disking. An experiment was then established using a randomized complete block design with irrigation as the main treatment in each of four main plots and N fertilizer as a subplot. In this region of the state and on this soil type, corn is grown under both irrigated and rainfed conditions; however, a preliminary experiment conducted at the site in 2008 found that completely unirrigated corn had a significant loss in yield (32–84%) compared with irrigated corn. Therefore, experiments in subsequent years compared standard irrigation to minimal irrigation applied only to prevent extreme water stress. Irrigation treatments were designated as (i) IRG, where main plots were irrigated based on the checkbook method for determining the frequency and amount of water inputs as described in Wright (2002), and (ii) DRY, where main plots were not irrigated except in mid-season (July and early August) when the soil matric potential at the 0.3-m depth was close to or below –50 kPa for two to four consecutive days and coincided with a matric potential of less than –100 kPa at the 1.2-m depth (amounts of irrigation applied to DRY plots are given below). Irrigation in all cases was applied using an aluminum solid-set overhead sprinkler system.

Each of four main IRG and DRY plots was subdivided into four 5- by 5-m subplots, which were assigned randomly to N fertilizer treatments consisting of: (i) split-U (46–0–0) applied in two and three separate applications in DRY and IRG plots, respectively, (ii) PCU (44–0–0) (ESN, Agrium Advanced Technologies) applied in a single preplant application, (iii) IU (46–0–0) containing the urease inhibitor *N*-(*n*-butyl)-thiophosphoric triamide and the nitrification inhibitor dicyandiamide (DCD) (Super U, Agrotain International) also applied in a single preplant application, and (iv) an unfertilized control. All N treatments, including the control, received liquid starter N fertilizer at planting at the rate of 5.6 kg N ha^{-1}as 10–34–0 (N–P–K). Corn was planted at a seeding rate of 79,000 seeds ha^{-1} on May 8 2009 and on Apr. 26 2010. Each fertilized treatment received a total of 180 kg N ha^{-1} (excluding starter), which is the recommended rate for this region (Rehm et al., 2008). The third application of split-U in the IRG plots was applied as urea–NH_4NO_3 to simulate a fertigation event, which is a recommended practice with irrigation but would not be advisable under dryland production (Rehm et al., 2008). A separate N rate study at the same site showed that an N rate of 180 kg N ha^{-1} was toward the lower end of a range of economically optimum N rates for irrigated corn and toward the higher end for water-stressed corn (unpublished data, 2008). Fertilizers were surface broadcast and incorporated using a cultivator except for the third split-U application in the IRG plots, which was irrigated immediately following surface application using 13 and 15 mm of water in 2009 and 2010, respectively. During application, the N_2O flux chamber measurement areas (described below) were initially covered. After the initial application, separately weighed portions of fertilizers were applied within the chamber measurement areas to ensure accurate application rates. Table 1 provides details of the date, source, and amount of fertilizers applied for both years. An on-site weather station was used to measure air temperature, wind speed, relative humidity, precipitation, and net solar radiation at 10-min intervals. Irrigation and precipitation water were periodically sampled and analyzed for the sum of NO_2^- plus NO_3^- (hereafter referred to as NO_3^-) using a flow-through colorimetric analyzer (QuickChem 8500 with ASX 520 Series autosampler, Lachat Instruments).

Nitrous Oxide Emissions

Soil-to-atmosphere N_2O fluxes were measured using static chamber methods (Venterea et al., 2005, 2010; Rochette et al., 2000). In 2009, fluxes were measured twice a week from May to October; in 2010, fluxes were measured once a week in April, September, and October and twice a week from May to August, for a total of 41 sampling dates each year. Sampling was generally made during 1000 to 1200 h local time when the soil temperature in the upper 0.10 m was close to its daily mean value. In 50% of the irrigation events in 2010 and 70% in 2009, N_2O flux samplings were performed within 24 h after irrigation. One stainless steel chamber anchor (0.50 by 0.29 by 0.086 m deep) was installed

Table 1. Date, source, and amount of fertilizer application.

Date	Irrigation treatment†	N source‡	N applied
			kg N ha^{-1}
	2009		
1 May	IRG, DRY	PCU, IU	180
8 May	IRG, DRY	starter	6
28 May	IRG, DRY	split-U	90
17 June	DRY	split-U	90
17 June	IRG	split-U	56
13 July	IRG	split-U	34
	2010		
23 Apr.	IRG, DRY	PCU, IU	180
26 Apr.	IRG, DRY	starter	6
26 May	IRG, DRY	split-U	90
9 June	DRY	split-U	90
9 June	IRG	split-U	56
8 July	IRG	split-U	34

† IRG, fully irrigated; DRY, minimum irrigated.

‡ Starter, 10–34–0 (N–P–K) fertilizer; PCU, polymer-coated urea; IU, stabilized urea with chemical inhibitors; split-U, split-applied urea. The third application of the split-U in the IRG plots was applied as urea–NH_4NO_3 to simulate a fertigation.

in each subplot, centered between corn rows with the short side parallel to the corn row and encompassing 70% of the interrow width. Because the fertilizers were uniformly applied, it was assumed that gas fluxes in the uncovered areas did not differ from the covered areas. On each sampling day, insulated and vented chamber tops (0.50 by 0.29 by 0.102 m high) were secured to anchors with binder clips, and samples were collected at 0, 0.5, and 1 h using a 12-mL polypropylene syringe. In 2010, a fourth sample was also collected after 1.5 h. Samples were immediately transferred to glass vials sealed with butyl rubber septa (Alltech) and analyzed within 2 wk using a headspace autosampler (Teledyne Tekmar) connected to a gas chromatograph (Model 5890, Agilent/Hewlett-Packard) equipped with an electron capture detector. The equipment was calibrated with analytical-grade standards (Scott Specialty Gases) each day when samples were analyzed. Gas concentrations in molar mixing ratios determined by the gas chromatograph were converted to mass per volume concentrations using the ideal gas law and air temperatures at the sampling time. Gas fluxes were calculated from the rate of change in gas concentration, the chamber volume, and the base area using quadratic regression (QR) as the default calculation scheme (Wagner et al., 1997) and using correction factors to account for suppression of the surface–atmosphere concentration gradient (Venterea, 2010). Linear regression was used in place of QR when time series gas concentration data had completely linear or positive curvature, i.e., when the second derivative of the QR results was ≥ 0 (Venterea, 2013; Venterea et al., 2009). The QR method was evaluated using the LINEST function in Microsoft Excel (version 2010).

Soil Water Nitrate Concentrations

Nitrate concentrations in the soil water were determined using suction cup lysimeters installed to a depth of 1.2 m, as described by Venterea et al. (2011a). Each lysimeter was constructed of a 1.3-m-long polyvinyl chloride pipe (48-mm i.d.) with one end fitted with epoxy to a round-bottom, 100-kPa high-flow porous ceramic cup (Soilmoisture Equipment Corp.) and the other end to a rubber stopper. Two sections of 5.35-mm-i.d. polyethylene tubing were inserted through the rubber stopper: one tube (the vent tube) was short and extended inside the lysimeter only to 0.1 m below the stopper, while the other (the sample tube) extended to 2 mm above the ceramic cup. The vent and sample tubes were connected to 6-mm-i.d. Tygon laboratory tubing equipped with polypropylene ratcheting clamps (Halkey-Roberts Corp.). The lysimeters were submerged in water under vacuum to fill them with water before installing them.

Each year within a week of planting, one lysimeter was installed in each subplot in a corn-planted row. A 1.3-m-deep borehole was made using an 83-mm-diameter soil auger. Silica flour slurry was added to a depth of 0.1 m before installing the lysimeters. Soil was poured back into the gap between the lysimeter and the sides of the hole in reverse order of its removal from the borehole. At a depth of 0.15 m, a 10-mm-thick layer of powdered bentonite was evenly applied around the lysimeter to prevent preferential water flow. On the following day, water was evacuated from each lysimeter by applying pressure through the vent tube while allowing water to exit the sample tube. The lysimeters were then prepared for subsequent water sampling by leaving them under a vacuum of 40 kPa for 1 wk. Water samples were collected once per week during the growing season in 50-mL polypropylene vials and stored at –5°C before being analyzed for NO_3^- using a flow-through colorimetric analyzer (QuickChem 8500 with ASX 520 Series autosampler, Lachat Instruments). Upon freeze-up in the fall, the vacuum was removed from the lysimeters, which were left in the field through the winter. Once the soil had thawed in early spring, the vacuum was restored to collect water samples as above. Depending on the conditions of the lysimeters in the soil, water samples were collected once a week for 6 wk in spring 2011 following 2010 corn and could be collected only one time in spring 2010 following 2009 corn.

Drainage and Nitrate Leaching

The amount of water draining below the root zone was estimated using a water mass balance equation as used in previous studies at this and other sites with excessively well-drained soils (Venterea et al., 2011a; Wilson et al., 2010; Waddell et al., 2000). Water balance and drainage rates were determined from

$$D-(P+I-\mathrm{ET})-\Delta S \quad [1]$$

where D is drainage (mm d^{-1}), P is precipitation (mm d^{-1}), I is irrigation water applied (mm d^{-1}), ET is evapotranspiration (mm d^{-1}), and ΔS is the daily change in soil water storage in the soil profile (mm d^{-1}). The value of P was determined using a National Weather Service catch can and gauge stick, and I was calculated based on the irrigation flow rate and the duration of application. The ET values were calculated as a product of a crop coefficient given by Stegman et al. (1977) based on the stage of corn growth and the potential ET estimated using the Penman–Monteith equation (Allen et al., 1998), with daily weather data recorded at the site. The value of S on any given day was assumed not to exceed field capacity (FC), which was measured to be 140 mm to a depth of 1.2 m (Gremy et al., 1993). The water content in a soil profile of 0 to 1.2 m was measured during the growing season a total of five times each year to confirm that it did not exceed FC. To determine D, Eq. [1] was expanded as follows:

$$D_n = (P_n + I_n - ET_n) + S_{n-1} - S_n \qquad [2]$$

where the subscripts n and $n - 1$ denote the current and previous day, respectively. The initial amount of water (S) in the soil profile at the start of the growing season was assumed equal to FC. Daily rates of NO_3^- leaching (mg NO_3^-–N d^{-1}) during the growing season were determined as the product of D and daily NO_3^- concentrations, which were estimated using linear interpolation of weekly NO_3^- concentrations measured in the lysimeter water samples as described above.

Yield and Plant Nitrogen Content

After physiological maturity, corn ears were harvested from 1.5 m in the middle two rows of each subplot. The ears were dried, shelled, and further dried for 3 d at 65°C, then weighed to obtain dry grain and cob yield. Stover was collected by cutting six plants just above their crowns where the corn ears were harvested. The stover was weighed, and the six plants from each subplot were subsampled and ground, weighed, and then dried for moisture content determination. Grain and stover samples were further ground with a grinding mill and analyzed with an elemental N combustion analyzer (VarioEL, Elementar) for total aboveground N.

Soil Physical and Chemical Properties

Soil temperature was measured on each N_2O flux measurement day using temperature probes (Fisher) inserted to the 0.05-m depth within 1 m of the chambers. Soil water content and bulk density were determined on samples collected from the control and split-U plots in both IRG and DRY treatments to the 0.05-m depth within 1 h of each flux measurement period by drying at 105°C. Bulk density values were used together with gravimetric water content to estimate the water-filled pore space (WFPS). Soil moisture sensors (6450WD, Spectrum Technologies, Inc.) were installed at depths of 0.3 and 1.2 m in one subplot each of the IRG and DRY plots. Probes were connected to a datalogger (3345WD, Spectrum Technologies, Inc.), from which high-frequency (every 10 min) data were collected and daily averages were calculated. These data are not presented but were used in determining when the DRY plots should be irrigated to prevent extreme water stress and crop failure.

Additional soil samples to a depth of 0.6 m were collected at the end of the season (post-harvest) for analysis of extractable inorganic N. Two cores from each subplot were pooled, homogenized, and refrigerated before analysis. Subsamples of ~10 g were extracted in 2 mol L^{-1} KCl, filtered (Whatman no. 42), and analyzed for NH_4^+ and NO_3^- using a flow-through injection colorimetric analyzer (Lachat Instruments).

Data Analysis and Statistics

Nitrous oxide fluxes measured on each sampling date for each subplot were used to estimate the cumulative area-based direct N_2O emissions (hereafter, N_2O emissions refer to direct soil-to-atmosphere emissions unless mentioned otherwise) using trapezoidal integration of flux vs. time. The fertilizer-induced emissions factor (FIEF) was calculated by subtracting the cumulative area-based N_2O emissions in the control treatment from that in each N treatment and then expressing the result as a percentage of the total amount of fertilizer N applied (180 kg N ha^{-1}). Yield-based N_2O emissions (g N Mg^{-1} yield) were calculated by dividing the cumulative area-based N_2O emissions by the grain yield. Nitrogen fertilizer recovery efficiency was calculated by subtracting the total aboveground N uptake in the control treatment from that in each N treatment and expressing the result as a percentage of the total fertilizer N applied.

Cumulative NO_3^- leaching (kg NO_3^-–N ha^{-1}) was estimated by summing the daily rates of NO_3^- leaching. A fertilizer-induced leaching factor (FILF) was calculated by subtracting the cumulative NO_3^- leaching in the control treatment from that in each N treatment and by expressing the result as a percentage of the total fertilizer N applied. Yield-based NO_3^- leaching was calculated by dividing the cumulative NO_3^- leaching by the grain yield. Indirect N_2O emissions due to NO_3^- leaching were estimated by multiplying the cumulative NO_3^- leaching by emission factors (EF_5 = 0.05, 0.75, and 2.5%), which represent the lower limit of the 95% confidence interval (CI), the best estimate, and the upper limit of the 95% CI, respectively, based on De Klein et al. (2006). The EF_5 value represents the percentage of leached NO_3^- that subsequently converts to N_2O in the groundwater, surface drainage, rivers, and estuaries. Indirect N_2O emissions were added to direct N_2O emissions from the same subplots to estimate DI N_2O emissions.

The effects of year, irrigation, and N source treatments were determined using Proc Mixed in SAS, with block, block × year, and block × year × irrigation treated as random effects and fertilizer, irrigation, and year as fixed effects (Littell et al., 2006; SAS Institute, 2003). When the main effect was significant, means comparisons were conducted using contrasts in SAS with significance criteria of $P < 0.05$, unless otherwise mentioned.

RESULTS

Climate, Soil Moisture, and Drainage

Total precipitation amounts during 1 April through 31 October in 2009 and 2010 were 532 and 732 mm, respectively, with the latter being greater than the 30-yr average (531 mm) by 38% (Fig. 1). Monthly rainfall patterns also varied between years. In 2009, precipitation from 1 April to 1 July was 208 mm, whereas in 2010 it was 458 mm. Irrigation was the equivalent of 41% of total water inputs in the IRG plots in 2009, compared with 27% in 2010. Irrigation was the equivalent of 6 and 2% of total water inputs in the DRY plots in 2009 and 2010, respectively. Irrigation was applied to the DRY plots on 13 July (13 mm), 15 July (8 mm), and 3 August (15 mm) in 2009 and 15 July (18 mm) in 2010. Total seasonal drainage in the IRG and DRY plots was the equivalent of 46 and 14%, respectively, of the total water inputs during the growing season in 2009 and 64 and 54%, respectively, in 2010 (Fig. 1). The mean daily temperature in 2010 was 17.4°C, compared with 15.8°C in 2009 (Fig. 2a). The soil WFPS at the time of N_2O flux sampling was <70% throughout the season in both years (Fig. 2b). The mean soil WFPS was 30 and 40% in the IRG plots in 2009 and 2010, respectively, compared with 22 and 30%, respectively, in the DRY plots.

Agronomic Responses

Averaged across N sources, grain yield was greater in 2009 than in 2010 and greater in the IRG than the DRY treatment (Table 2). Averaged across years and irrigation treatments, yield was greater for all three N sources than the control and was significantly greater with split-U than with PCU or IU (Table 2).

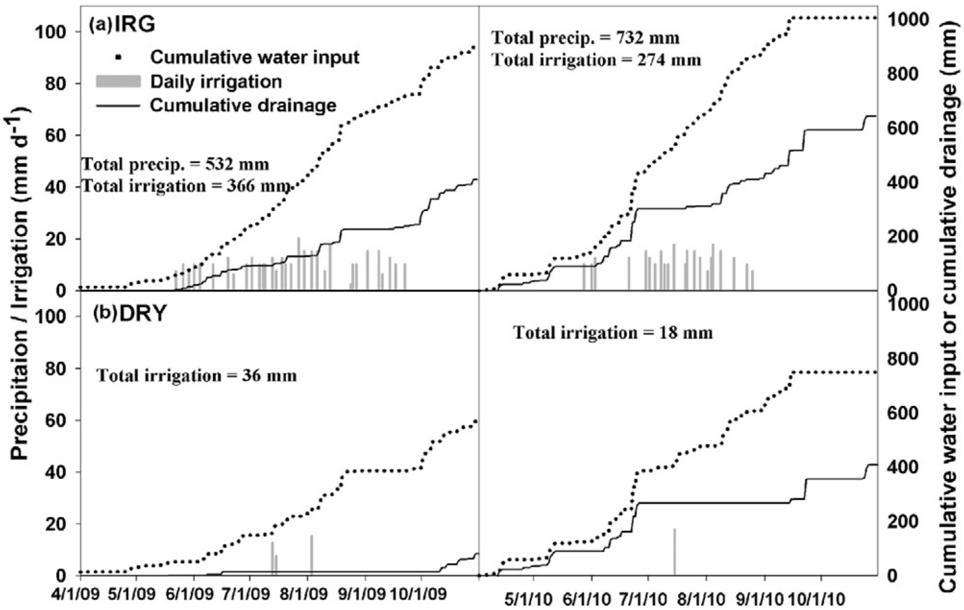

Fig. 1. Daily irrigation and cumulative water input and drainage in (a) fully irrigated (IRG) and (b) minimum-irrigated (DRY) plots during 2009 and 2010.

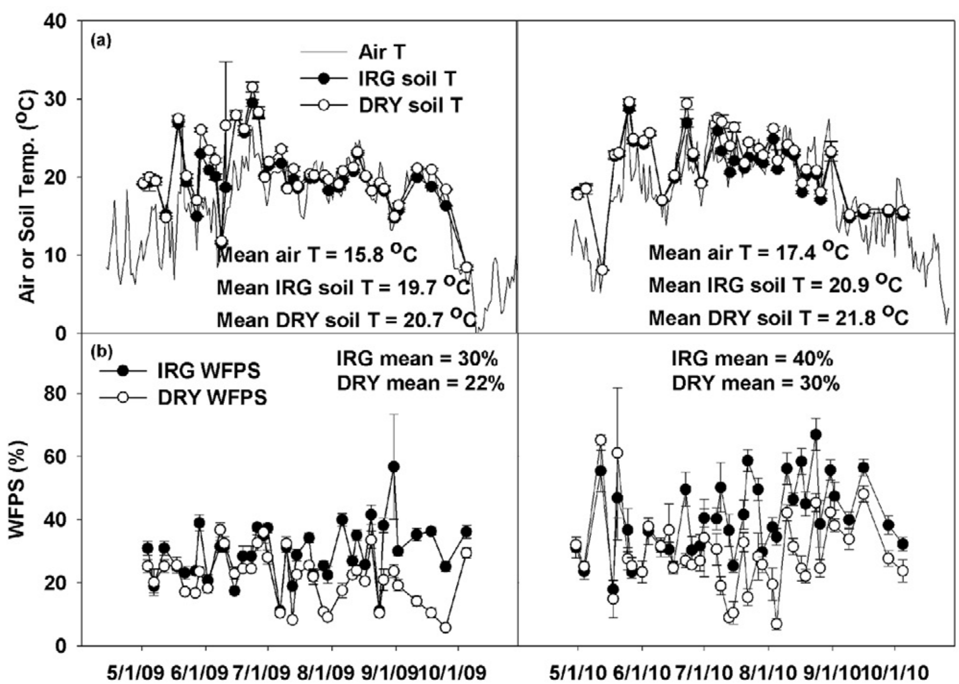

Fig. 2. (a) Air temperature and mean soil temperature, and (b) mean water-filled pore space (WFPS) at the 0.05-m depth at the time of N_2O sampling in fully irrigated (IRG) and minimum-irrigated (DRY) plots during 2009 and 2010. Standard errors are denoted by vertical bars.

The three-way interaction effect of year, irrigation, and N source was significant for aboveground N uptake and NFRE (Table 2). Aboveground N uptake was greater in IRG plots than in DRY plots in 2010 for all N sources, including the control, whereas in 2009, it was greater only for the split-U treatment (Table 3). Aboveground N uptake was always greater for split-U than any other N treatment in both IRG and DRY plots each year. In 2010, NFRE did not differ by irrigation for any of N sources, and split-U had greater NFRE than PCU or IU in both IRG and DRY treatments. In 2009, NFRE was greater in DRY than IRG treatments for PCU and IU, but the reverse was true for split-U.

Direct Nitrous Oxide Emissions

During each growing season, fluxes >20 μg N m^{-2} h^{-1} were observed in the months of May, June, and July (Fig. 3). There was no significant difference in area-based N_2O emissions by year or irrigation (Table 2). Cumulative area-based N_2O emissions were greater for all fertilized treatments than the control. Among fertilized treatments, area-based N_2O emissions were significantly

Table 2. Results of statistical analyses with means for different dependent variables as affected by year, irrigation, and N source.

Source of effects	Grain yield	Aboveground N uptake	NFRE†	N_2O emissions	Yield-scaled N_2O emissions	FIEF†	NO_3 leaching	Yield-scaled NO_3 leaching	FILF†
	Mg ha^{-1}	kg N ha^{-1}	%	kg N ha^{-1}	g N Mg^{-1} grain	%	kg N ha^{-1}	kg N Mg^{-1} grain	%
Year (Y)									
2009	9.8 (0.5) a‡	143.9 (9.6) a	64.2 (2.7) a	0.33 (0.02)	30.3 (1.6)	0.08 (0.01)	15.8 (2.8) b	1.6 (0.3) b	4.5 (1.3)
2010	7.7 (0.6) b	114.5 (8.6) b	50.0 (3.1) b	0.28 (0.02)	47.4 (6.7)	0.07 (0.01)	30.3 (2.8) a	5.0 (0.7) a	8.5 (2.0)
Significance	**	**	*	ns	*P* = 0.07	ns	*	**	*P* = 0.07
Irrigation (I)§									
IRG	10.2 (0.5) a	139.5 (8.8) a	55.2 (3.3)	0.30 (0.02)	30.3 (1.6) b	0.08 (0.01)	30.6 (2.1) a	3.1 (0.2)	8.4 (1.4)
DRY	7.4 (0.6) b	118.9 (9.9) b	59.0 (3.2)	0.31 (0.02)	52.5 (6.4) a	0.07 (0.01)	15.5 (3.3) b	3.4 (0.9)	4.6 (2.0)
Significance	***	**	ns	ns	**	ns	**	ns	P = 0.08
N source (N)¶									
Control	4.4 (0.4) c	52.1 (4.7) c	–	0.20 (0.01) c	61.5 (11.8) a	–	14.6 (2.3) c	5.0 (1.4) a	–
PCU	9.9 (0.5) b	147.2 (7.0) b	52.8 (3.9) b	0.41 (0.03) a	42.5 (4.3) b	0.11 (0.02) a	29.7 (5.7) a	3.3 (0.8) b	8.7 (2.9)
IU	9.8 (0.6) b	146.6 (8.7) b	52.5 (4.2) b	0.28 (0.02) b	30.0 (2.8) c	0.04 (0.01) b	26.8 (4.8) ab	2.8 (0.5) b	6.9 (1.9)
Split-U	11.0 (0.6) a	170.9 (6.8) a	66.0 (3.0) a	0.34 (0.03) b	31.6 (2.4) bc	0.07 (0.01) ab	21.0 (3.3) bc	2.0 (0.4) b	3.9 (1.0)
Significance	***	***	***	***	***	**	**	**	ns
Interaction									
N × Y	ns	***	**	ns	*	ns	ns	*	ns
N × I	ns	**	**	ns	**	ns	ns	ns	ns
N × Y × I	ns	**	**	ns	*	ns	ns	*	ns

* Significant at *P* < 0.05; ns, not significant.
** Significant at *P* < 0.01.
*** Significant at *P* < 0.001.
† NFRE, N fertilizer recovery efficiency; FIEF, fertilizer-induced emission factor; FILF, fertilizer-induced leaching factor.
‡ Means with standard errors in parentheses. Means in a column followed by the same letter are not significantly different (*P* < 0.05).
§ IRG, fully irrigated; DRY, minimum irrigated.
¶ Starter, 10–34–0 (N–P–K) fertilizer; PCU, polymer-coated urea; IU, stabilized urea with chemical inhibitors; split-U, split-applied urea.

Table 3. Means for variables where significant three-way interaction effects of year, irrigation (IRG, fully irrigated; DRY, minimum irrigated), and N source were found.

N source†	2009 IRG	2009 DRY	2010 IRG	2010 DRY
		Aboveground N uptake, kg N ha^{-1}		
Control	65.2 (8.2) f‡	49.5 (12.8) fg	64.9 (14.3) f	29.0 (11.7) g
PCU	160.8 (8.3) bc	179.0 (9.6) ab	136.3 (25.2) d	112.6 (6.7) e
IU	162.1 (8.4) bc	181.7 (3.0) ab	145.8 (25.2) cd	97.0 (12.5) e
split-U	199.4 (28.0) a	154.0 (22.0) cd	181.7 (3.1) ab	148.6 (13.1) cd
		N fertilizer recovery efficiency, %		
Control	–	–	–	–
PCU	43.7 (6.6) cdef	72.0 (6.1) ab	39.7 (15.0) ef	46.4 (7.3) def
IU	53.1 (6.3) cde	73.5 (8.7) ab	44.9 (13.1) def	37.8 (13.0) f
split-U	74.5 (16.0) a	58.1 (12.9) bcd	64.9 (9.5) abc	66.4 (5.3) abc
		Yield-scaled direct N_2O emissions, g N kg^{-1}		
Control	35.9 (1.8) bcd	52.3 (16.8) bc	31.9 (11.4) cd	126.1 (55.2) a
PCU	37.7 (7.8) bcd	39.4 (6.8) bcd	32.9 (6.40) cd	60.2 (27.7) b
IU	27.5 (9.8) cd	24.3 (7.7) d	25.9 (9.2) d	42.2 (9.7) bcd
split-U	29.4 (11.0) cd	36.7 (4.6) bcd	21.3 (4.0) d	39.1 (7.1) bcd
		Yield-scaled NO_3 leaching, g N Mg^{-1}		
Control	3.2 (0.7) cdef	0.4 (0.1) def	4.0 (0.6) bc	12.3 (3.4) a
PCU	3.0 (0.4) cdef	0.2 (0.1) ef	3.3 (0.5) cde	6.8 (2.2) b
IU	3.0 (0.7) cdef	0.4 (0.1) def	4.3 (0.7) bc	3.7 (0.9) bc
split-U	2.1 (0.2) cdef	0.1 (0.1) f	2.3 (0.2) cdef	3.5 (0.7) cd

† Starter, 10–34–0 (N–P–K) fertilizer; PCU, polymer-coated urea; IU, stabilized urea with chemical inhibitors; split-U, split-applied urea.
‡ Mean with standard error in parentheses. Means in a column followed by the same letter are not significantly different (*P* < 0.05).

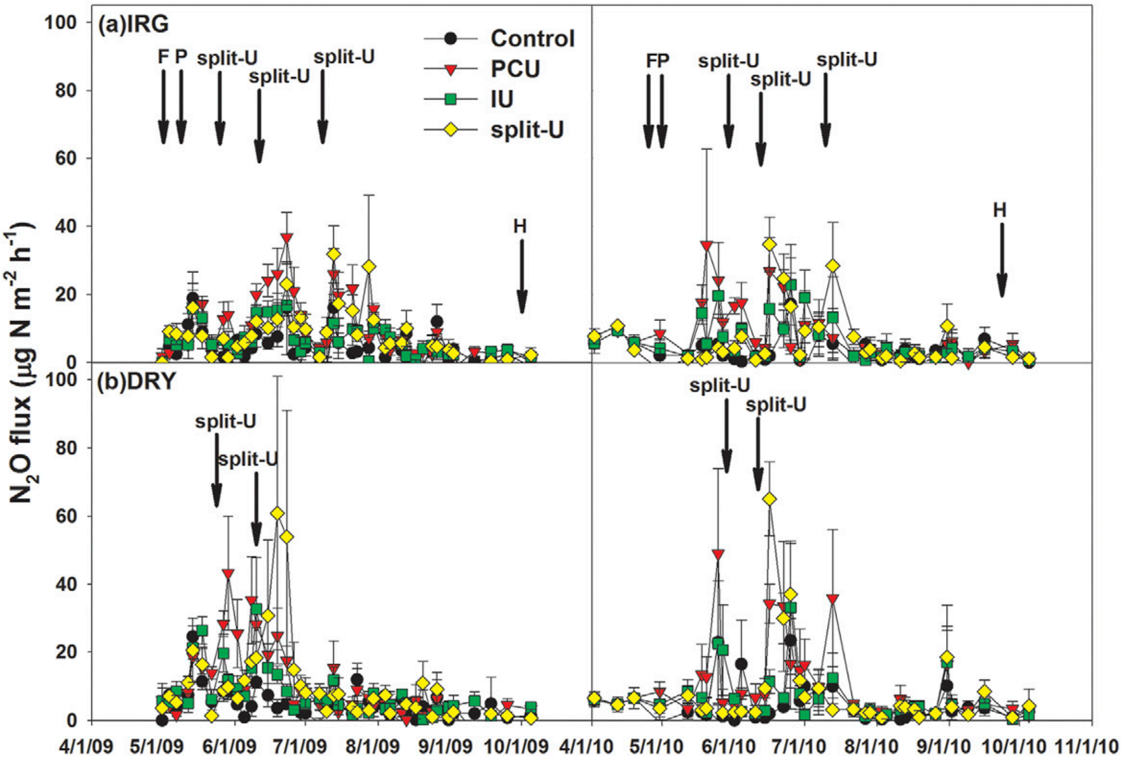

Fig. 3. Mean N_2O emissions in (a) fully irrigated (IRG) and (b) minimum irrigated (DRY) plots under different N sources: no N (control), polymer-coated urea (PCU), stabilized urea with inhibitors (IU), and split-applied conventional urea (split-U) during 2009 and 2010. Downward-pointing arrows indicate dates of planting (P), split-U application (split-U), PCU/IU fertilizer application (F), and harvest (H). Standard errors are denoted by vertical bars.

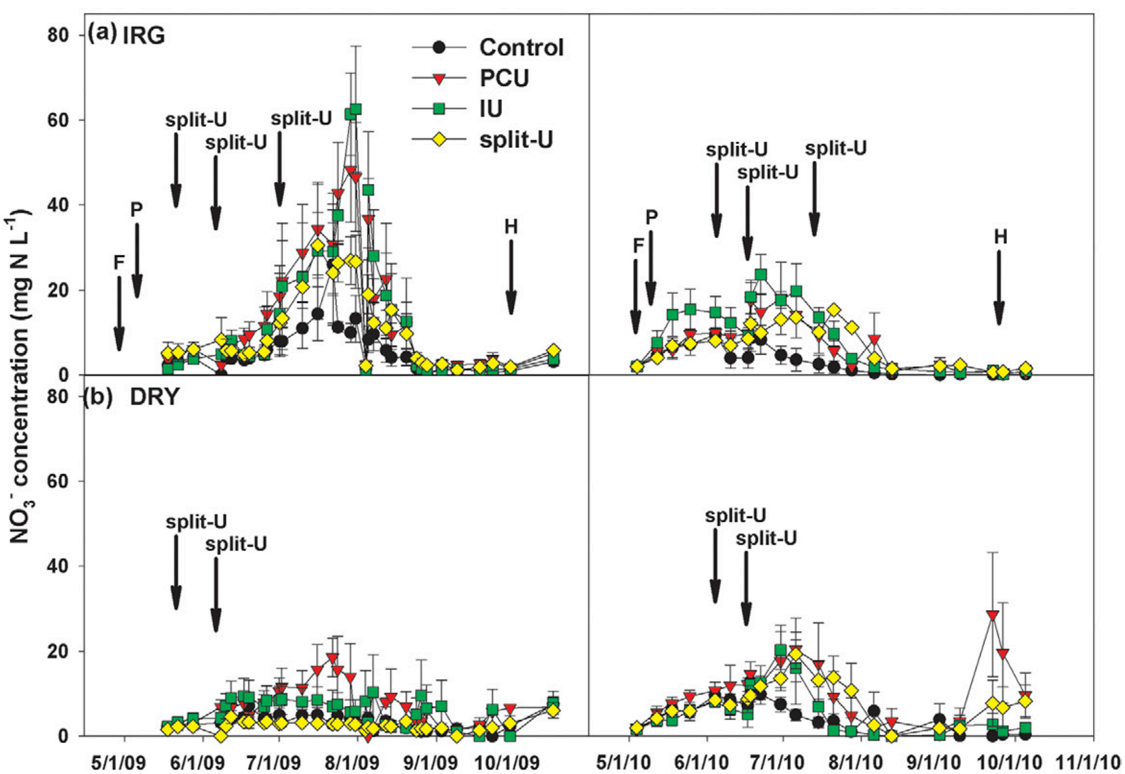

Fig. 4. Daily mean NO_3^- concentrations in lysimeter water samples from (a) fully irrigated (IRG) and (b) minimum-irrigated (DRY) plots under different N sources: no N (control), polymer-coated urea (PCU), stabilized urea with inhibitors (IU), and split-applied conventional urea (split-U) during 2009 and 2010. Downward-pointing arrows indicate dates of planting (P), split-U application (split-U), PCU/IU fertilizer application (F), and harvest (H). Standard errors are denoted by vertical bars.

greater with PCU than with IU or split-U (Table 2). There was also a trend ($P = 0.08$) for greater emissions with split-U than with IU.

When N_2O emissions were expressed per unit of grain yield, there was a significant 3-way interaction effect of year, irrigation and N source (Table 2). Yield-based direct emissions were greater in DRY treatment than in IRG in 2010 for the control and PCU treatments. This trend was not observed in 2009 (Table 3). The control treatment in IRG plots in 2010 had greater yield-based N_2O emissions than any other N sources in both irrigation systems (Table 3). The FIEF did not differ by year or irrigation (Table 2). Among N sources, the FIEF with PCU was significantly greater than with IU or split-U. There was a trend ($P = 0.09$) for greater FIEF with split-U than with IU.

Nitrate Leaching

Soil water NO_3^- concentrations varied during the season from <1 to 63 mg N L^{-1}, and all fertilizer treatments had their maximum soil water NO_3^- concentrations in the IRG plots in 2009 (Fig. 4). In each season, NO_3^- concentrations seemed to level to baseline at the beginning of September, except for PCU, which had NO_3^- concentrations as high as 29 mg N L^{-1} in the DRY plots in September to October 2010. The June to August period accounted for 60 to 98% of the total amount of NO_3^- leached during the season each year, except for the DRY plots in 2009, where cumulative leaching during the season was only about 2 kg N ha^{-1}. Averaged across N sources, cumulative NO_3^- leaching varied significantly by year (2010 > 2009) and irrigation (IRG > DRY) (Table 2). The PCU and IU treatments had greater cumulative NO_3^- leaching than the control, while among the fertilizer treatments, PCU had greater cumulative NO_3^- leaching than split-U (Table 2).

When NO_3^- leaching was expressed per grain yield, there was a three-way interaction effect of year, irrigation, and N source (Table 2). Yield-based NO_3^- leaching was greater in the DRY treatments than IRG in 2010 for the control and PCU treatments. This trend was not observed in 2009 (Table 3). The FILF was significantly different by year (2010 > 2009) at $P = 0.07$ and by irrigation (IRG > DRY) at $P = 0.08$ (Table 2). The FILF was not affected by N sources at $P = 0.05$, but there was a trend for greater FILF with PCU compared with split-U ($P = 0.10$) and greater FILF with IU compared with split-U ($P = 0.12$).

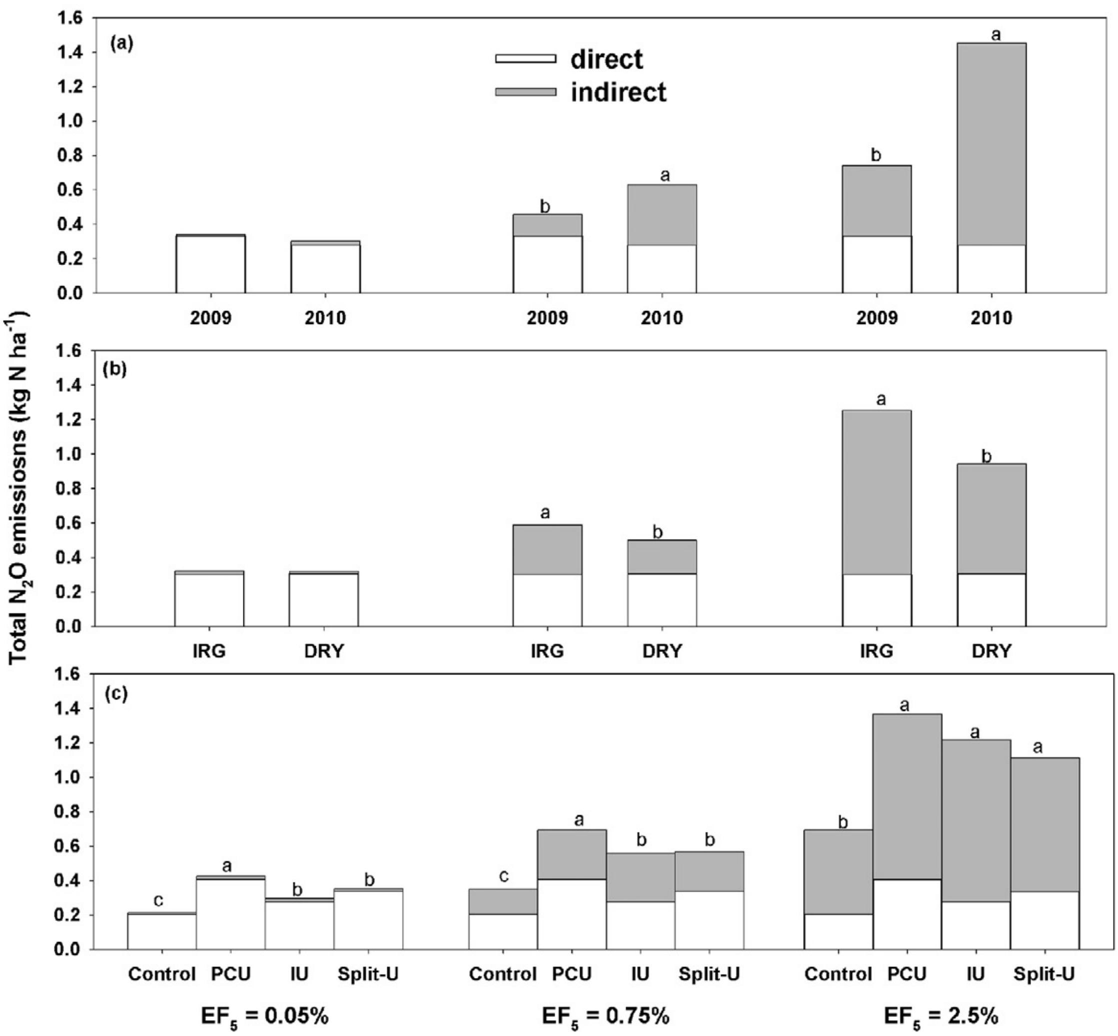

Fig. 5. Mean total (direct plus indirect) N_2O emissions estimated using different default emission factors (EF_5) published by the Intergovernmental Panel on Climate Change of 0.05, 0.75, and 2.5% by: (a) year; (b) irrigation regime: fully irrigated (IRG) or minimum irrigated (DRY); and (c) N source: no N (control), polymer-coated urea (PCU), stabilized urea with inhibitors (IU), and split-applied conventional urea (split-U) during 2009 and 2010. For each EF_5 value, bars having the same letter are not significantly different ($P < 0.05$).

Direct plus Indirect Nitrous Oxide Emissions

Figure 5 shows DI N_2O emissions in three different scenarios of indirect emissions estimated using EF_5 of 0.05% (lower limit), 0.75% (default value), and 2.5% (upper limit). At an EF_5 of 0.05%, indirect emissions accounted for only 5 to 8% of DI emissions, while at EF_5 values of 0.75 and 2.5%, indirect emissions accounted for 44 to 54 and 73 to 80% of DI emissions, respectively. Averaged across years and irrigation treatments, fertilized treatments always had greater DI emissions than the control at all EF_5 values. At EF_5 values of 0.05 and 0.75%, PCU had significantly greater DI emissions than IU or split-U, whereas the fertilized treatments did not differ in DI emissions at an EF_5 of 2.5%. At an EF_5 of 0.05%, DI emissions did not differ by year or irrigation. At EF_5 values of 0.75 and 2.5%, DI emissions were greater in 2010 than in 2009 and greater in the IRG than the DRY treatment.

Post-Harvest Soil Nitrogen and Soil Water Nitrate in the Spring

The soil profile of 0 to 0.6 m had greater residual NO_3^- and less residual NH_4^+ (post-harvest) in 2009 than in 2010 (Table 4). Total residual soil N (NO_3^- + NH_4^+) did not differ by year but was greater in the DRY than the IRG treatment. There was no significant N source effect on residual soil N, individually or together. The mean NO_3^- concentration in the soil water sampled in early spring the year following corn harvest differed by year (2009 > 2010) and by irrigation (DRY > IRG). There was no difference in NO_3^- concentration in spring soil water among fertilized treatments.

DISCUSSION

Direct Nitrous Oxide Emissions

Averaged across all N sources and both years, there was no significant irrigation effect on area-based N_2O emissions. To our knowledge, there is only one study that compared N_2O emissions in irrigated and unirrigated systems. Horvath et al. (2010) reported that area-based N_2O emissions from irrigated plots were 70% greater than from unirrigated plots on a loess soil in a drier than normal year, with the WFPS in the irrigated plots almost twice that in the unirrigated plots (87 vs. 47%). In a normal year, Horvath et al. (2010) observed that the mean WFPS in irrigated and unirrigated plots differed by only 5% (61 vs. 56%), with no irrigation effect on N_2O emissions. In the current study, the difference in the mean WFPS under regular and minimal irrigation was within 10%. This small difference in WFPS may have been the reason why the effect of irrigation on area-based emissions was not significant.

Averaged across years and irrigation, IU or PCU did not reduce area-based N_2O emissions compared with split-U; instead, PCU had greater emissions than split-U; however, it is important to note that unlike PCU or IU, which were applied preplant and all in one application, split-U was applied two times in the DRY plots and three times in the IRG plots. When all N sources were applied in same manner (one-time application and at the same time), many studies have shown that compared with urea, PCU and/or IU reduced N_2O emissions (Halvorson et al., 2010; 2013; Jumadi et al., 2008; Delgado and Mosier, 1996). Limited or no effectiveness of these products has been reported in other studies (Sistani et al., 2011; Venterea et al., 2011b). Different N management practices, such as the timing of N application (post-emergence application

Table 4. Results of statistical analyses with mean (standard error) for post-harvest residual soil inorganic N and NO_3^- concentration in water sampled in early spring following corn harvest.

Source of effects	Post-harvest soil inorganic N			NO_3^- conc. of water sampled in spring
	NO_3^-	NH_4^+	Total N	
	kg N ha^{-1}			mg N L^{-1}
Year				
2009	12.6 (0.7) a†	10.8 (0.9) b	23.4 (1.3)	10.5 (0.7) a
2010	7.6 (0.3) b	25.2 (1.4) a	32.8 (1.4)	5.3 (0.4) b
Significance	*	*	P = 0.06	*
Irrigation‡				
IRG	9.7 (0.7)	16.7 (1.6)	26.4 (1.4)	7.1 (0.5)
DRY	10.4 (0.7)	19.3 (1.9)	29.8 (1.7)	8.7 (0.9)
Significance	ns	ns	P = 0.06	P = 0.07
N source§				
Control	9.5 (1.2)	18.3 (2.3)	27.7 (2.2)	6.4 (0.8)
PCU	11.1 (1.2)	17.4 (2.0)	28.5 (1.6)	8.4 (1.5)
IU	9.8 (0.7)	17.2 (2.5)	27.1 (2.0)	8.5 (1.0)
Split-U	9.9 (0.8)	19.1 (3.1)	29.0 (3.1)	8.2 (0.6)
Significance	ns	ns	ns	ns

* Significant at $P < 0.05$; ns, not significant.

† Mean with standard error in parentheses. Means in a column followed by the same letter are not significantly different ($P < 0.05$).

‡ IRG, fully irrigated; DRY, minimum irrigated.

§ Starter, 10–34–0 (N–P–K) fertilizer; PCU, polymer-coated urea; IU, stabilized urea with chemical inhibitors; split-U, split-applied urea.

in the case of Venterea et al., 2011b) or the application method itself (surface broadcast without incorporation, as in Sistani et al., 2011) may limit the effectiveness of PCU or IU in mitigating N_2O emissions. Site specifics and climatic conditions may also explain some differences observed in their effectiveness in mitigating emissions. These products are designed to release N more gradually during the course of the season compared with urea to minimize N susceptibility to loss and improve synchrony between soil N availability and crop N demand. Soluble urea, when split applied, also serves the same purpose and, as was observed in the current study, performed better than PCU in relation to mitigating N_2O emissions; however, there was still a trend ($P = 0.08$) for greater emissions with split-U than with IU. This result signifies that even though split-U reduced emissions compared with PCU, one-time preplant application of IU can be an alternative to labor-intensive and time-consuming split-U in terms of mitigating N_2O emissions.

The IU treatment significantly reduced N_2O emissions compared with PCU. Similar results were reported by Venterea et al. (2011b) in rainfed corn and Halvorson et al. (2010, 2011) in irrigated corn. These observations suggest that the chemical inhibition of urea hydrolysis and nitrification in the IU treatment is more effective than physical inhibition of N release in the PCU treatment in reducing N_2O emissions.

The FIEF was in the range of 0.04 to 0.11%, which is lower than the values reported in other studies, which were close to 1% (Stehfest and Bouwman, 2006; Akiyama et al., 2006). The default emission factor published in the IPCC guidelines for national greenhouse gas inventories to estimate N_2O emissions from managed soils is also 1% but has a wide variability (95% CI = 0.3–3%). The mean growing season area-based N_2O emissions in the current study were only 0.30 and 0.31 kg N ha^{-1}

for IRG and DRY treatments, respectively. Linn and Doran (1984) noted a linear relationship for N_2O production between WFPS of 30 and 70%, and WFPS values in the current study were toward the lower end of the range (30–70%) most of the season. Accumulation of NO_2^-, a precursor to N_2O emissions, is decreased at low soil pH, as was the case in the current study (pH ~ 5.7 in 1:1 soil/water mixture) and also when PCU or IU is applied or urea is split applied (Van Cleemput and Samater, 1995). The acidic and sandy nature of the soil combined with a low WFPS and subsequently possible low NO_2^- accumulation might explain the low emissions that were observed in the current study. Burton et al. (2008) also attributed less N_2O emission (0.5 kg N ha^{-1}) in clay loam soil vs. clay (1.8 kg N ha^{-1}) to differences in soil texture and moisture. The composition, abundance, and spatial distribution of different functional groups of soil microorganisms in the soil can also affect emissions (Inselsbacher et al., 2011). Compared with PCU, IU had a significantly smaller FIEF. This was evident by greater N_2O emissions with the PCU treatment than with the IU.

Nitrate Leaching

Abundant irrigation and/or precipitation can greatly increase NO_3^- leaching, especially on sandy soils (Petrovic, 2004; Morton et al., 1988). The timing and intensity of precipitation and irrigation could also be vital and induce greater N loss through NO_3^- leaching. In a rainfall simulation experiment, NO_3^- leaching was shown to be greater after a larger rainfall (pulse of 15 mm in 1 d) compared with smaller ones (three pulses of 5 mm each on three consecutive days) (Yahdjian and Sala, 2010). In the current study, there were 12 rainfall events in 2010 that were >20 mm d^{-1} compared with only six such rainfall events in 2009. In 2010 when precipitation and total water inputs were greater than in 2009 by 26 and 5%, respectively, NO_3^- leaching was correspondingly significantly greater in 2010 than in 2009.

Irrigation had a significant effect on NO_3^- leaching when expressed per unit area. When NO_3^- leaching was expressed per unit yield, irrigation had no effect on it, except for the PCU and control treatments in 2010 when the DRY treatment had greater yield-based NO_3^- leaching than the IRG treatment (Table 3). This, combined with an increase in yield with irrigation, indicates that if irrigation is minimized or avoided in fertilized agriculture on sandy soils to reduce N loss through leaching, which is important from the perspective of groundwater contamination, then a minimum-irrigated system would generate more NO_3^- leaching to grow the same amount of crops as an irrigated system. In addition to this, post-harvest residual soil N and NO_3^- concentrations in water collected in the spring showed that there was greater residual N in the soil and subsequently a greater potential for post-seasonal NO_3^- leaching in the DRY than the IRG treatment. These findings support the conclusion that similar grain yields would result in greater N loss through leaching in the DRY than the IRG treatment.

Venterea et al. (2011a) reported no difference in NO_3^- leaching under split-U and PCU (with two different polymer formulations) in irrigated potato (*Solanum tuberosum* L.) production at the same research station where the current study was conducted; however, one type of PCU still had greater residual N in the soil and greater soil water NO_3^- concentration in the following spring, which suggested possible greater total (seasonal plus post-season) NO_3^- leaching in that PCU treatment compared with split-U. The total N applied was also higher than in the current study (270 vs. 180 kg N ha^{-1}) and thus, although split applied, the advantages of split-U compared with PCU that was observed in the current study could have been undermined in their study. In a field experiment on a permanent pasture, Zaman et al. (2008) found that urea with only urease inhibitor or with both urease and nitrification inhibitors (as in the IU in the current study) reduced NO_3^- leaching compared with urea alone. Diez et al. (2010) also reported significantly lower NO_3^- leaching with the use of DCD with a traditional N source. In the current study, greater NO_3^- leaching with PCU than with split-U and the trend for greater NO_3^- leaching with IU compared with split-U were most likely due to better synchrony of the N application with crop demand for split-U.

Direct plus Indirect Nitrous Oxide Emissions

At EF_5 values of 0.05 and 0.75%, the estimated DI N_2O emissions were significantly greater with PCU than with IU or split-U. The same fertilizer effect was observed for direct N_2O emissions. Indirect N_2O emissions due to NO_3^- leaching accounted for >50% of DI emissions at an EF_5 of 2.5%. Therefore, the irrigation effect on NO_3^- leaching was carried over to DI emissions. These estimates show how indirect emissions due to NO_3^- leaching can be significant in N_2O inventory and cannot be ignored; however, there is a wide range of uncertainty in currently available emission factors in estimating indirect emissions and there is a great need of improvement.

In addition to NO_3^- leaching, other possible sources of indirect N_2O emissions include NH_3 volatilization and NO_x flux, which were not measured here (Intergovernmental Panel on Climate Change, 2006). Incorporation of urea mechanically or with water (rain or irrigation) is recommended to reduce NH_3 volatilization (Dawar et al., 2011; Rochette et al., 2001). Field studies have reported the effectiveness of PCU and IU in reducing NH_3 volatilization loss (Connell et al., 2011; Rochette et al., 2009). The default emission factor of 1% to estimate indirect N_2O emissions due to NH_3 volatilization loss plus NO_x flux also has a high uncertainty (0.2–5%) (De Klein et al., 2006). Hence, more robust studies are needed that include all N losses and estimate what fraction of those N losses convert into N_2O within the receiving ecosystems.

Agronomic Responses

Grain yields were significantly greater in 2009 than in 2010. More precipitation and more frequent large impulses of precipitation, with subsequently greater NO_3^- leaching, in 2010 than in the previous year apparently affected yield. Similar results were reported by Errebhi et al. (1998) for irrigated potato. Grain yields were significantly greater in IRG plots than DRY plots, as reported in other studies (Simsek et al., 2011; Yi et al., 2011; Follet et al., 1978). Because irrigation was well timed according to crop need according to the checkbook method, it ensured water availability based on crop need during the season and had a positive effect on agronomic responses. Yields were significantly greater with split-U than PCU or IU. Our study plots also had subplots where urea was also applied as a single preplant application and had significantly lower grain yields (8.6 and 5.8 Mg ha^{-1} in IRG and DRY treatments respectively) than with preplant PCU or IU (unpublished data, 2010). Therefore, split applications of N fertilizer appear to be an effective practice for increasing agronomic response (Rosen and Bierman, 2008; Abdin et al., 1996).

Plant N uptake is generally considered to be a function of soil water status (Djaman et al., 2013). In the current study, the IRG treatment had greater aboveground N uptake than the DRY treatment in 2010 and for split-U in 2009; however, there was no irrigation effect on N uptake in 2009 for the control, PCU, and IU treatments. Buljovcic and Engels (2001) reported that N uptake by corn was not affected at moderate levels of soil drought (10% w/w water content). Plant N uptake can sometimes be more dependent on applied N than on water supply (Pandey et al., 2000). In this study, no irrigation effect on N uptake in the control, PCU, and IU treatments in 2009 was observed due to greater N concentration in the grain in the DRY than the IRG treatments. Hons et al. (1986) also noted that a sorghum [*Sorghum bicolor* (L.) Moench] cultivar that produced less biomass had higher nutrient concentrations and vice versa. In the current study, irrigation increased grain yield but decreased N concentrations in the grain. A positive irrigation effect on N uptake was observed for all N treatments in 2010 and for split-U in 2009 because of the significant increase in biomass yields (26–49%) rather than N concentrations in the biomass. In 2009, because biomass yields for the control, PCU, and IU treatments in IRG treatments were greater than in DRY treatments by <14% (compared with 26–49% mentioned above), and N concentration in the grain was greater in DRY than IRG treatments, there was no irrigation effect on N uptake.

In 2010, NFRE did not differ by irrigation, while in 2009, NFRE was greater in the DRY than the IRG treatment for the PCU and IU treatments and the reverse was observed for split-U. Nitrogen fertilizer recovery efficiency was calculated based on the difference in aboveground N uptake in fertilized plots and in the control. That would make it possible that NFRE was greater in DRY than in IRG treatments in some cases because aboveground N uptake for the control treatment in the DRY plots was almost half of that in the IRG plots.

CONCLUSIONS

An important finding of this study was that irrigation did not increase and in some cases decreased N_2O and NO_3^- losses when emissions were expressed on a yield basis. This result points out the limitations of reporting environmental impacts of agricultural practices only on an area-scaled basis. In the current study, urea was split applied, whereas PCU and IU were applied as a single preplant application. Thus, the greater N_2O and NO_3^- losses observed with PCU and the lower NFRE observed with both PCU and IU compared with split-U need to be interpreted with this in mind. Depending on the value of EF_5 assumed to account for off-site conversion of NO_3^- to N_2O, estimated indirect N_2O emissions due to NO_3^- leaching accounted for 5 to 80% of the total (direct plus indirect) N_2O emissions. The wide range and high upper limit of these estimates point out the need for improved methods of quantifying indirect N_2O emissions in evaluating management effects on total greenhouse gas budgets.

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