

## Enhanced-Efficiency Fertilizers in Nitrous Oxide Emissions from Urea Applied to Sugarcane

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### Abstract

The environmental benefits of producing biofuels from sugarcane have been questioned due to greenhouse gas emissions during the biomass production stage, especially nitrous oxide ( $N_2O$ ) associated with nitrogen (N) fertilization. The objective of this work was to evaluate the use of nitrification inhibitors (NIs) dicyandiamide (DCD) and 3,4 dimethylpyrazole phosphate (DMPP) and a controlled-release fertilizer (CRF) to reduce  $N_2O$  emissions from urea, applied at a rate of  $120 \text{ kg ha}^{-1}$  of N. Two field experiments in ratoon cycle sugarcane were performed in Brazil. The treatments were (i) no N (control), (ii) urea, (iii) urea+DCD, (iv) urea+DMPP, and (v) CRF. Measurements of  $N_2O$  fluxes were performed using static chambers with four replications. The measurements were conducted three times per week during the first 3 mo and biweekly afterward for a total of 217 and 382 d in the first and second seasons, respectively. The cumulative  $N_2O$ -N emissions in the first ratoon cycle were  $1098 \text{ g ha}^{-1}$  in the control treatment and  $1924 \text{ g ha}^{-1}$  with urea (0.7% of the total N applied). Addition of NIs to urea reduced  $N_2O$  emissions by more than 90%, which did not differ from those of the plots without N. The CRF treatment showed  $N_2O$  emissions no different from those of urea. The results were similar in the second ratoon: the treatment with urea showed  $N_2O$  emissions of 0.75% of N applied N. Application of NIs resulted in a strong reduction in  $N_2O$  emissions, but CRF increased emissions compared with urea. We therefore conclude that both NIs can be options for mitigation of greenhouse gas emission in sugarcane used for bioenergy.

**S**UGARCANE ETHANOL has been recognized as environmentally friendly due to the reduction of greenhouse gas (GHG) emissions when it replaces fossil fuel (Boddey et al., 2008; Galdos et al., 2010; Lisboa et al., 2011). However, nitrous oxide ( $N_2O$ ) emission associated with N fertilization during biomass production can offset these benefits (Crutzen et al., 2008).

In Brazil,  $N_2O$  is the most important GHG emitted from agricultural soils (Cerri et al., 2009; MCTI, 2013). The global warming potential of  $N_2O$  is 298 times greater than  $CO_2$  over a 100-yr period. In addition,  $N_2O$  is the main source of nitric oxide, which causes depletion of the stratospheric ozone layer (IPCC, 2007).

The default value for  $N_2O$  emitted by N fertilizers is 1% of the N applied (IPCC, 2006), but the actual percentage can vary. Crutzen et al. (2008) reported emission factors of 3 to 5% of the total N applied. Lisboa et al. (2011), compiling data from Australia, Hawaii, and Brazil, suggested a mean emission factor of 3.9% of N applied in sugarcane fields. Although background values were not discounted, these  $N_2O$  emissions may represent 40% of the total GHG emission for systems in which ethanol is produced from sugarcane (Lisboa et al., 2011). In Brazil, Carmo et al. (2013) found that the proportion of N emitted can be influenced by sugarcane trash retention and averaged 1.1% of N applied. However, when vinasse, a residue of ethanol production, was applied, the N fertilizer emission factor increased to 3%. In two other regions in Brazil, Signor et al. (2013) reported higher losses of  $N_2O$  in sugarcane fields than those reported by Carmo et al. (2013).

Emissions of  $N_2O$  in soils mainly occur due to nitrification and denitrification processes (Stevens and Laughlin, 1998). Many factors are involved in estimating the amount of  $N_2O$  emitted, including (i) management practices (e.g., fertilizer source, rate, placement, timing, other chemicals, crop, irrigation, presence of plant residues) and (ii) environmental and soil factors (e.g., temperature, rainfall, soil moisture, organic C, oxygen

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**Abbreviations:** CRF, controlled release fertilizer; DCD, dicyandiamide; DMPP, 3,4-dimethylpyrazole phosphate; EEf, enhanced-efficiency fertilizers; GHG, greenhouse gas; NI, nitrification inhibitor; PSCU, polymer and sulfur-coated urea; UR, urea.

concentration, porosity, pH, and microorganisms) (Carmo et al., 2013; Eichner, 1990; Snyder et al., 2009; Vargas et al., 2014).

One way to reduce N<sub>2</sub>O emissions due to the use of N fertilizers is by the addition of nitrification inhibitors (NIs). Nitrification inhibitors maintain N in soil in the NH<sub>4</sub><sup>+</sup> form for a period of time by suppressing microbial oxidation of ammonium (Subbarao et al., 2006). The crop may then take up NH<sub>4</sub><sup>+</sup>-N, reducing N<sub>2</sub>O emission due to nitrification and denitrification (Hu et al., 2013; Liu et al., 2013; Snyder et al., 2009). Several NIs are commercially available, including nitrapyrin, dicyandiamide (DCD), and 3,4-dimethylpyrazole phosphate (DMPP) (Trenkel, 2010).

Controlled-release fertilizers (CRFs) also can reduce N<sub>2</sub>O emissions. Akiyama et al. (2010) compiled data from 35 studies to evaluate CRF effects in N<sub>2</sub>O emissions and found an overall reduction of 35% compared with conventional and organic sources of N. The N release synchronized with plant demand can increase N use efficiency and thereby reduce N<sub>2</sub>O emissions (Hyatt et al., 2010; Yang et al., 2012). Controlled-release fertilizers have small market participation because of high prices, but their importance has increased due to agronomic and environmental benefits (Chien et al., 2009).

Nitrification inhibitors and CRFs are recognized as options of GHG mitigation. IPCC (2001) assumes an average reduction of 30% in N<sub>2</sub>O emissions when NI and CRFs are used. However, higher reductions have been reported. Snyder et al. (2009) listed studies with reductions between 40 and 90% by addition of NIs to conventional fertilizers. However, the extent of the effect of NIs is not clear, especially in warm tropical soils. No study has been done to compare the efficiency of NIs and CRFs in sugarcane used for bioenergy in Brazil, the largest producer in the world, with 9 million ha cultivated with this crop. Sugarcane is a long-cycle crop, with very high biomass production, grown in tropical and subtropical conditions that may affect N<sub>2</sub>O emissions from N fertilizer. Therefore, the aim of this study was to evaluate the efficiency of DCD, DMPP, and CRFs in reducing N<sub>2</sub>O emissions from urea applied to sugarcane.

## Materials and Methods

Three enhanced-efficiency fertilizers were tested. The treatments were: (i) no N (control), (ii) urea (UR), (iii) UR+DCD, (iv) UR+DMPP, and (v) polymer and sulfur-coated urea (PSCU), a CRF. The fertilizers were evaluated in two consecutive cycles, under field conditions, in ratoon cane in 2011/2012 and 2012/2013. In the second ratoon cycle, the treatments were applied in the same plots, but two additional treatments were included (UR+DCD and UR+DMPP) in new

plots in the same field to test the hypothesis that NIs could be less efficient if reapplied in the same area.

Sugarcane yields were not measured because gaseous N losses as N<sub>2</sub>O are relatively small, and no NH<sub>3</sub> volatilization was expected in this study because urea was incorporated into the soil. Leaching losses, which could be reduced by the NI or CRF treatments, are considered to be of little significance for sugarcane grown in the southeastern region of Brazil (Ghiberto et al., 2009, 2011). To minimize soil variability and to focus on the GHG evaluations, the treatments were concentrated in a small area of a sugarcane field with a uniform plant stand.

The experiment was installed in a sugarcane field grown with the variety SP791011, spaced 1.5 m between rows, at Agronomic Institute in Campinas, Brazil (22°52'15" S, 47°04'57" W). The soil is classified as a Typic Hapludox or Red Latosol (Empresa Brasileira de Pesquisa Agropecuária, 2006). The chemical (van Raij et al., 2001) and physical properties (Camargo et al., 1986) of the 0- to 20-cm layer are shown in Table 1.

The experimental units were 1-m sections of sugarcane rows with a gas chamber installed in the middle of the fertilizer band. It was assumed that the chemical and biological reactions that cause N<sub>2</sub>O emissions take place in a small soil area; large plots would not bring additional benefit because of the high spatial variability of N<sub>2</sub>O emissions in soils (Mathieu et al., 2006). The experiment followed a complete randomized design with four replications, resulting in 20 plots and 20 chambers.

Fluxes of N<sub>2</sub>O were measured using PVC static chambers, 20 cm in height and 30 cm in diameter, according to the method used by Rochette and Ericksen-Hamel (2008) and Carmo et al. (2013). The chambers were inserted 5 cm into the soil and 10 cm from the sugarcane rows.

The N fertilizer treatments were applied at rate of 120 kg ha<sup>-1</sup>, which is in the range of recommendations for sugarcane in Brazil (van Raij et al., 1997). Lime, phosphorus, potassium, sulfur, zinc, and boron were common to all plots and were applied separately from the N fertilizer treatments.

The NIs were added to UR in the laboratory at Agronomic Institute. Analytical-grade DCD (Sigma Aldrich) in powder form containing 650 g kg<sup>-1</sup> of N was weighed individually and mixed with urea for each plot at a rate corresponding to 5% of DCD-N in relation to urea-N (Soares et al., 2012; Subbarao et al., 2006; Weiske et al., 2001). The DMPP, also analytical grade and in powder form, was used at a rate of 1% in relation to urea-N (Liu et al., 2013; Subbarao et al., 2006; Weiske et al., 2001).

Polymer sulfur-coated urea (390 g N kg<sup>-1</sup> and 110 g S kg<sup>-1</sup>) (Produquímica) has two coating layers composed of elemental sulfur and water-insoluble, polyacrylate-derived resin.

**Table 1. Properties of the 0- to 20-cm layer of the Red Latosol of the experimental area.**

pH (CaCl <sub>2</sub> ; 0.0125 mol L <sup>-1</sup> )	OC†	P‡	K	Ca	Mg	H+AlS	CEC¶	Soil texture#		
								Clay	Silt	Sand
5.6	g dm <sup>-3</sup>	mg dm <sup>-3</sup>	mmol <sub>c</sub> dm <sup>-3</sup>			g kg <sup>-1</sup>				
	12	8	2.7	22	12	19	55.9	410	175	415

† Organic carbon (oxi-reduction).

‡ Phosphorus, K, Ca, and Mg were extracted with ion exchange resin.

§ Buffer solution (pH 7.0).

¶ Cation exchange capacity.

# Soil texture determined by the densimeter method.

The trash left after the harvest of the previous sugarcane crop was removed from the field to simulate plant residue collection for energy production. In the second year, little trash remained in the soil because the cane had been burned before harvest.

To prevent  $\text{NH}_3$  volatilization, the fertilizers were banded and incorporated to the soil in a small furrow made with a hoe, about 5 cm deep, because NIs can increase  $\text{NH}_3$  losses from urea (Soares et al., 2012) and could cause an underestimation of  $\text{N}_2\text{O}$  emissions (Snyder et al., 2009). The fertilizer band was parallel to and distant around 0.2 m from the sugarcane row, as is commonly done in sugarcane fields in Brazil. The spot in the middle of the fertilized band where the chambers for GHG measurement were placed (0.3 m in diameter) received individually weighed amounts of the fertilizer treatments, also incorporated at 5 cm, so that the  $\text{N}_2\text{O}$  emission factor could be directly calculated:

$$\text{N}_2\text{O-N factor} = \frac{\text{N}_2\text{O-N}_{\text{treat.}} - \text{N}_2\text{O-N}_{\text{control}}}{\text{N}_{\text{applied}}}$$

where  $\text{N}_2\text{O-N}_{\text{treat.}}$  and  $\text{N}_2\text{O-N}_{\text{control}}$  are the cumulative emissions of the fertilized and unfertilized chambers, respectively, and  $\text{N}_{\text{applied}}$  is the mass of N fertilizer added to the chamber. The whole field  $\text{N}_2\text{O}$  emission was calculated using the background  $\text{N}_2\text{O}$  emission data obtained from the unfertilized chambers and data of the fertilizer treatments. The fertilized area corresponded to 16% of the total area, equivalent, for every sugarcane row, to a strip of land 0.3 m wide (i.e., the width of the chamber corrected for the chamber's actual circular area). Conversely, 84% of the field was assumed to have just the background emission.

Gas samples were collected in the mornings (Alves et al., 2012) three times per week for the first 3 mo after fertilizer application. Subsequently, the sampling was done weekly or biweekly. For the samplings, the chambers were closed with a 7-cm cap. The caps have two openings, each fitted with a valve, one for gas sampling and other to equilibrate internal and external pressure. Gases were sampled with plastic syringes (60 mL) at three time intervals (1, 15, and 30 min) after the chambers were closed (Mosier et al., 2006). The samples were transferred and stored in pre-evacuated Exetainers vials (12 mL). During each gas sampling, air and soil temperature and atmospheric pressure were measured. Climatic data were obtained from a meteorological station located 300 m from the experiment.

The samples were analyzed in a gas chromatograph (model GC-2014, Shimadzu Co.) with an electron capture detector for  $\text{N}_2\text{O}$  determination (Hutchinson and Mosier, 1981). Nitrous oxide flux was calculated by linear interpolation of the three sampling times. Daily  $\text{N}_2\text{O}$  fluxes were plotted using Sigma Plot software, version 10 (Systat Software, 2006). Cumulative emissions were calculated by linear interpolation between adjacent sampling dates (Allen et al., 2010). Total cumulative emission was submitted to ANOVA, and means were compared (Tukey  $p \leq 0.05$ ) using SISVAR statistical software.

In the first cycle, GHG measurements were conducted for a total of 217 d from April 2012 to November 2012, when the cane was harvested. In the second cycle, the evaluation period was 382 d, from November 2012 to November 2013. In the 2011/2012 cycle, the fertilizer treatments were applied in April in a ratoon crop, where plants were approximately 1.5 m tall. The

previous cycle (cane plant) was harvested in December 2011. Therefore, the N fertilization was done 4 mo after harvest, later than recommended for this region (van Raij et al., 1997). After an accidental fire, the cane of the 2011/2012 cycle was harvested in November 2012. For the 2012/2013 cycle, the treatments were applied 15 d after the harvest. At this time point, the cane plants were smaller (0.5 m) than in 2011/2012.

## Results

The climatic conditions of the experimental period are shown in Fig. 1 and 2. Mean air temperature varied between 15 and 30°C, and total rainfall amounts were 540 and 1255 mm in the first and second seasons, respectively.

In the 2011/2012 cycle, the dry period was typical of the south-central region of Brazil. From July until September (100–165 d after fertilizer application), total rain precipitation was <30 mm (Fig. 1). The 2012/2013 season was wetter than average. Rainfall in the dry and cool period from May to October (170–311 d after fertilizer application) was 239 mm (Fig. 2).

Emissions of  $\text{N}_2\text{O}$  were low in the first 10 d after fertilizer application in 2011/2012 (<5 g  $\text{ha}^{-1} \text{d}^{-1}$  of N) (Fig. 1). The treatment with urea had a peak  $\text{N}_2\text{O}$  emission on the 17th day, corresponding to 70 g  $\text{ha}^{-1} \text{d}^{-1}$  of N. After this, two other emission peaks (40 and 30 g  $\text{ha}^{-1} \text{d}^{-1}$ ) occurred after rain events; between these peaks, the  $\text{N}_2\text{O-N}$  emissions were approximately 15 g  $\text{ha}^{-1} \text{d}^{-1}$ . The treatments with NIs had smaller  $\text{N}_2\text{O}$  fluxes, similar to the control treatment, which was around 5 g  $\text{ha}^{-1} \text{d}^{-1}$  of N. Polymer and sulfur-coated urea showed lower  $\text{N}_2\text{O}$  emission (30 g  $\text{ha}^{-1} \text{d}^{-1}$ ) than conventional urea on the 17th day, but in the other two peaks, 60 and 80 d after fertilizer application, the emissions were similar to those of urea (Fig. 1).

In the period between 80 and 160 d after fertilizer application, emissions in all treatments were low, compatible with the drier and colder months of the year (Fig. 1). When rainfall started again in October 2012, the treatment with PSCU had greater emission, showing a peak of 30 g  $\text{ha}^{-1} \text{d}^{-1}$  of  $\text{N}_2\text{O-N}$ , probably because of the gradual release of N from the fertilizer. The other treatments showed low  $\text{N}_2\text{O-N}$  emissions (near 10 g  $\text{ha}^{-1} \text{d}^{-1}$ ) (Fig. 1).

The  $\text{N}_2\text{O}$  emissions in the 2012/2013 cycle were low in the first 10 d, similar to those of the previous cycle. The treatment with urea had a peak of 80 g  $\text{ha}^{-1} \text{d}^{-1}$  of N on the 14th day; thereafter, two other periods of high emissions occurred around 20 and 37 d after fertilizer application after rain events (60 and 40 g  $\text{ha}^{-1} \text{d}^{-1}$  of  $\text{N}_2\text{O-N}$ , respectively) (Fig. 2). Polymer and sulfur-coated urea showed lower  $\text{N}_2\text{O}$  emission than urea in the first 20 d, but after this period the other two peaks of both treatments were similar, and PSCU had higher emissions than all treatments at 40 d after fertilizer application, probably due to gradual N release (Fig. 2).

Treatments with NIs showed low  $\text{N}_2\text{O-N}$  emissions (around 5 g  $\text{ha}^{-1} \text{d}^{-1}$  of N), similar to the control treatment without N, and did not differ from the treatments where urea with NIs was applied in the same area of the previous year (Fig. 2).

After 217 d in the 2011/2012 cycle, the cumulative  $\text{N}_2\text{O-N}$  emission of the control was equivalent to 1.1 kg  $\text{ha}^{-1}$ . The treatment with urea emitted almost 2 kg  $\text{ha}^{-1}$  of  $\text{N}_2\text{O-N}$ , which corresponded to 0.7% of total N applied. The addition of NIs

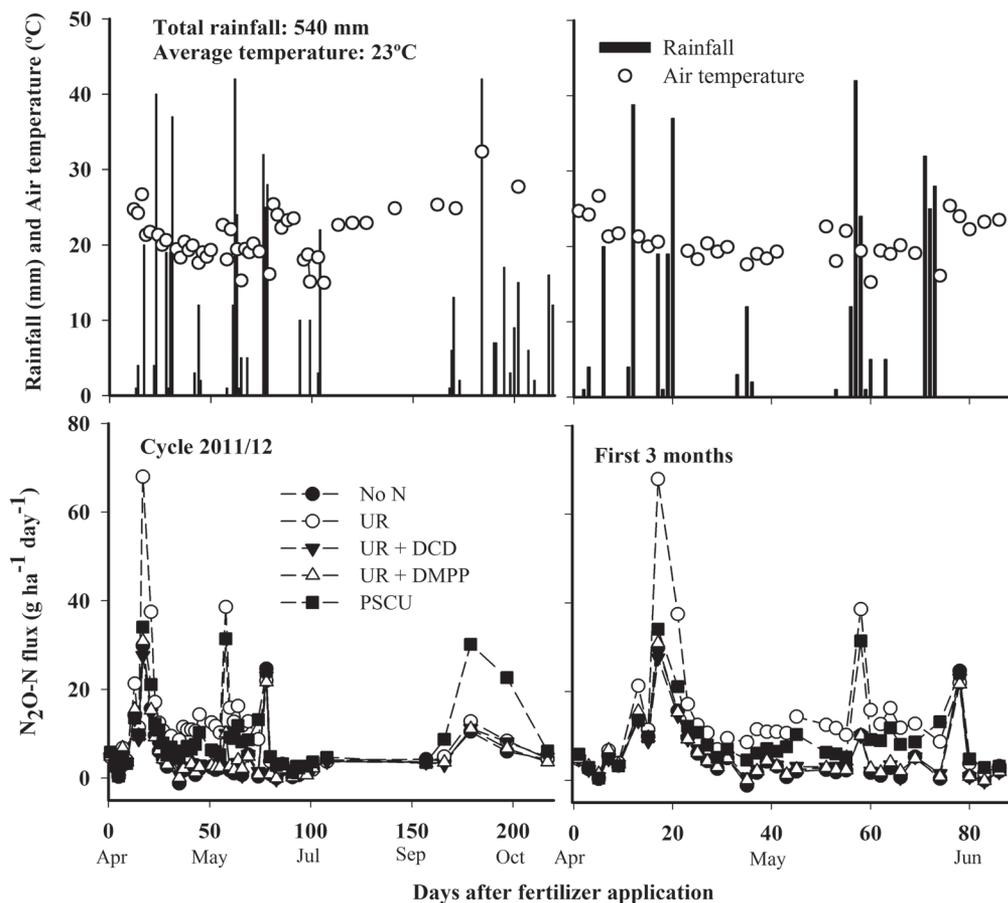


Fig. 1. Rainfall, air temperature, and  $N_2O$  emissions from urea (UR), incorporated in a Red Latosol, with or without nitrification inhibitors (dicyandiamide [DCD] and 3,4-dimethylpyrazole phosphate [DMPP]) or polymer sulfur-coated urea (PSCU) applied to ratoon cane, cycle 2011/2012.

to urea resulted in a strong reduction in  $N_2O$  emissions, which did not differ from those of the control treatment. Controlled-release fertilizers showed cumulative emissions similar to those of conventional urea (Table 2).

In the second year, the cumulative  $N_2O-N$  emission in the plots without N was  $600 \text{ g ha}^{-1}$  after 382 d. Urea treatment produced a  $N_2O-N$  emission of  $1.5 \text{ kg ha}^{-1}$ , which is equivalent to 0.75% of the total N applied. Application of PSCU resulted in cumulative  $N_2O$  emission greater than that of conventional urea: almost  $2 \text{ kg ha}^{-1}$  were emitted as  $N_2O-N$ , which represents approximately 1% of the N applied. Nitrification inhibitors reduced  $N_2O$  emission from urea by 81 to 100%, which did not differ from the control treatment without N; a similar reduction in  $N_2O$  emissions took place in the plots where the inhibitors were reapplied. There were no differences between DCD and DMPP (Table 3).

## Discussion

Nitrous oxide emissions from plots with no N fertilizer were 1.1 and  $0.6 \text{ kg ha}^{-1}$  of N in the first and second seasons, respectively, close to the background emissions values of approximately  $1 \text{ kg}^{-1} \text{ ha}^{-1} \text{ yr}^{-1}$  of  $N_2O-N$  estimated by Bouwman (1996). Bouwman pointed out that background emissions from agricultural soils are not from a “natural” ecosystem but rather include the effects of crop residues and previous soil amendments. Accordingly, in our study, the soil had been

regularly fertilized in previous years. The lower background emissions in the second cycle could be explained by the small amounts of plant residues left on the soil because sugarcane was burned before the harvest in the previous cycle. Sugarcane trash has been shown to increase  $N_2O$  emissions (Vargas et al., 2014).

High daily fluxes of  $N_2O$  were observed for the UR treatment 2 to 3 mo after fertilizer application. Similar results were reported by Carmo et al. (2013) in a sugarcane field in the same region in Brazil. High  $N_2O$  emissions were usually associated with rainfall events, especially in the weeks that followed fertilizer applications. However, after about 100 d of fertilization, emissions were low for all treatments despite the relatively frequent rains (Fig. 2). Other researchers also showed greater  $N_2O$  emissions in the first weeks after N fertilizer application, attributing this effect to increased N availability for nitrification and denitrification processes and favorable environmental conditions for  $N_2O$  emissions such as rainfall, high soil moisture, temperature, and available C (Jumadi et al., 2008; Linzmeier et al., 2001; Menéndez et al., 2006; Signor et al., 2013; Weitz et al., 2001; Zaman et al., 2008).

Cumulative emission of  $N_2O$  in this study was 0.7% of total N applied in the treatment with conventional urea. This value is close to the default value of 1% of the N applied used by the IPCC (IPCC, 2006) but lower than those of other field studies with sugarcane (Allen et al., 2010; Carmo et al., 2013; Denmead et al., 2010; Signor et al., 2013; Weier et al., 1998). Carmo et al.

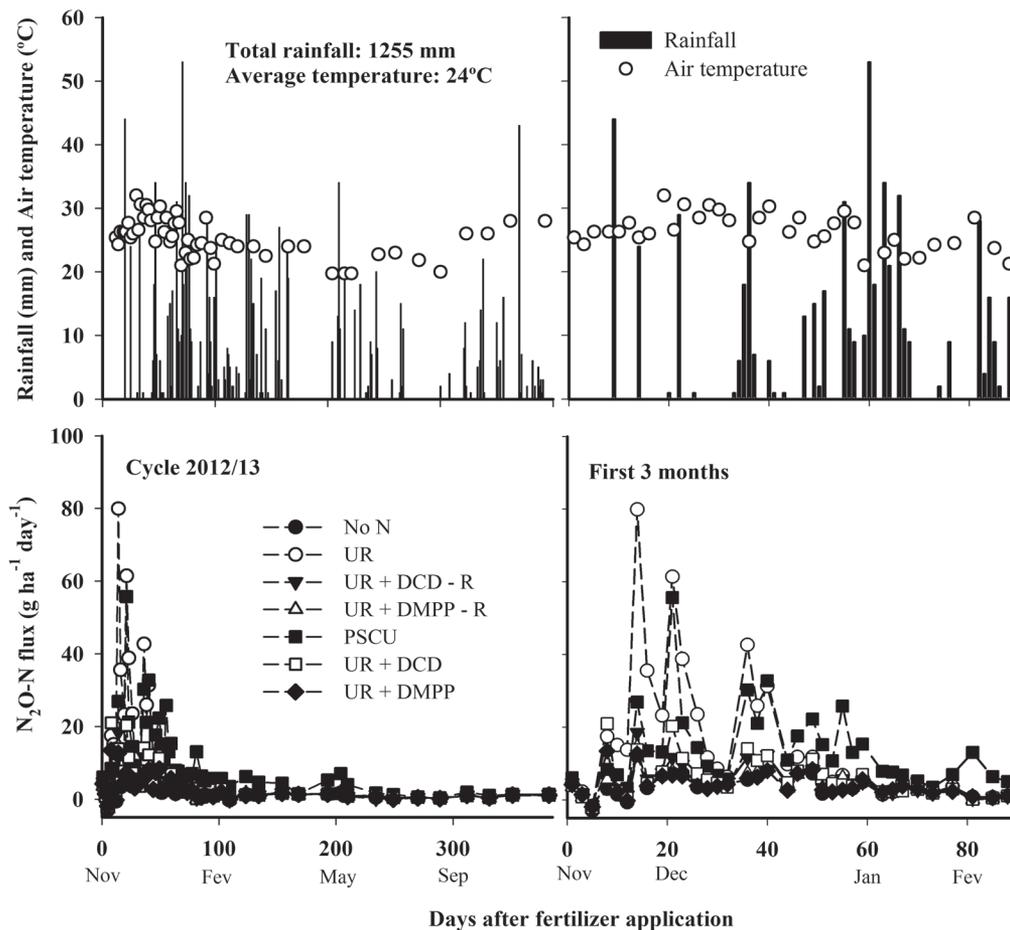


Fig. 2. Rainfall, air temperature, and  $N_2O$  emissions from urea (UR), incorporated in a Red Latosol, with or without nitrification inhibitors (dicyandiamide [DCD] and 3,4-dimethylpyrazole phosphate [DMPP]) or polymer sulfur-coated urea (PSCU) applied to ratoon cane, cycle 2012/2013. R indicates inhibitor reapplied in same plot of previous cycle.

(2013) found an emission factor of 0.7% of N applied as urea in sugarcane fields in Brazil, but the fertilizer emission factor increased to 3% when vinasse and harvest trash were present. Lisboa et al. (2011) also listed several studies with sugarcane with a mean emission factor of 3.9% (values of 2.0–29%; background values were not subtracted). As in the present study, other studies in Brazil have reported  $N_2O$  emission factors lower than the IPCC default value. This has been attributed to the high

drainage capacity of Oxisols, which prevent water accumulation in the soil profile for extended periods of time (de Morais et al., 2013; Jantalia et al., 2008).

The default value of the IPCC (IPCC, 2001) for reduction of  $N_2O$  emission due to the use of enhanced-efficiency fertilizers

Table 2. Cumulative nitrous oxide emissions for 217 d from urea, incorporated in the Red Latosol, with or without nitrification inhibitors (dicyandiamide and 3,4-dimethylpyrazole phosphate) or polymer and sulfur-coated urea applied to ratoon cane, 2011/2012.

Treatments†	Cumulative $N_2O-N$ emissions		Differences from urea¶
	$g\ ha^{-1}\ddagger$	% of N applied§	
No N (control)	1098b	–	–
UR	1924a	0.69	–
UR+DCD	1142b	0.04	–95
UR+DMPP	1112b	0.01	–98
PSCU	2213a	0.93	+35

† DCD, dicyandiamide; DMPP, 3,4-dimethylpyrazole phosphate; PSCU, polymer and sulfur-coated urea; UR, urea.

‡ Values followed by the same lowercase letter are not significantly different at  $P \leq 0.05$  using the Tukey test.

§ Results from treatment without N were subtracted for this calculation.

¶ (–) reduction, (+) increase; coefficient of variation: 15%.

Table 3. Cumulative nitrous oxide emissions for 382 d from urea, incorporated in the Red Latosol, with or without nitrification inhibitors (dicyandiamide and 3,4-dimethylpyrazole phosphate) or polymer sulfur coated-urea applied to ratoon cane 2012/2013.

Treatments†	Cumulative $N_2O-N$ emissions		Differences from urea¶
	$g\ ha^{-1}\ddagger$	% of N applied§	
No N (control)	587c	–	–
UR	1484b	0.75	–
UR+DCD-R	674c	0.07	–90
UR+DMPP-R	643c	0.05	–94
UR+DCD	759c	0.14	–81
UR+DMPP	584c	0.00	–100
PSCU	1901a	1.09	+46

† DCD, dicyandiamide; DMPP, 3,4-dimethylpyrazole phosphate; PSCU, polymer and sulfur-coated urea; R, inhibitor reapplied in same plot of previous cycle; UR, urea.

‡ Values followed by the same lowercase letter are not significantly different at  $P \leq 0.05$  using the Tukey test.

§ Results from treatment without N were subtracted for this calculation.

¶ (–) reduction, (+) increase; coefficient of variation: 17%.

is 30%. Results presented in this study showed much higher reductions: NIs lowered  $N_2O$  emission from urea by 90%, as a mean of two seasons, which is in the upper limit of the values compiled by Snyder et al. (2009). These researchers listed decreases in the  $N_2O$  emission ranging from 40 to 96% with the addition of NIs to conventional N fertilizers.

The variation in  $N_2O$  reduction caused by NIs is explained by the complex combination of factors that affect the action of such compounds in the soils and the drivers of  $N_2O$  emission (e.g., soil pH, organic matter, porosity, temperature, and soil moisture) (Halvorson et al., 2014; Singh et al., 2008; Subbarao et al., 2006; Trenkel, 2010; Vargas et al., 2014; Weiske et al., 2001). For example, Singh et al. (2008) showed 90% reduction in  $N_2O$  emissions by the addition of DCD in urine to a soil with low organic carbon ( $3.4 \text{ g kg}^{-1}$ ), but the reduction decreased to 45% when applied to a soil with high organic carbon ( $8 \text{ g kg}^{-1}$ ) in 60 d of measurement. In this way, depending on environmental conditions and site characteristics, the nitrification inhibitor is degraded in soil faster than plants can take up  $NH_4^+$ , thus increasing  $N_2O$  emissions after the period during which NIs are effective (Hu et al., 2013; Jumadi et al., 2008; Liu et al., 2013; Weiske et al., 2001).

Sugarcane is a fast-growing plant, capable of accumulating between 30 and  $60 \text{ t ha}^{-1}$  of dry matter in one season (Cantarella et al., 2012). The demand of N is high during the initial stages of ratoon growth (Franco et al., 2011). In 2011/2012, the fertilizers were applied at the end of the summer when plants were already 1.5 m tall and growing fast; in 2012/2013, N was applied 15 d after harvest, at the end of the spring but during a period that was warm and rainy enough (Fig. 2) for fast plant growth. Therefore, even if the NIs did not have a lasting inhibitory effect because of the high soil temperatures, the  $NH_4^+$  preserved as a consequence of lower nitrification rate would have a fair chance of being readily taken up by the sugarcane plants. This may explain the high efficiency of both NIs in reducing  $N_2O$  emission in the present study.

The sugarcane harvesting season spans from April to November in Brazil. From April to September (late fall to early spring in the southern hemisphere), rainfall is somewhat scarce, and temperatures are mild for sugarcane development and, thus, for N uptake. It is not possible to foresee whether NIs will show the same effectiveness to reduce  $N_2O$  emission if applied in these drier months as compared with the results reported here. Because of the long harvesting season, many fields are fertilized in the dry months; therefore, the study of NIs under such conditions deserves attention.

Reapplication of NIs on the same site of the previous year did not affect the capacity of DCD or DMPP to reduce  $N_2O$  losses (Table 3). Rajbanshi et al. (1992) showed that DCD was degraded faster in soils after reapplication, which could decrease its effectiveness to inhibit  $NH_4^+$  oxidation. However, the interval between reapplications was shorter than the 1 yr used in our study. Other researchers have reported opposite results, indicating that reapplication of DCD after 57 d (Wakelin et al., 2013) or repeated application over a 3-yr period (Weiske et al., 2001) did not affect the persistence of the NIs. Therefore, most results indicate that the continuous use of NIs poses no risk of decreased efficiency to reduce  $N_2O$  emission.

Dicyandiamide and DMPP showed similar capacities to reduce  $N_2O$  emissions (Table 3). Weiske et al. (2001) showed that DMPP was more efficient than DCD because DCD was degraded in soil faster than DMPP. Subbarao et al. (2006) pointed out that the mobility of DCD in soil was higher than that of  $NH_4^+$ , whereas the relative mobility of DMPP is about the same as  $NH_4^+$ , which may make DMPP more effective than DCD. However, in the present study both NIs were very efficient in mitigating  $N_2O$  emissions, probably due to favorable environmental conditions.

The controlled release fertilizer used in this study failed to reduce  $N_2O$  emissions as compared with urea. This was somewhat unexpected, although it is not a new finding in the literature. In the second experiment,  $N_2O$  emissions of PSCU were even higher than those of the regular UR (Table 3). The reasons for these results are not clear. Under laboratory conditions we observed that N from PSCU was not readily released and that the two coating layers remained mostly intact for at least 50 d (unpublished results). The gradual release of N prevents peaks of nutrient concentration above the capacity of plants to take it up, reducing the N available for microbial processes of nitrification and denitrification that lead to  $N_2O$  emissions (Delgado and Mosier, 1996). Increasing the rate of N application, depending on soil C availability, may exponentially increase  $N_2O$  emission (Kim et al., 2013). Thus, slow N release from CRFs or split application of N can reduce  $N_2O$  emissions depending of environmental conditions and product properties (Akiyama et al., 2010; Burton et al., 2008; Halvorson et al., 2014; Hyatt et al., 2010; Yang et al., 2012).

The complex interactions of time of N release of CRFs, environmental conditions, and N uptake by plants can affect the amounts of nutrient in the soil and, therefore, the risks of  $N_2O$  fluxes to the atmosphere (Venterea et al., 2012). In the first year, the N fertilizer treatments were applied in April, at the end of the rainy season. Nitrous oxide emissions of the plots with PSCU were lower than those of conventional UR in the first 60 d (Fig. 1), when probably less N from the PSCU was available. However, after the dry season (i.e., in October), a peak of  $N_2O$  emission (Fig. 1) indicates that the N that remained in the granules of PSCU probably had been let out. In the second year, the fertilizers were applied before the long, hot, and rainy summer, and the N from PSCU probably was released sooner: at about 40 d after fertilization, the  $N_2O$  emissions from the PSCU treatments prevailed over those of UR (Fig. 2). Therefore, the chain of events controlling N release from PSCU did not favor this N source, and, ultimately, the cumulative emissions of  $N_2O$  from PSCU were similar or higher than those of UR.

Other researchers have also reported situations in which  $N_2O$  emissions from soils treated with slow- or controlled-release N fertilizers were similar to those of readily available N sources (Delgado and Mosier, 1996; Halvorson et al., 2014; Hu et al., 2013; Jumadi et al., 2008; Venterea et al., 2011), mainly because of the lack of synchrony of N release and plant use.

In the present study, we conducted intense measurements of  $N_2O$  emissions for two consecutive seasons to compare emissions derived from a conventional N fertilizer (urea) with those of urea amended with two NIs and that of a CRF. Our results indicated a smaller  $N_2O$  emission factor for the conventional fertilizer than most results reported in the international literature for sugarcane,

suggesting that N<sub>2</sub>O emissions from highly permeable Oxisols in this region of Brazil may be lower than from most other soils. We also demonstrated that NIs sharply decreased N<sub>2</sub>O emissions but that the CRF was ineffective at reducing N<sub>2</sub>O emissions. Our results are among the first in the literature to test these classes of compounds in tropical soils and in sugarcane in particular. The effectiveness of NIs to reduce N<sub>2</sub>O emissions in sugarcane must be tested further, including when fertilizer is applied in the dryer months of the year and in combination with vinasse and trash—common practices in most sugarmills—which substantially increase N<sub>2</sub>O emissions (Carmo et al., 2013).

There is growing interest of the international community in data of GHG emissions in sugarcane used for bioethanol from Brazil because soil emissions of N<sub>2</sub>O are an important component of calculated net GHG emissions from ethanol production (Boddey et al., 2008; Macedo et al., 2008). Therefore, NIs may be an option to increase sugarcane ethanol sustainability indicators. There are indications that sugarcane prefers NH<sub>4</sub><sup>+</sup> over NO<sub>3</sub><sup>-</sup> in mineral nutrition (DeArmas et al., 1992; Parashar et al., 1980), which could further justify the use of NIs. However, NIs are not commonly used in Brazil because they add cost to fertilizers and because these products do not always bring yield increases (Trenkel, 2010), especially in situations where N loss by nitrate leaching is low. Cantarella (2007), Ghiberto et al. (2009), and Ghiberto et al. (2011) observed very little NO<sub>3</sub><sup>-</sup> leaching from N fertilizers in sugarcane using fertilizers labeled with <sup>15</sup>N. Although losses of N as N<sub>2</sub>O are environmentally important, they are a small fraction of fertilizer costs, and sugarcane growers may not be willing to pay the cost of NIs if no yield increases accompany this environmental benefit. Mitigating N<sub>2</sub>O emissions from agriculture may, therefore, require broader approaches, such as the internationalization of costs of GHG abatement (Cavigelli et al., 2012; Venterea et al., 2012), in addition to the technical solutions found by researchers.

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