Nitrous oxide emission from N fertilizer and vinasse in sugarcane

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Abstract
Nitrous oxide (N_2O) emissions from nitrogen fertilizers may strongly affect the sustainability indicators of ethanol produced from sugarcane and there are evidences that the application of vinasse could enhance the emission of GHGs from N fertilizers. The strategy of separating the application of N fertilizer and vinasse in time was tested in three field experiments in Brazil. Vinasse – both regular and concentrated – was applied a) at the same time as the fertilizer, b) anticipated by one month or c) delayed by one month. Intense measurements of N_2O emissions were carried out using static chambers. The N_2O-N fertilizer emission factor (EF) varied from 0.08% to 0.52%, whereas the average EF of regular and concentrated vinasse were 0.68% and 0.33% respectively. Application of concentrated vinasse in the same day of the mineral N fertilization caused high N_2O emissions than when the fertilizer was applied alone; simultaneous application of regular vinasse increased N_2O emission in 2 out of 3 experiments. The strategy of anticipating or postponing the application of both regular and concentrated vinasse by about 30 days with respect to N fertilization in most cases granted lower N_2O emissions.

Key Words
Greenhouse gases, sugarcane residues, emission factor

Introduction
About half of the sugarcane grown in Brazil is directed to ethanol production to replace gasoline in light vehicles. The sustainability of biofuels depends on how much greenhouse gases (GHG) emission they can avoid compared to that of the fossil fuels. Nitrogen fertilizers alone can account for 25% of the energy consumed to produce sugarcane (Boddey et al., 2008) and the nitrous oxide (N_2O) emissions from N fertilizers are responsible for up to 40% of the total GHGs emissions from sugarcane ethanol. High N_2O emissions from N fertilizers can, in some cases, negate the benefits of biofuels replacing fossil fuels (Crutzen et al., 2008). A previous study showed that vinasse – a liquid residue of the ethanol production - applied to sugarcane fields could increase up to threefold the N_2O emissions from N fertilizers (Carmo et al., 2013). Vinasse is generated at a rate of 10 to 13 L/L of ethanol and its application to sugarcane fields is not only a common practice but is desirable in order to recycle nutrients and add organic matter to the soil. Therefore, the knowledge of the interaction between vinasse and N fertilization is important to ascertain how much GHGs are emitted in sugarcane production systems as well as to establish strategies to mitigate such emissions.

Methods
Experimental sites
The study comprised three field experiments in sugarcane ratoons in different seasons in Piracicaba, Brazil (22º41′S; 47º33′W) with the sugarcane variety RB86-7515 harvested without burning, i.e. leaving about 10 t/ha of trash on the soil. The soils were Red Latosols in experiments in the rainy (2013/2014 cycle) and dry seasons (2014/2015 cycle), and Rhodic Nitisol for the experiment in the rainy season, 2014/2015 cycle. The clay content of the soils used varied from 514 to 631 g/kg. The study sites have average annual precipitation around 1390 mm, and annual average temperature near 21°C.

Treatments
The treatments (Table 1) consisted of a combination of time of vinasse and N fertilizer application so that vinasse was applied a) at the same time as the fertilizer, b) anticipated by one month or c) delayed by one month. The purpose was to verify whether the separation in time of both inputs could be a strategy to decrease the GHGs emission. Two types of vinasse were used: regular vinasse (V) containing 3 to 4 g/kg K, or concentrated vinasse (CV) with K content varying from 14 to 23 g/kg K. The experiments followed a

randomized block design with ten treatments and four blocks totaling 40 plots in an area over 3.000 m^2. Each plot was 7.5 x 10 m and contained five rows planted with sugarcane spaced at 1.5 m. The N fertilizer treatments were applied at the rate of 100 kg N/ha as ammonium nitrate. All plots were fertilized with phosphorus and potassium. Regular vinasse was sprayed over the entire experimental plot (i.e., not only in rows) at a rate of 100 m^3/ha, using a motorized pump. Concentrated vinasse was applied in amount equivalent to 17.2 m^3/ha. The mineral fertilizers and concentrated vinasse were surface-applied in a 0.2-m wide band about 0.1 m from the plant row. Fluxes of N_2O were measured using PVC static chambers, 20 cm in height and 30 cm in diameter, according to the method used by Carmo et al. (2013) and Soares et al. (2015). Gases were sampled with plastic syringes (60 mL) at three time intervals (1, 15, and 30 min) after the chambers were closed and were analyzed in a gas chromatograph model GC-2014, Shimadzu Co. Nitrous oxide flux was calculated by linear interpolation of the three sampling times (Carmo et al., 2013).

Results

Nitrous oxide emissions varied with season, as expected, because of climate differences, especially rainfall. Net N_2O emissions from the N fertilizer without vinasse varied from 76 to 118 g N/ha in the three experiments. However, when concentrated vinasse was applied at the same time as ammonium nitrate emissions rose to 928 to 2107 g N/ha, significantly higher than that of N fertilizer alone, even taking into account the N contained in the vinasse. When regular vinasse was used with N fertilizer emissions were also higher than those of treatments with fertilizer alone in two out of three experiments. However, in the rainy season of 2013/14 regular vinasse had low emissions even when vinasse was applied with N in the same day, which is somewhat unexpected given the results of previous studies (Carmo et al., 2013) (Table 2). Anticipating both types of vinasse application caused a decrease in N_2O emissions in the dry season as compared to adding both inputs at the same time. Postponing vinasse application by 27 days also reduced N_2O losses in the rainy season of 2014/15, but more so for the concentrated vinasse (Table 2).

The results of the three field experiments with intense GHGs measurements during almost one year in each allowed the calculation of EF that are relevant for the ethanol industry. The N_2O-N fertilizer EF varied from 0.08% to 0.52% of the N applied as fertilizer (100 kg/ha N). These results are in line with others obtained in recent field experiments in the State of São Paulo (Carmo et al, 2013, Soares et al, 2015), and are lower than the default value of 1% used by the IPCC. It was also possible to calculate the EF for vinasse – both regular and concentrated. The N_2O-N for concentrated vinasse were low, varying from 0.18% to 0.57% (average 0.33%) of the N contained in the vinasse, whereas for regular vinasse the EF values varied from 0.07% to 1.84% (n=6), with an average of 0.66% (Table 2). To our knowledge there is only one study reporting values of EF for concentrated vinasse in the literature (Pitombo et al, 2015). They found EF values for concentrated vinasse higher that in the present study (1.36% to 1.86%) but still, as here, lower than those obtained with regular vinasse.

Table 1. Schedule of application of mineral fertilizer (AN: ammonium nitrate) and vinasse (V: Regular Vinasse and CV: Concentrated Vinasse) in sugarcane ratoons. Experiments implemented in the rainy and dry seasons

Treatments[1]	First and second experiments Rainy season 2013/14 and Dry season 2014/15		Third experiment Rainy season 2014/15	
	13 Nov or 15 Jul	13 Dec or 15 Aug	14 Oct	10 Nov
Control	-	-	-	-
N	-	AN	AN	-
V_b	Regular vinasse	-	-	-
CV_b	Conc. vinasse	-	-	-
V_b+N	Regular vinasse	AN	-	-
CV_b+N	Conc. vinasse	AN	-	-
V	-	Regular vinasse	Regular vinasse	-
CV	-	Conc. vinasse	Conc. vinasse	-
V+N	-	Regular vinasse + AN	Regular vinasse + AN	-
CV+N	-	Conc. Vinasse + AN	Conc. Vinasse + AN	-
V_a	-	-	-	Regular vinasse
CV_a	-	-	-	Conc. vinasse
V_a+N	-	-	AN	Regular vinasse
CV_a+N	-	-	AN	Conc. vinasse

[1]: $_b$ Vinasse application 30 days before N fertilization; $_a$ Vinasse application 27 days after N fertilization.

Table 2. Cumulative nitrous oxide emissions, N fertilizer emission factor (EF) and GWP (CO_2 equivalent) based on rates of N fertilizer applied to sugarcane. (standard error of the mean)

Treatments¶	Rainy season 1, 2013/2014 [1]			Dry season, 2014/2015 [1]			Rainy season 2, 2014/2015 [2]		
	Cumulative N_2O–N emissions		GWP CO_2-eq	Cumulative N_2O–N emissions		GWP CO_2-eq	Cumulative N_2O–N emissions		GWP CO_2-eq
	(g N/ha)	(% of N applied)	(kg CO_2 eq/ha/yr)	(g N/ha)	(% of N applied)	(kg CO_2 eq/ha/yr)	(g N/ha)	(% of N applied)	(kg CO_2 eq/ha/yr)
CV_b	-	-	-	133 ±82	0.44 ±0.27	63 ±39	-	-	-
CV	87 ±28	0.18 ±0.06	41 ±13	297 ±79	0.57 ±0.15	140 ±37	157 ±7	0.34 ±0.02	74 ±3
CV_a	-	-	-	-	-	-	73 ±19	0.21 ±0.05	34 ±9
V_b	35 ±95	0.07 ±0.18	16 ±44	438 ±123	0.87 ±0.24	205 ±58	-	-	-
V	-3 ±62	0.00 ±0.12	-2 ±29	1639 ±391	1.84 ±0.44	768 ±183	583 ±168	0.79 ±0.23	273 ±79
V_a	-	-	-	-	-	-	576 ±213	0.37 ±0.14	270 ±100
N	118 ±18	0.12 ±0.02	55 ±8	516 ±97	0.52 ±0.10	242 ±45	76 ±5	0.08 ±0.00	36 ±2
CV_b+N	-	-	-	741 ±82	0.57 ±0.06	347 ±39	-	-	-
CV+N	2107 ±505	1.42 ±0.34	987 ±237	1225 ±486	0.81 ±0.32	573 ±227	928 ±283	0.64 ±0.19	434 ±133
N+CV_a	-	-	-	-	-	-	364 ±59	0.27 ±0.04	170 ±28
V_b+N	126 ±19	0.08 ±0.01	59 ±9	969 ±131	0.64 ±0.26	454 ±61	-	-	-
V+N	191 ±23	0.13 ±0.02	89 ±11	2202 ±75	1.16 ±0.04	1031 ±35	929 ±73	0.53 ±0.04	435 ±34
N+V_a	-	-	-	-	-	-	772 ±21	0.30 ±0.01	362 ±10

¶ Results from Control treatment (without N and vinasse) were subtracted for these calculations;
[1] Second vinasse application (concentrated or regular vinasse) was 30d before ammonium nitrate in the soil;
[2] Second vinasse application (concentrated or regular vinasse) was 27d after ammonium nitrate in the soil

Table 3 shows the effect of the interaction of vinasse and inorganic fertilizer on N_2O emissions. Concentrated vinasse produced much higher N_2O emissions than those of the mineral fertilizer in the three experiments. The relatively small effect of the regular vinasse to increase the N_2O emission of N fertilizer contrasts with the high stimulus to N_2O emission observed by Carmo et al. (2013). However, in the study of Carmo et al. (2013) very high emissions (EF > 3) were only found over high trash (20 t/ha of dry matter), whereas in the present study the trash cover varied from 9 to 16 t/ha. In the study of Siqueira Neto et al. (2015) vinasse did not increase N_2O emissions when applied with urea. Paredes et al. (2014) also examined the effect of vinasse and fertilizer. The EF for urea was 0.2% but reached 0.6 and 0.7% when urea and vinasse were applied in the same area with a difference of two days. In another recent study in which vinasse, trash, and fertilizers were combined, the EF for ammonium nitrate increased from 0.21% and 1.06% (with and without trash but without vinasse) to 1.34 and 2.41% respectively when 100 m^3/ha of vinasse were added soon after fertilization (Pitombo *et al.*, 2015).

The results obtained in the present study show, however, that anticipating the vinasse application by 30 days with respect to the mineral fertilizer application usually decreased or negated the stimulating effect of vinasse over N_2O emissions from N fertilizer, including that of concentrated vinasse (Table 3). Postponing vinasse application by 27 days after mineral N fertilizer application also decreased N_2O emissions compared to those observed when both amendments were applied in the same day, however, N_2O emissions were still higher than those of the N fertilizer without vinasse (Table 3). It is likely that when vinasse was applied 27 days after N fertilization in the rainy season of 2014/15, part of the N was still in the soil; under these conditions, the easily available C present in the vinasses could stimulate the microbiota responsible for N_2O production.

Table 3. Increments of cumulative N_2O emissions due to the application of vinasse and nitrogen in the same plot (standard error of the mean).

Treatments[¶]	Rainy season 1, 2013/2014[1]	Dry season, 2014/2015[1]	Rainy season 2, 2014/2015[2]
	Cumulative N_2O–N emissions (g N/ha)		
N	118 ± 18	516 ± 97	76 ± 5
CV_b+N	-	608 ± 82	-
CV+N	2020 ± 506	928 ± 486	771 ± 283
N+CV_a	-	-	291 ± 59
V_b+N	91 ± 19	532 ± 131	-
V+N	194 ± 23	562 ± 75	346 ± 73
N+V_a	-	-	196 ± 21

[¶] Results from treatment without N and/or correspondent vinasse (CV_b, CV, CV_a, V_b, V or V_a) were subtracted for this calculation.
[1] Second vinasse application (concentrated or regular vinasse) was 30d before ammonium nitrate in the soil.
[2] Second vinasse application (concentrated or regular vinasse) was 27d after ammonium nitrate in the soil.

Conclusion

The effect of N fertilization and vinasse on N_2O emissions was highly affected by environmental conditions, especially soil moisture (rain). The N_2O-N fertilizer (100 kg N/ha) emission factors (EF) estimated for sugarcane in three field experiments when no vinasse was applied was on average 0.25% of the N applied, well below the 1% used as default by IPCC. Anticipating or postponing vinasse application with respect to N fertilization decreased the fertilizer-associated N_2O emissions as compared to using both inputs in the same day and may be considered a viable strategy to maintain good sustainability indicators of ethanol production.

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