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ORIGINAL ARTICLE

Nitrogen sources and application rates affect emissions of N_2O and NH_3 in sugarcane

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Abstract Best management practices for N fertilization should increase yields while reducing negative environmental effects such as losses by ammonia (NH_3) volatilization and emission of greenhouse gases, especially nitrous oxide (N_2O). We studied the impact on sugarcane of two N sources (UR: urea and CAN: calcium ammonium nitrate) in three N rates (30, 60, and 90 kg N ha^{-1} in the plant cane cycle and 60, 120, and 180 kg N ha^{-1} in ratoons) on a sugarcane field grown on a Red Latosol soil in southeastern Brazil. We measured sugarcane yields and N_2O, CO_2 and CH_4 emissions in three crop cycles (plant cane, 2nd and 3rd ratoons), and NH_3 in two crop cycles (2nd and 3rd ratoons). The accumulated emission of N_2O from UR was significantly higher in comparison with those of CAN in all three crop cycles. The average emission factors for UR were 0.8% (plant cane), 1.1% (2nd ratoon) and 0.8% (3rd ratoon) and the corresponding figures for CAN were 0.4%, 0.7% and 0.5%, respectively. The N_2O intensity was higher for UR (20.3 mg N–N_2O kg^{-1} sugarcane stalk) than CAN (16.2 mg N–N_2O kg^{-1} sugarcane stalk). The NH_3 volatilization losses for CAN were less than 1% compared to 5–16% of the N applied as UR. Stalk

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yield increased with N application, but no difference was observed between UR and CAN. We concluded that CAN has the potential to reduce both NH_3 and N_2O losses compared with urea and is the preferred N source for sugarcane.

Keywords Ammonia volatilization · Calcium ammonium nitrate · Nitrous oxide · Straw · Sugarcane yield · Urea

Introduction

Sugarcane is cultivated on 10 Mha in Brazil, which uses 17–23% of the N fertilizer employed in Brazilian agriculture (CONAB 2018). Urea (UR), ammonium nitrate (AN) and ammonium sulfate are the main sources of N for this crop (Cantarella et al. 2007).

Urea, the most-used N fertilizer, is subject to high losses of N through ammonia (NH_3) volatilization when surface-applied to soils. Under the warm conditions in Brazil, this can reach 60% of the N applied (Pan et al. 2016; Cantarella et al. 2007; Chien et al. 2009), and may reduce sugarcane yields (Vitti et al. 2007; Costa et al. 2003). For this reason, other sources of N fertilizer may be preferable for sugarcane, especially when applied to ratoon cycles, in which a thick mulch of plant residues (10–20 Mg ha^{-1} dry mass) remains on the soil surface, making it difficult to incorporate urea to prevent NH_3 volatilization loss. In this context, calcium ammonium nitrate (CAN 27-00-00) containing 4% Ca and 2% Mg, is a promising N fertilizer for sugarcane in Brazil.

The amount of NH_3 lost can vary substantially depending on soil management and climate. For instance, Cantarella et al. (2008) observed volatilization of NH_3 from 1 to 25% of the N surface-applied as urea to seven sugarcane fields. Although high amounts of harvest residues remain on the soil surface, fertilization of this crop often occurs in periods with dry and mild temperatures, which may reduce the potential for NH_3 losses. Therefore, the information about NH_3 loss in sugarcane must be refined for specific situations, such as areas with thick trash mulch, and mitigation strategies must be developed (Cantarella et al. 2018; Otto et al. 2016). In addition, the volatilized NH_3 deposited in other places may lead to soil acidification and indirect N_2O emission (Behera et al. 2013).

The N_2O emissions from N fertilizers and residues range from 0.3 to 2% of the N applied in sugarcane fields in Brazil (Filoso et al. 2015). High N_2O emissions are undesirable especially if the crop is used to produce biofuels meant to replace fossil fuels and to decrease greenhouse gases emission; such emissions may even negate the beneficial effect of the CO_2 savings from biofuels (Crutzen et al. 2008). N_2O may represent up to 40% of the total greenhouse gases emitted in the production of ethanol from sugarcane (Lisboa et al. 2011).

Recent studies show that the N_2O emissions in sugarcane fields in Brazil occur mainly due to the nitrification process rather than denitrification (Lourenço et al. 2018a; Soares et al. 2016). For this reason, sources of N containing ammonium may have higher N_2O emission than those containing nitrate (Soares et al. 2016; Tenuta and Beauchamp 2003). Snyder et al. (2009) suggested that the emission of N_2O with urea is generally higher than that from other N sources, due to the accumulation of nitrite over time in the soil (Venterea et al. 2015), but there is no clear tendency. For instance, Harty et al. (2016) compared N sources in wet temperate grasslands and found higher N_2O emissions with AN than with UR. In addition, if an N source results in higher crop yields—i.e., by increasing the efficiency of fertilizer use—the emission of greenhouse gases (GHG) per unit of product may be lowered.

The amount of N applied to crops affects both NH_3 loss and N_2O emissions. The NH_3 volatilization usually shows an exponential effect as a function of the N application rate (Pan et al. 2016; Rochette et al. 2009). In general, this also applies to N_2O emissions. For national inventories, the use of a linear relationship is recommended, between the N application rate and N_2O emissions (IPCC 2006). However, Snyder et al. (2009) reported a linear response at typical N fertilization rates and an exponential increase when the N rate is substantially higher than the plant demand. Furthermore, in a meta-analysis, Kim et al. (2013) showed that the N_2O can be linear or nonlinear depending on the availability of C and the N demand by microorganisms and plants.

Today, in the State of São Paulo, over 95% of the 5 Mha of sugarcane are harvested without burning. Nitrogen fertilizers are applied on top of sugarcane straw, but questions remain whether urea underperforms in such system and at what extent to justify its substitution by other N fertilizers. Best management practices for N fertilization not only influence productivity but also N gaseous losses. Therefore, the objective of the present work was to evaluate the effect of N sources and rates on NH_3 volatilization, N_2O emissions, and sugarcane yield in Brazil in three crop cycles conducted in a field with mechanical harvest and straw preserved over the soil.

Material and methods

Experiment and treatments

This study was conducted in a traditional area of sugarcane cultivation at the São Paulo Agency of Agribusiness Technology—APTA in Piracicaba, southeastern Brazil (22°41′02″S, 47°38′44″W, 547 m above sea level), with long-term (100 year) average rainfall and air temperature of 1297 mm and 22.5 °C, respectively. The region is classified as Koppen's CWA humid subtropical climate, with dry winters and hot and wet summers.

The soil in the experimental site has a 4–5% slope and was classified as Red Latosol (Embrapa 2013). Samples of the 0–0.20 m layer were collected yearly from 2013 to 2017 and analyzed for chemical and physical properties (Van Raij et al. 2001) showing the following average values: pH $CaCl_2$: 5.0, OM: 19 g dm^{-3}, CEC: 64 $mmol_c$ dm^{-3}, bulk density = 1.4 Mg m^{-3} clay: 519 g kg^{-1}, silt: 146 g kg^{-1}, sand: 335 g kg^{-1} (Table 1).

The area has been continuously grown with sugarcane harvested without burning for more than 10 years. The former sugarcane crop was desiccated in November 2012 and the soil was plowed and disked for the new crop. In March 2013, the IAC-5000 variety was planted with pre- sprouted seedlings, in plots containing 5 rows, 15 m in length, spaced by 1.5 m. The plant cane was initially irrigated until 30–45 days after planting and thereafter, including the ratoons, the crop was rain-fed.

The treatments comprised two N sources (UR and CAN) and four N rates. The N rates, termed control, low, medium and high, were 0, 30, 60, and 90 kg ha^{-1} in the plant cane cycle, and 0, 60, 120, and 180 kg ha^{-1} in the ratoons, and were defined based on the N response of the sugarcane crop to this nutrient in Brazil (van Raij et al. 1996).

The experimental design was a randomized block with four replicates. The control treatment (without N) was common to both N sources. Granular urea (45% N) and CAN (ammonium nitrate with limestone containing 27% N with 1:1 NH_4 to NO_3 ratio, 4% Ca, and 2% Mg) were used. Other nutrients were applied at common rates to all treatments: P (65 kg ha^{-1} in plant cane and 20 kg ha^{-1} in the ratoons) as single superphosphate, K, (120 kg ha^{-1}) as potassium chloride, Zn (10 kg ha^{-1}) as zinc sulfate, B (1 kg ha^{-1}) as boric acid, and Mo (0.4 kg ha^{-1}) as sodium molybdate.

In the plant cane cycle the fertilizers were applied into the planting furrow and incorporated at a depth of 0.2 m; in the ratoons, the fertilizers were surface-applied over the harvest straw, in bands approximately 0.2 m from the sugarcane rows. The treatments were reapplied in the same plots from 2013 to 2017.

Plants were harvested manually in Aug/Sept of each year (Table 2). The dry leaves and green tops were separated from the stalk and left on the soil as straw. This material was homogeneously distributed over the field. The stalks were weighted with a load

Table 1 Chemical and physical properties of the Red Latosol soil of the experimental area (0–0.20 m depth)

Year	pH $CaCl_2$	OM	P	K	Ca	Mg	H + Al	CEC	BS %	Clay	Silt	Sand
		g dm^{-3}	mg dm^{-3}	$mmol_c$ dm^{-3}						g kg^{-1}		
2013–2014	4.9	19	15	0.8	28	14	31	74	58	519	146	335
2015–2016	5.0	19	17	1.0	19	15	24	58	58			
2016–2017	5.0	19	24	1.1	20	15	28	63	56			

pH $CaCl_2$ (0.0125 mol L^{-1}); OM: organic matter; P, K, Ca, Mg: extracted with ion exchange resin; H + Al: buffer solution at pH 7.0; CEC: cation exchange capacity; BS: base saturation; Soil texture: pipette method

Table 2 Dates of key operations, mean air temperature and total rainfall in the experimental site (2013 to 2017)

Year	Straw from previous harvest (Mg ha^{-1})	N fertilization	Harvest	NH_3 measurement	GHG measurement	Average air temperature (°C)	Rainfall (mm)
Plant cane	–	19 Mar 2013	22 Sep 2014	–	20 Mar 2013 to 22 Sept 2014	23.1 ± 3.4	1134
First ratoon	13	18 Nov 2014	18 Sep 2015	–	–	23.8 ± 3.3	1442
Second ratoon	14	04 Nov 2015	02 Aug 2015	05 Nov 2015 to 01 Dec 2015	05 Nov 2015 to 11 Jul 2016	22.7 ± 3.8	1426
Third ratoon	15	08 Oct 2016	01 Aug 2016	09 Oct 2015 to 04 Nov 2016	08 Oct 2016 to 03 Jul 2017	22.3 ± 3.3	1430

Mean daily air temperature ± standard deviation. Detailed air temperature and rainfall data in the periods of N_2O emission are presented in Fig. 6S, 7S, and 8S

cell coupled to a tractor to estimate stalk yields. Samples of straw left on the soil were randomly collected using a 1 by 1 m wooden frame and dried at 60 °C to constant weight in the laboratory. The average dry biomass values of the straw were 13, 14 and 15 Mg ha^{-1} for the three ratoon cycles (Table 2).

NH_3 emission

Ammonia volatilization was measured for 27 days in all UR plots and in one CAN plot (180 kg ha^{-1}) during the two ratoon cycles. Ammonia was not measured in the plant cane cycle since the fertilizers were incorporated into the soil, a condition in which significant losses are not expected.

The N losses by NH_3 volatilization were measured using a semi open chamber made of PVC cylindrical tubes 0.40 m in height × 0.20 m in diameter, placed over PVC bases 0.10 m height and 0.19 m in diameter and following the procedure described by Cantarella et al. (2003, 2008). The chamber bases (10 per plot) were inserted 0.05 m into the soil, and 0.20 m from the sugarcane rows, maintaining the straw inside each chamber. The amounts of N for each treatment were previously weighed in the laboratory using an analytical balance. The chambers were fitted with two polyethylene foam discs (0.002 m in height × 0.2 m diameter), previously soaked with phosphoric acid and glycerin solution (Cantarella et al. 2003). The first disc was placed in the lower part of the chamber at a height of 0.15 m from the ground to capture the volatilized NH_3 from the soil and fertilizer treatments. The other disc, placed in the upper part of the chamber 0.25 m from the ground, captured the NH_3 from the external environment and avoided the contamination of the lower disc. A protective cap was placed on the top of the chamber to prevent rain from reaching the foam discs.

The NH_3 trapping discs were collected 1, 3, 5, 7, 9, 11, 15, 17, 21, and 27 days after N application. After each sampling, the chamber was moved to an adjacent base where the fertilizers had been exposed to the weather as the remainder of the plot to ensure that the measurements reflect the multifactorial conditions that affect NH_3 losses (rain, wind, and temperature) and decrease the interferences of the chamber.

The NH_3 trapped in the foams was extracted with successive portions of KCl solution (1 mol L^{-1}), transferred to a volumetric flask, and the volume was made to 500 mL. A 25 mL aliquot was transferred to a 200 mL distillation flask and NaOH (10 M) was added to raise the pH to > 7.5. The distillate was collected in 10 mL of a boric acid solution containing a pH indicator and then titrated with 0.0025 mol L^{-1} sulfuric acid (Cantarella et al. 2003). Daily (mg day^{-1}) and cumulative NH_3 losses (kg ha^{-1}) were calculated to express the percentage loss in relation to the N applied.

N_2O emission

The static chambers consisted of PVC cylinders 0.20 m in height and 0.30 m in diameter installed in the fertilizer band as described by Carmo et al. (2013) and Soares et al. (2015).

The fluxes of greenhouse gases (GHG) were measured in the plant cane and in the 2nd and 3rd ratoon cycles starting 1 day after N fertilization. To decrease the GHG data variation, the amount of N fertilizer was weighed separately for each chamber.

Gas samples were collected daily for 7 days following N application. After that, the samples were collected three times a week during the first 2 months, twice a week in the third month, once a week in the fourth month, and subsequently every 15 or 30 days. In addition, samples were also collected 1 day after rain events.

For the GHG sampling, the chambers were closed for 30 min. The cover lids are fitted with two valves, one for collecting gases and the other to equalize the internal and external pressures. The gas samples were collected using nylon syringes (60 mL) in three time intervals after the closing of the chambers, i.e. 0, 15, and 30 min according to Mosier et al. (2006) and stored in 12-mL Exetainer® vials (Labco Limited, United Kingdom) for no more than 2 weeks before analysis.

The samples were analyzed with a GC-2014 Shimadzu gas chromatograph (Shimadzu Corp., Japan) with simultaneous determination of N_2O using an EC detector operating at 325 °C (Hutchinson and Mosier 1981) and of CH_4 and CO_2 using an FID operating at 250 °C. The gas concentrations were corrected for the atmospheric pressure and temperature measured at the time of sampling. The fluxes were calculated as described by Denmead et al. (2010). The cumulative nitrous oxide emission was calculated by linear interpolation between adjacent sampling dates. The emission factor (EF) was calculated using Eq. (1) as follows:

$$EF = \frac{(N_2O - Ntreatment - N_2O - N\ control)}{N\ mineral\ applied} * 100 \tag{1}$$

The N_2O intensity was calculated considering the emission of N_2O from the treatment and control plots in relation to the stalk yield in each plot, according to Eq. (2):

$$N_2O - N\ intensity = \frac{(Emission\,factor\mathrm{N_2O} \times applied\ \mathrm{N}\ rate) + Emission\ \mathrm{N_2O}\ control}{Stalk\,yield\ in\ \mathrm{kg\ m^{-2}}} \tag{2}$$

The EF was also represented in relation to the net emission for each treatment, discounting the N loss by NH_3 volatilization as follows:

$$EFnet = \frac{(N_2O - N\ \mathrm{treatment}\ - N_2O - N\ \mathrm{control})}{\mathrm{N\ mineral\ applied}\ - \mathrm{NH_3 - N\ \ volatilized}} * 100 \tag{3}$$

Soil sampling

Soil samples at a depth of 0–0.10 m were collected weekly in the fertilization band and close to the chambers on the same day as the GHG samples. Three subsamples per plot were collected to measure soil moisture, NO_3^- and NH_4^+ (mineral N). The mineral N concentration was determined by steam distillation after extraction with KCl (1 M), according to Van Raij et al. (2001). Soil moisture was determined after drying the samples at 100 °C to constant weight. The water-filled pore space (WFPS) was estimated as follows:

$$\mathrm{WFPS}\ (\%) = 100 * (\mathrm{GWC} \times \mathrm{BD})/\mathrm{SP} \tag{4}$$

where GWC is the gravimetric water content (Mg Mg^{-1}), BD is the bulk density (1.4 Mg m^{-3}), and PS is the soil porosity (0.48 m^3 m^{-3}). BD and SP were determined in four replicates per block, once a year.

Statistical analysis

Data for stalk yield and the cumulative emissions of NH_3, N_2O, CO_2, and CH_4 were checked for a normal distribution of residues and stability of the variance (Rawlings et al. 1998), submitted to analysis of variance (ANOVA) and were compared by orthogonal contrasts ($P \leq 0.05$). The softwares used were SAS, version 9.2, and Sigma Plot, version 12.5 (Systat Software, Inc.).

Results

NH_3 emissions

NH_3 volatilization losses were measured in the 2nd and 3rd ratoon crops, immediately following the surface application of N fertilizers, which was done in the middle of spring, 3 and 2 months after the sugarcane of the previous cycles had been harvested without burning, respectively. Approximately 14–15 Mg ha^{-1} of straw was left on the soil (Table 2). At that time, the rainy season was starting, and temperatures were already high. In both years, daily maximum temperatures were above 30 °C (results not shown).

Losses from the urea treatments varied from 6.4 to 28.8 kg ha^{-1} N in the 2nd ratoon and 7.7–15.0 kg ha^{-1} NH_3-N in the 3rd ratoon for rates of application ranging from 60 to 180 kg N ha^{-1} (Fig. 1). As a proportion of the N application rates, the NH_3 losses varied from 10.8 to 16.0% in the 2nd ratoon and from 6.9 to 10.8% in the 3rd ratoon (Fig. 2).

In both years, the NH_3 losses observed in the treatments with the highest N application rate (180 kg ha^{-1}) as urea were higher than those obtained with 60 and 120 kg ha^{-1}, but these did not differ significantly (Tukey $P \leq 0.1$) (Fig. 1). However, NH_3 losses expressed as a percentage of the applied N varied little in both ratoons (Fig. 2): the large amounts of straw on the soil caused the experimental error to be high, especially in the 2nd ratoon (CV = 62%).

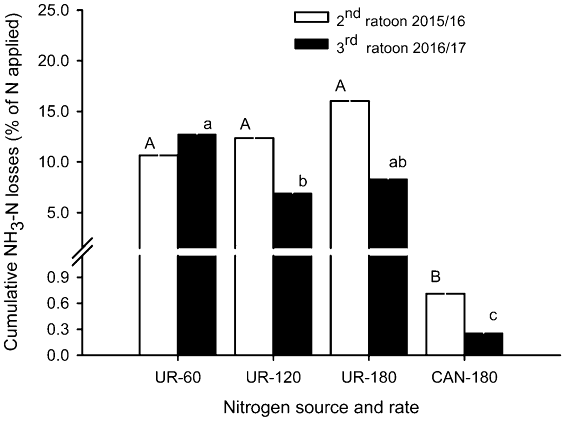

Fig. 2 Ammonia volatilization losses as a percentage of the N applied over the straw blanket as affected by sources of N and application rates in two sugarcane ratoon cycles. UR: urea; CAN: calcium ammonium nitrate; 60, 120, and 180 are N application rates (kg ha^{-1}). Uppercase and lowercase letters compare the means (Tukey, $P \leq 0.05$) for the 2nd and 3rd ratoons, respectively

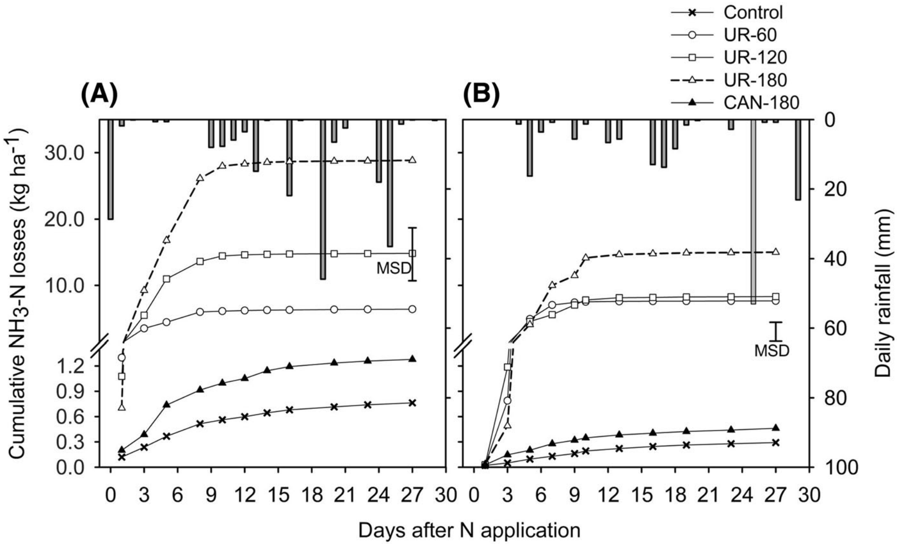

Fig. 1 Ammonia volatilization losses during the 2nd ratoon 2015/2016 (**a**) and 3rd ratoon 2016/2017 (**b**) as affected by N sources and application rates. Control (without N), UR: urea; CAN: calcium ammonium nitrate. The values 60, 120, and 180 are N application rates, in kg ha^{-1}. Vertical gray bars in the chart represent daily rainfall. Vertical bars inside each graphic indicate minimum significant difference—"MSD" (Tukey, $P \leq 0.05$). The results for each treatment were adjusted with the model $[y = a(1 - e^{-bx})]$

Nonetheless, the increasing NH_3 losses as the urea rates increased were as expected.

In the plots with CAN, NH_3 losses were very small: 0.7% and 0.3% of the applied N at the rate of 180 kg ha^{-1}, not significantly different from the control and much lower than those observed for the urea treatments (Fig. 1). The lower volatilization with CAN is due to the lower amount of NH_4^+-N compared to hydrolyzed urea. Besides, part of the granules of CAN that fall through the straw end up on the acidic soil (pH in $CaCl_2$: 4.9–5.0) (Table 1), which does not lead to relevant NH_3 losses from CAN.

N_2O emissions

Fertilization was performed in November, 2 months (3rd ratoon) and in October, 3 months (2nd ratoon) after the previous crop harvest (Table 2), when plants were approximately 0.5 m high. At that time, the raining season was starting and rain events were frequent (Fig. 3). Most of the peaks of N_2O emissions occurred in the first 30 to 40 days after the N fertilizer application during the three seasons when these measurements were performed (Fig. 3). The main driver of N_2O emissions was the combination of rain events (Fig. 3), which determined the time when the peaks occurred and the availability of inorganic NH_4^+ and NO_3^- in the soil. After 40 days the N_2O emissions declined following the decline of the concentration of soil inorganic N, since soil moisture (rainfall) was not limiting. Emissions tended to be higher in plots fertilized with urea than CAN and responded to the N application rates (Fig. 3). Data of soil inorganic N, soil moisture and the daily fluxes of N_2O are in the Supplementary Material.

The cumulative N_2O emission of the control treatment (without N) was much lower ($P \leq 0.001$) than those of the fertilized plots in both the plant cane and the ratoon measurements. The cumulative amounts of N_2O emitted in the plant cane (552 days), 2nd ratoon (250 days), and 3rd ratoon (269 days) were 168, 53, and 29 mg N_2O-N m^{-2} year^{-1}, respectively (Table 3). As there was at time span of at least 6 months after the previous sugarcane crop and the cane plant cycle of the present study, the higher emission in the control treatment in plant cane than in ratoons was probably caused by mineralization of soil organic N stimulated by the plowing and disking operations before planting. The soil remained undisturbed in the ratoon cycles.

The values of N_2O emission reported refer to measurements performed in the fertilizer band, which

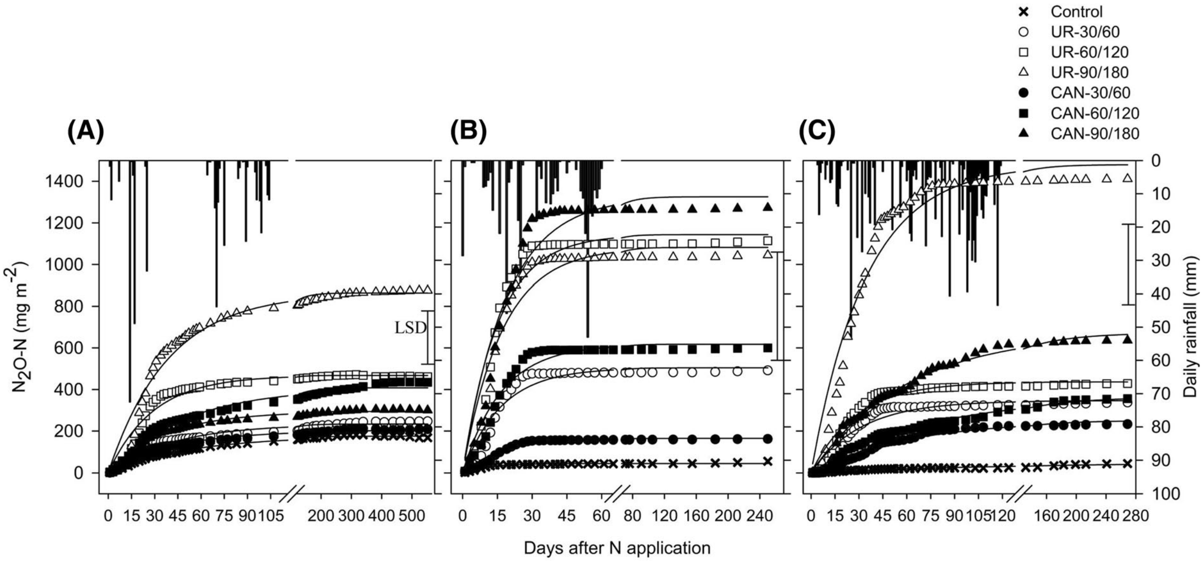

Fig. 3 Cumulative emissions of N_2O-N as affected by sources of N and application rates. UR: urea; CAN: calcium ammonium nitrate; 30, 60, and 90 are N rates in kg ha^{-1} applied to the plant cane and 60, 120, and 180 kg ha^{-1} are N rates applied to ratoons. Plant cane 2013/2014 (**a**), 2nd ratoon 2015/2016 (**b**) and 3rd ratoon 2016/2017 (**c**) cycles. Vertical black bars represent daily rainfall for the early sampling period. LSD is the least significant difference from the *t* test ($P \leq 0.05$). The results for each treatment were adjusted to the model $[y = a(1 - e^{-bx})]$

Table 3 Cumulative emissions of N_2O-N and N fertilizer emission factor (EF) as affected by N fertilizer sources and rates. N sources: urea (UR) and calcium ammonium nitrate (CAN); low, medium and high N rates for plant cane (30, 60, and 90 kg N ha^{-1}) and ratoons (60, 120, and 180 kg N ha^{-1}), respectively. Emissions reported for the fertilizer band

N rate	N_2O emission in sugarcane cycle					
	plant cane		2nd ratoon		3rd ratoon	
	UR mg N_2O-N m^{-2} (% of applied N[†])	CAN	UR	CAN	UR	CAN
Control (N = 0)	168		53		29	
Low	247 (0.41)	209 (0.21)	492 (1.14)$^{\#1.31}$	161 (0.28)	290 (0.68)$^{\#0.79}$	255 (0.59)
Medium	461 (0.77)	435 (0.70)	1114 (1.39)$^{\#1.59}$	600 (0.71)	393 (0.48)$^{\#0.52}$	327 (0.39)
High	876 (1.24)	300 (0.23)	1045 (0.86)$^{\#1.04}$	1265 (1.06)	1322(1.13)$^{\#1.25}$	698 (0.52)
Mean values	528 (0.81)	315 (0.38)	884 (1.13)$^{\#1.31}$	675 (0.68)	668 (0.76)$^{\#0.85}$	427 (0.50)
Contrasts	Matrix of orthogonal contrasts for treatments (N sources and rates) *Pr > F*[*]					
Control vs N treat.	0.0013		< 0.0001		< 0.0001	
UR vs CAN	0.0005		0.0558		0.0051	
$UR_{Linear\ Effect}$	< 0.0001		0.0058		< 0.0001	
$UR_{Quadratic\ Effect}$	0.2013		0.0364		0.0019	
$CAN_{Linear\ Effect}$	0.3085		< 0.0001		0.0034	
$CAN_{Quadratic\ Effect}$	0.0282		0.4697		0.2036	

[†] Numbers in parentheses are the N fertilizer emission factor

[#] Net emission factor (%), subtracting the N lost as NH_3 from the N rate applied

[*] Significance probability of F test

represents approximately 20% of the field area. The mean cumulative N_2O emission in the three cycles was significantly lower in the plots with CAN than in those with urea (Table 3). The average N_2O-N emission for the three N application rates applied as CAN was 315 mg m^{-2} $year^{-1}$, 675 mg m^{-2} $year^{-1}$, and 427 mg m^{-2} $year^{-1}$, for plant cane and 2nd and 3rd ratoons, respectively. The corresponding values for the urea treatments were 528 mg m^{-2} $year^{-1}$, 884 mg m^{-2} $year^{-1}$ and 668 mg m^{-2} $year^{-1}$ (Table 3).

Considering the average of all three N application rates, the fertilizer N_2O emission factor (EF), expressed as a percentage of the applied N, varied from 0.76 to 1.13% for urea and from 0.38 to 0.68% for CAN, that is, the EF for CAN was on average 42% lower than that for urea (Table 3). The EF for urea was also calculated considering the amount of N lost as NH_3. In this case, the NH_3-N lost was subtracted from the N amount applied as urea. The EF corrected for NH_3 losses were, for the 2nd and 3rd ratoons respectively, 1.31% and 0.85%, whereas those calculated from the full N application rate were 1.13% and 0.76%. The fertilizer N_2O EF, in general, increased with increasing N rates except for the UR treatments in the 2nd ratoon, which showed relatively high EF at lower N fertilizer rates (Fig. 4).

Sugarcane productivity and N_2O intensity

Except for the plant cane cycle, when there was no yield response to N fertilization, N application

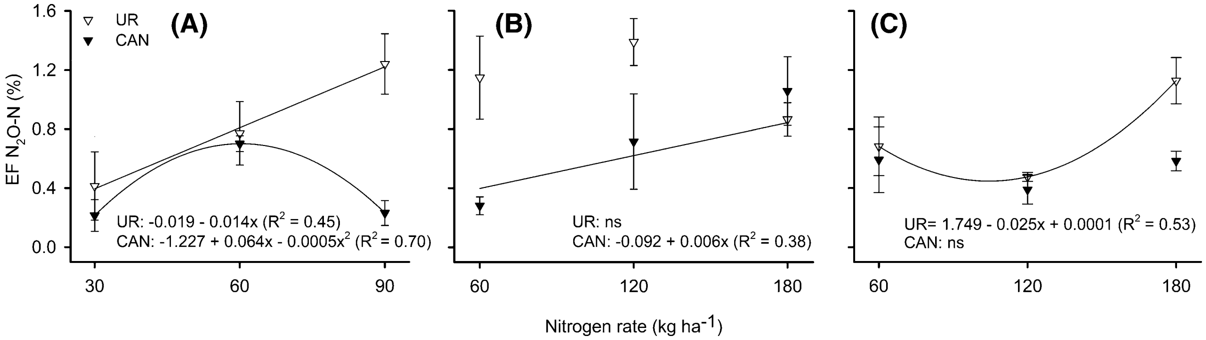

Fig. 4 Emission factor N_2O-N emission factor (EF) during the plant cane (**a**), 2nd ratoon (**b**), and 3rd ratoon (**c**) cycles as affected by N sources and application rates. UR: urea; CAN: calcium ammonium nitrate; 30, 60, and 90 are N rates in kg ha^{-1} applied to the plant cane and 60, 120, and 180 kg ha^{-1} are N rates applied to ratoons. Bars indicate the mean standard error (n = 4)

significantly increased stalk yields in the 2nd and 3rd ratoons, as well as in the sum of the three cycles (Table 4). The main difference in stalk yield was between the unfertilized control and the fertilized plots but the response to N application rates (60, 120, and 180 kg N ha^{-1} in the ratoon cycles) was of little significance. In addition, there was no effect of the N source on yields in any of the cycles evaluated: the cumulative stalk yields obtained with UR and CAN were 269.3 and 269.8 t ha^{-1} (Table 4). The results of the 1st ratoon are not reported because in that cycle NH_3 and GHG were not measured. However, the

Table 4 Sugarcane yield and N_2O–N intensity of plant cane and ratoons as affected by N fertilizer sources and rates. N sources: urea (UR) and calcium ammonium nitrate (CAN); low, medium and high N rates for plant cane (30, 60, and 90 kg N ha^{-1}) and ratoons (60, 120, and 180 kg N ha^{-1}), respectively

Treatment	Sugarcane yield				N_2O intensity†			
	Plant Cane Mg ha^{-1}	2nd Ratoon	3rd Ratoon	Three cycles	Plant Cane mg N_2O-N kg^{-1} sugarcane	2nd Ratoon	3rd Ratoon	Three cycles
Control (N = 0)	90.3	79.2	49.9	219.4	18.6	6.8	5.9	11.4
UR-Low	89.7	98.4	71.5	259.6	19.3	12.4	9.9	14.2
UR-Medium	90.4	107.3	76.5	274.2	22.5	20.5	11.3	18.8
UR-High	94.2	102.4	77.4	274.0	31.0	20.4	29.9	26.8
CAN-Low	90.6	102.2	70.2	263.0	19.6	6.9	9.5	12.2
CAN-Medium	93.7	103.6	73.0	270.3	23.3	13.4	10.5	16.0
CAN-High	95.1	104.0	77.0	276.1	20.1	23.4	18.0	20.8
Contrast	Matrix of orthogonal contrasts for treatments (N sources and rates)							
	Pr > *F*$^{\#}$							
Control vs Treat.	0.6303	< 0.0001	< 0.0001	< 0.0001	0.0134	0.0006	0.0011	< 0.0001
UR vs CAN	0.4398	0.8642	0.6029	0.6669	0.0139	0.0859	0.0249	0.0017
$UR_{Linear\ Effect}$	0.4224	0.4989	0.3073	0.5845	< 0.0001	0.0132	< 0.0001	< 0.0001
$UR_{Quadratic\ Effect}$	0.4048	0.1948	0.6820	0.2621	0.1945	0.1214	0.0044	0.2443
$CAN_{Linear\ Effect}$	0.2178	0.7672	0.2416	0.2638	0.9809	< 0.0001	0.0122	< 0.0001
$CAN_{Quadratic\ Effect}$	0.7400	0.9136	0.9072	0.9061	0.0509	0.4506	0.2344	0.7511

$^{\dagger}N_2O{-}N\ intensity = \frac{(Emission factor N_2O \times Applied N Rate) + Emission N_2O control}{Stalk\ Yield\ in\ \mathrm{kg\ m^{-2}}}$

#Significance probability of F test

yields followed the same trend, that is, there was a significant difference between unfertilized (82.5 t ha^{-1}) and fertilized plots (average yields of all N application rates: UR, 94.7 t ha^{-1}; CAN, 97.1 t ha^{-1}).

Yields of the 3rd ratoon were unexpectedly low: the stalk yield of the control treatment was only 49.9 t ha^{-1} whereas those for UR and CAN (average of the three N application rates) were 75.1 t ha^{-1} and 73.4 t ha^{-1}, respectively. The reason for this was an infestation of spittle bug (*Mahanarva fimbriolata*), probably induced by the high amounts of straw (approximately 14 Mg ha^{-1} of dry matter) close to the plants, that was perceived and treated only in the mid-season when substantial damage had already occurred.

The fertilizer treatments did not affect the sugar concentration in stalks in any season; therefore, the sugar yields (not presented) were proportional to the stalk yields reported in Table 4.

The N_2O intensity, expressed in mg N_2O-N per kg of sugarcane stalk produced, was significantly affected by both the N fertilizer application rate and the source of N used in all cycles evaluated (Table 4). In the average of three harvests, 11.4 mg N-N_2O was emitted for every kilogram of stalk in the unfertilized control; the corresponding figures for plots fertilized with UR and CAN were 19.9 mg kg^{-1} and 16.3 mg kg^{-1}, respectively (Table 4). Increasing the N application rates for both sources of N caused a significant increase in the N_2O intensity (Table 4).

CO_2 and CH_4 emissions

The accumulated CO_2 emission varied from 780 to 1180 g m^{-2} in the three seasons and, except for the plant cane cycle, it was not affected by the treatments. In the plant cane cycle, the application of N increased CO_2 emission although this seems to be due to an outlier observed in plots fertilized with 90 kg N ha^{-1} as urea. There was little variation in the average CO_2 emission in the three cycles.

In general, the soil was a sink rather than an emitter of CH_4. Except for an increase in CH_4 consumption with increasing rates of N as urea in the plant cane and the 3rd ratoon cycle, the effects of the source of N fertilizer and application rates were not statistically significant. Data of CO_2 and CH_4 emissions are in the supplementary material (Table S3 and S4).

Discussion

NH_3 volatilization

Sugarcane straw mulch tends to enhance NH_3 losses because it acts as a barrier to incorporation of urea into the soil and because part of the losses may come directly from the urea that stays in the mulch (Pinheiro et al. 2018). These authors found, in two studies, that NH_3 losses increased by 1.5% and 2.6% of the applied N per metric ton of straw left on the field. In addition, the magnitude of NH_3 losses when urea is surface-applied to sugarcane fields is highly dependent on the weather and therefore on specific site conditions. The straw blanket may also retain moisture and increase the urease activity. Freney et al. (1992) reported maximum losses of 32–39% of the applied urea–N in Australia. In Brazil (Costa et al. 2003) observed losses of 36% of the urea-N (100 kg ha^{-1}) applied over the straw. For this same rate of urea-N applied over sugarcane straw, NH_3 losses of 20% were reported by Otto et al. (2017) and from 14 to 33% in five sites by Mira et al. (2017), within the range of values found in the present study.

Higher application rates of N or localized (band *vs* broadcast) application usually increases NH_3 losses expressed as a percentage of the applied N because of the concentration effect of urea hydrolysis on the soil pH in the vicinity of the fertilization zone (Cantarella et al. 2003; Vitti et al. 2007). However, if excess urea saturates the active sites of urease in the soil or in straw, the effect of increasing N application rates may not hold. Mariano et al. (2012) reported NH_3 losses of 16% of the urea-N applied at 50 kg ha^{-1} over sugarcane straw but the losses were in the range of 24% as N application rates increased from 100 kg ha^{-1} up to 200 kg ha^{-1}. In the present study, NH_3 losses increased from 11 to 16% as the N application rates increased from 60 to 180 kg ha^{-1} in one year but did not vary in the following year. Uneven fertilizer distribution may also explain such results. However, all these studies indicate that significant amounts of N may be lost as urea is applied to sugarcane fields with preserved straw.

The differences in the amounts and pattern of NH_3 volatilization in the 2 years of observation are explained by the climate conditions, especially the rain regime at the time of fertilizer application. In the 2nd ratoon experiment, NH_3 volatilization from the urea treatments started soon after fertilization: in the third and fourth days, respectively, 9.2 and 16.8 kg ha^{-1} NH_3–N had been lost from the urea applied at 180 kg ha^{-1} N (Fig. 1). In that experiment rain totaling 40 mm occurred in the 4 days that preceded the fertilizer application. The moist soil combined with maximum daily temperatures above 30 °C drives NH_3 losses up. Interestingly, the 28.6 mm precipitation that occurred on the day of the fertilizer application was not enough to stop NH_3 volatilization (Fig. 1). The losses continued up to approximately the 9th day when they leveled off, probably because of cumulative rain events.

Usually, it is assumed that 10–20 mm of rain is enough to incorporate urea into the soil, thereby reducing or even controlling NH_3 volatilization losses (Holcomb et al. 2011). However, the nature of the sugarcane straw (large particles), its amounts and arrangement over the soil may affect how rain acts to reduce losses. Rain may go through preferential channels in the straw and may not effectively wash the urea to the soil (Freney et al. 1994). This may explain why 28.6 mm of rain did not stop NH_3 losses in our study as well as other cases of rain greater than 20 mm that had only a small effect on reducing losses from urea applied to sugarcane blankets (Cantarella et al. 2007).

Nonetheless, soil moisture and rain play an important role in determining NH_3 losses from urea used in sugarcane fields. Cantarella et al. (2008) reported NH_3 losses varying from 1 to 25% of the applied N in seven field studies with sugarcane; most of the variation could be explained by the weather conditions. Urea applied to dry soil—common when sugarcane fertilization is done in the winter—resulted in very little NH_3 losses as the urea remained unhydrolyzed on the soil/straw for approximately 20 days (Cantarella et al. 2008; Mira et al. 2017). We can derive associations between the weather and NH_3 losses observed in our study. In the 3rd ratoon experiment, the soil was dry when the fertilizer treatments were applied; no rain had been registered in 5 days. In the 4 days that followed fertilization practically no rain occurred. Consequently, NH_3 losses were very small in the measurements done on the 1st and the 3rd days after fertilization. However, NH3 volatilization increased sharply after the 5th day (Fig. 1), which coincided with rain events that supplied the water necessary to cause urea hydrolysis. As in the previous year, NH_3 volatilization tended to decrease after 9–10 days due to several consecutive rain events.

Urea incorporation into the soil is an effective way to reduce NH_3 volatilization losses (Rochette et al. 2013), including on sugarcane blanketed soils (Cantarella et al. 1999) but this operation is time-consuming and requires high-powered machines in fields with large amounts of straw; therefore, mechanical incorporation of urea is seldom done by farmers in Brazil.

Acidic soils such as those of our study are not prone to NH_3 volatilization losses from nitrogen fertilizer compounds that contain N as ammonium or nitrate, such as CAN. Indeed, the NH_3 losses found in our study were 0.3% and 0.7% of the N applied as CAN (Fig. 2). Because of the negligible NH_3 volatilization losses, ammonium nitrate is the fertilizer of choice of the sugarcane sector when surface-applied. However, there are increasing legal restrictions to ammonium nitrate trade and storage because of its use in the manufacture of explosives; for this reason, a major fertilizer company operating in Brazil stopped selling this product recently. CAN has fewer restrictions because it contains limestone, which reduces its potential as an explosive material, but its price is higher than that of urea.

Despite its drawback as a N source when surface-applied, urea is unlikely to be totally displaced in sugarcane because urea is the less expensive N fertilizer and comprises approximately 60% of the N in the Brazilian and the international market. In addition to management practices such as soil incorporation, options to reduce NH_3 losses include the use of urease inhibitors (Cantarella et al. 2018). The use of NBPT (N-(n-butyl) thiophosphoric triamide), a urease inhibitor, reduced NH_3 losses by 35% as an average of five experiments in sugarcane fields with straw-covered soils (Cantarella et al. 2008). Controlled-release fertilizers can also reduce losses and increase N use efficiency but currently they are not price-competitive for sugarcane (Verburg et al. 2016). Moreover, the results of the use of controlled-release fertilizer in sugarcane are variable, but increasing testing and use may turn them more reliable and economic (Verburg et al. 2016).

Sugarcane yield

Despite the loss of NH_3 ranging between 7% and 16% of the N applied as UR and the insignificant losses observed with CAN (0.3–0.7%) (Fig. 2), the source of N did not affect stalk yield in either the 2nd or 3rd ratoon (Table 4). The same occurred in the 1st ratoon (results not shown). However, it is risky to conclude that UR and CAN have the same efficiency in supplying N to sugarcane grown in soils covered with straw. Sugarcane has a long cycle (in our study 18 months in plant cane and 12 months in the ratoons); the contribution of N fertilizer to the overall N supply to sugarcane tends to be low. Therefore, the amounts of N lost as NH_3 may have a limited effect on crop nutrition on the short term.

Vitti et al. (2011) reported that 30% of the N applied as urea was recovered by sugarcane plants at the end of the cycle. Similar results were reported by Ng Kee Kwong and Deville (1987) in Mauritius. Usually, the amount of fertilizer-derived N is higher in the early stages of sugarcane growth but declines as the plant matures. Franco et al. (2011) found that in young sugarcane plants 40% and 70% of the plant N was derived from fertilizer in plant cane and ratoon, respectively. However, these proportions decreased to 10% and 30% in mature plants, that is, most of the N at the end of the cycle had come from other sources, more likely the soil. In a recent review of the sugarcane literature in Brazil, Otto et al. (2016) reported that on average only 26% of the N taken up by sugarcane plants comes from fertilizer but 32% of the N applied as fertilizer ends up immobilized in the soil organic fractions. Thus, part of the N that is not lost as NH_3 probably will accumulate in the soil and form the stock of soil organic N that will mineralize and supply the crop in subsequent years (Meier et al. 2006; Ng Kee Kwong et al. 1987) even though the short-term yield response may not be clear. The N lost as NH_3 may also affect the yield, despite the low fertilizer-N recovery by this crop, as reported by Vitti et al. (2007). In their study, plots fertilized with ammonium sulfate (not subject to NH_3 losses in acidic soils) yielded 73 t ha^{-1} of stalks, significantly higher than the yields obtained with UR (60 t ha^{-1}). However, the yield with ammonium nitrate was 64 t ha^{-1}, similar to that of urea.

The fact that the soil supplies part or even most of the crop N tends to mask the effect of losses. A review about urease inhibitors (Cantarella et al. 2018) showed that NBPT added to urea reduced NH_3 volatilization losses by 52% in an average of 35 studies with different crops but yields increased by only 6%; in the 11 studies with sugarcane, the effect of the urease inhibitor on sugarcane yield was null.

When N was applied in October or November (Table 2) the plants were approximately 0.5 m tall and growing rapidly, that is, intensively taking up N. A tall plant canopy may also absorb part of the NH_3 that volatilizes. Between 3 and 15% of the NH_3 volatilized from the soil-applied urea was taken up by corn plants, the highest proportion being when the plants were fertilized at a later growth stage, presenting 10 expanded leaves (Schoninger et al. 2018). However, it is difficult to establish how foliar uptake of volatilized NH_3 can affect the urea-N budget in sugarcane.

The fertilizers were applied on top of the straw, which should lead to a higher efficiency of CAN because of the insignificant NH_3 losses. However, a recent study showed that incorporation of ammonium nitrate under the straw layer increased sugarcane yields by approximately 12% compared to band application over the straw (de Castro et al. 2017), as done in our study, suggesting that part of the fertilizer N may be immobilized by the high C:N ratio in the sugarcane harvest residue, which might reduce the advantage of this N source over UR, although both fertilizers may be subject to the same immobilization process.

GHG emission

The N_2O emission observed for UR was higher than for CAN ($P \leq 0.01$) and increased with increasing N application rates for both N fertilizers (Table 3). The average N_2O-N emission factor (EF) for UR was 0.90% (ranging from 0.41 to 1.39%) and for CAN was 0.52% (ranging from 0.21 to 1.06%). The effect of N rate on EF was less clear but, in general, EF values increased with increasing N rates (Fig. 4). The climate conditions, especially rain near the time of fertilizer application, play an important role in determining the magnitude of the N_2O losses. However, the average EF values for both sources of N were lower than the IPCC default value (1%). This has been reported in most studies of sugarcane done in Brazil (Borges et al. 2019; Carmo et al. 2013; da Silva et al. 2017; Gonzaga et al. 2018; Lourenço et al. 2019; Paredes et al. 2014; Pitombo et al. 2017; Soares et al. 2015). The relatively low EF values have been attributed, among other reasons, to the good drainage of Brazilian Oxisols

(Jantalia et al. 2008). However, straw mulch may increase the N_2O emissions from N fertilizers (Carmo et al. 2013; Gonzaga et al. 2018), as was the case in the present study.

In our study, the N_2O emissions from CAN were lower than those of UR but the effect of the fertilizer source is probably site- and climate-dependent and there is no clear difference in the various studies reported in the literature (Snyder et al. 2009). For instance, Roche et al. (2016), working with barley fertilization, did not find a significant difference between the EF for UR and CAN. Martins et al. (2015) in a study with maize in an Oxisol similar to the soil used in our study also reported similar emissions for urea and a nitrate-based fertilizer (calcium nitrate), whereas Harty et al. (2016) reported much higher EF values for CAN (1.49%, ranging from 0.58 to 3.81%) than for UR (0.25%, ranging from 0.10 to 0.49%). Their study was conducted in pastures in Ireland, a wetter region than Central-South Brazil and presumably on a very different soil type. One possible reason for the lower emissions with CAN in our study is the prevalence of nitrification over denitrification as the main process driving N_2O emissions in sugarcane in our region (Lourenço et al. 2018a, b; Soares et al. 2016). In fact, Soares et al. (2016) found that N_2O emissions in plots of sugarcane fertilized with calcium nitrate were as low as those of the unfertilized control, as opposed to the plots with UR, where the EF was 1.68%. Siqueira Neto et al. (2016) also reported lower N_2O emissions in sugarcane with ammonium nitrate than with urea.

The effect of N fertilizer on biomass production may offset the GHG emissions if expressed per unit of crop produced (Snyder et al. 2014). However, in our study, the N_2O emission per unit of sugarcane stalk was significantly higher ($P \leq 0.01$) in the fertilized plots than in the unfertilized control, and higher ($P \leq 0.01$) for UR than for CAN: the N_2O intensity for the unfertilized control was, on the average of three cycles, 11.4 mg N_2O–N kg^{-1} of sugarcane stalk, whereas the corresponding values for UR and CAN were 19.9 and 16.3 mg N_2O–N kg^{-1} stalk (Table 4). Therefore, CAN had a lower carbon footprint than UR but, because the relatively small yield gains of the fertilized plots and lower N_2O emissions (Table 4) the lowest emissions per unit of stalk produced were still obtained in the unfertilized plots. Similar results were reported by Borges et al. (2019) and by Gonzaga et al. (2018) in studies with sugarcane fertilized with 120 kg N ha^{-1} conducted in the same region.

Our data corroborate others cited above, indicating that in most cases N_2O emissions in sugarcane are lower than 1%. These results will be useful to support future estimates of the Brazilian GHG inventory, currently based on IPPC's default values (IPCC 2013).

Although net cumulative CH_4 emissions were observed in the control and the low fertilizer N treatments in the 2nd and 3rd ratoon cycles, they were small and, in most treatments, the soil was a sink of CH_4 (Table 4S). Except under conditions of poor drainage (Denmead et al. 2010), sugarcane soils act mostly as sinks for this gas (Bento et al. 2018; Borges et al. 2019; Carmo et al. 2013; Lourenço et al. 2019). Therefore, CH_4 has little contribution to the net GHG emissions of sugarcane.

Conclusion

Losses of NH_3 by volatilization and N_2O emissions were higher when UR was surface-applied over sugarcane straw harvest residue, as compared with CAN. However, stalk yields were not affected by the source of N and were little affected by application rates above 60 kg N ha^{-1}. At least from an environmental point of view CAN should be preferred as a source of N for sugarcane grown under conditions similar to those of the present study because N dynamics in soils are site-specific.

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