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**Patrick Leal Pinheiro**

**INTERAÇÃO ENTRE REMOÇÃO DE PALHA E ADUBAÇÃO  
NITROGENADA SOBRE A VOLATILIZAÇÃO DE NH<sub>3</sub> E EMISSÃO DE  
N<sub>2</sub>O NA CULTURA DA CANA-DE-AÇÚCAR**

Santa Maria, RS  
2018

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SOBRE A VOLATILIZAÇÃO DE NH<sub>3</sub> E EMISSÃO DE N<sub>2</sub>O NA CULTURA DA  
CANA-DE-AÇÚCAR**

Tese apresentada ao Curso de Doutorado do Programa de Pós-Graduação em Ciência do Solo, da Universidade Federal de Santa Maria (UFSM, RS), como requisito parcial para obtenção do título de **Doutor em Ciência do Solo**

Orientador: Prof. Dr. Sandro José Giacomini

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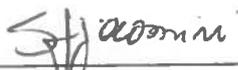
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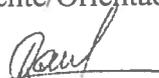
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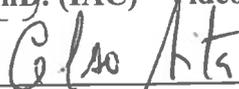
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*“Não acredite em algo simplesmente porque ouviu. Não acredite em algo simplesmente porque todos falam a respeito. Não acredite em algo simplesmente porque está escrito em seus livros religiosos. Não acredite em algo só porque seus professores e mestres dizem que é verdade. Não acredite em tradições só porque foram passadas de geração em geração. Mas depois de muita análise e observação, se você vê que algo concorda com a razão, e que conduz ao bem e benefício de todos, aceite-o e viva-o.”*

*(Buda)*

## RESUMO

### INTERAÇÃO ENTRE REMOÇÃO DE PALHA E ADUBAÇÃO NITROGENADA SOBRE A VOLATILIZAÇÃO DE NH<sub>3</sub> E EMISSÃO DE N<sub>2</sub>O NA CULTURA DA CANA-DE-AÇÚCAR

AUTOR: Patrick Leal Pinheiro  
ORIENTADOR: Sandro José Giacomini

O Brasil possui uma área de 8,74 milhões de hectares cultivada com cana-de-açúcar. Atualmente, cerca de 90% dessa área é colhida mecanicamente sem despalha a fogo, o que resulta em grande quantidade de palha (7 a 25 Mg MS ha<sup>-1</sup>) que permanece sobre o solo após a colheita. A remoção total ou parcial da palha para fins energéticos é uma prática que vem sendo estudada em razão do potencial desta matéria prima na produção de etanol de segunda geração e bioeletricidade. No entanto, pouco se sabe sobre os efeitos desta prática na perda de nitrogênio (N) por volatilização de amônia (NH<sub>3</sub>) após a fertilização nitrogenada e nas emissões de óxido nítrico (N<sub>2</sub>O) do solo. O objetivo do presente trabalho foi avaliar a interação entre diferentes taxas de remoção de palha e adubação nitrogenada sobre a volatilização de NH<sub>3</sub> e a emissão de N<sub>2</sub>O no sistema de cultivo de cana-de-açúcar. Dois estudos foram realizados a campo na Universidade Federal de Santa Maria, com delineamento experimental em blocos ao acaso, em esquema fatorial 4x2, com quatro repetições. O primeiro fator: 0, 4, 8 e 12 Mg ha<sup>-1</sup> de palha (100, 67, 33 e 0% de remoção). O segundo fator: 0 e 100 kg ha<sup>-1</sup> de ureia-N, o que resultou em 8 tratamentos: 0S, 0S+N, 4S, 4S+N, 8S, 8S+N, 12S e 12S+N. A ureia foi aplicada em dose única aos 52 dias em 2016 e 60 dias em 2017 após a colheita da cana-planta. Nos dois anos, durante aproximadamente duas semanas após a aplicação do N-ureia foram realizadas medições de volatilização de NH<sub>3</sub>, N inorgânico do solo, NH<sub>4</sub><sup>+</sup> e N total solúvel em água da palha. No primeiro ano, foram realizadas avaliações da emissão de N<sub>2</sub>O, N inorgânico do solo, conteúdo de água e temperatura do solo e C e N remanescentes na palha desde a adição da palha ao solo até a colheita da cana-soca. A volatilização de NH<sub>3</sub> diferiu entre os dois anos avaliados e a quantidade de N-NH<sub>3</sub> perdida reduziu com o aumento dos níveis de remoção de palha (12S > 8S > 4S > 0S). Isso foi relacionado a diminuição da barreira física da palha que dificulta a infiltração do N-ureia no solo. Essa hipótese foi confirmada pelas dinâmicas do N na camada superficial do solo e na palha, o que sugere maior retenção de N-ureia com aumento das quantidades de palha. Além disso, parte da NH<sub>3</sub> volatilizada ocorre diretamente a partir da palha. Foi observado dois “hot moments” (HM) de emissão de N<sub>2</sub>O do solo, o primeiro após a colheita da cana e o segundo após adubação nitrogenada. No primeiro HM, as emissões de N<sub>2</sub>O foram fortemente relacionadas com o espaço poroso saturado por água (EPSA) e a quantidade de C disponível e no segundo HM, além desses, o NO<sub>3</sub><sup>-</sup> resultante da adição do N-ureia influenciaram as emissões. A remoção da palha reduziu a emissão acumulada de N<sub>2</sub>O nos tratamentos sem N e com N. Efeito semelhante foi observado para o fator de emissão calculado para a palha e para o N-ureia. Diante desses resultados, fica demonstrado que o aumento na taxa de remoção da palha na superfície do solo diminui significativamente a volatilização de NH<sub>3</sub> e as emissões de N<sub>2</sub>O. Entretanto, a remoção indiscriminada de palha não é uma prática recomendada sendo necessário estudos em diferentes aspectos ambientais e agronômicos para definir a quantidade ideal de palha a ser removida.

**Palavras-chave:** resíduo cultural, gases do efeito estufa, perdas de nitrogênio, bioenergia

## ABSTRACT

### INTERACTIONS BETWEEN STRAW REMOVAL AND N FERTILIZATION ON NH<sub>3</sub> VOLATILIZATION AND N<sub>2</sub>O EMISSION IN SUGARCANE CROPPING SYSTEM

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Brazil has an area of 8.74 million hectares cultivated with sugarcane. Currently, 90% of this area is mechanically harvested without fire which results in large amounts of straw (7 to 25 Mg DM ha<sup>-1</sup>) remaining on the soil surface after harvest. The total or partial removal of the straw is a practice that has been studied due to the potential of straw as a raw material in the production of second generation ethanol and bioelectricity. However, little is known about the effects of this practice on nitrogen (N) loss by ammonia (NH<sub>3</sub>) volatilization after N fertilization and nitrous oxide (N<sub>2</sub>O) emissions from soil. The objective of the present work was to evaluate the interaction between different rates of straw removal and N fertilization on NH<sub>3</sub> volatilization and N<sub>2</sub>O emission in the sugarcane cropping system. Two field experiments were carried out at the Federal University of Santa Maria, with a randomized block design, in a 4x2 factorial scheme, with four replications. The first factor: 0, 4, 8 and 12 Mg ha<sup>-1</sup> of straw (100, 67, 33 and 0% removal). The second factor: 0 and 100 kg ha<sup>-1</sup> of urea-N, which resulted in 8 treatments: 0S, 0S + N, 4S, 4S + N, 8S, 8S + N, 12S and 12S + N. Urea was applied in a single dose at 52 days in 2016 and 60 days in 2017 after cane harvest. In two years, during approximately two weeks after urea-N application were performed measurements of NH<sub>3</sub> volatilization, soil inorganic N, water-soluble NH<sub>4</sub><sup>+</sup> and total N of straw. In the first year, were performed measurements of N<sub>2</sub>O emission, soil inorganic N, moisture and temperature, and remaining straw C and N from the addition of the straw to the soil until the cane harvest. NH<sub>3</sub> volatilization were different according to rain pattern of each year and NH<sub>3</sub>-N losses reduced with increased straw removal levels (12S > 8S > 4S > 0S). This was related to the decrease of straw physical barrier that hinders urea-N infiltration in the soil. This hypothesis was confirmed by N dynamics in the top-soil and straw which suggested a higher retention of urea-N with increasing amounts of straw. In addition, part of NH<sub>3</sub> volatilization occurs directly from the straw. Two “hot moments” (HM) for N<sub>2</sub>O emission were observed, the first one after the cane harvest and the second after nitrogen fertilization. In the first HM, N<sub>2</sub>O emissions were strongly related to the water-filled pore space (WFPS) and the amount of C availability and in the second HM, besides that, the NO<sub>3</sub><sup>-</sup> resulted from urea-N application influenced the emissions. Straw removal reduced cumulative N<sub>2</sub>O emissions in treatments with and without N. A similar effect was observed for the calculated emission factor for straw and urea-N. These results demonstrate that increase straw removal rate significantly reduce NH<sub>3</sub> volatilization and N<sub>2</sub>O emission. However, indiscriminate straw removal is not a recommended practice and it is necessary to study different environmental and agronomic aspects to define the ideal quantity of straw to be removed.

**Keywords:** crop residues, greenhouse gas, nitrogen loss, bioenergy

## LISTA DE FIGURAS

### ARTIGO I

**Figure 1.** Wind speed, air temperature and rainfall (a), soil water content (b) and  $\text{NH}_3\text{-N}$  losses (c) in the first ratoon cane (2016) after 100 kg urea-N  $\text{ha}^{-1}$  (N) application over the different straw (S) quantities (0, 4, 8 and 12 Mg  $\text{ha}^{-1}$ ). The vertical bars represent the least significant difference (LSD) between the treatments ( $P < 0.05$ ) ..... 37

**Figure 2.** Wind speed, air temperature and rainfall (a), soil water content (b) and  $\text{NH}_3\text{-N}$  losses (c) in the first ratoon cane (2017) after 100 kg urea-N  $\text{ha}^{-1}$  (N) application over the different straw (S) quantities (0, 4, 8 and 12 Mg  $\text{ha}^{-1}$ ). The vertical bars represent the least significant difference (LSD) between the treatments ( $P < 0.05$ ) ..... 38

**Figure 3.** Net cumulative  $\text{NH}_3\text{-N}$  losses in the first ratoon sugarcane (2016 and 2017) after 100 kg urea-N  $\text{ha}^{-1}$  (N) application over the different straw (S) quantities (0, 4, 8 e 12 Mg  $\text{ha}^{-1}$ ). The vertical bar represents the least significant difference (LSD) between the treatments ( $P < 0.05$ ). ..... 39

**Figure 4.** Relationship between straw quantities (0, 4, 8 e 12 Mg  $\text{ha}^{-1}$ ) and  $\text{NH}_3\text{-N}$  losses in the first ratoon sugarcane (2016 and 2017) after 100 kg urea-N  $\text{ha}^{-1}$  (N) application. Vertical error bars indicate the standard mean deviation. \*significant difference with t test ( $P < 0.05$ ). ..... 40

### ARTIGO II

**Figure 1.** Mean daily air temperature and rainfall (a), WFPS in 0-5 cm soil layer (b), WFPS in 5-10 cm soil layer (c), temperature on soil surface (d), soil temperature in 0-5 cm soil layer (e) and soil temperature in 5-10 cm soil layer (f) in first sugarcane ratoon..... 67

**Figure 2.** Dynamics of straw-C (a) straw-N (b) on soil from harvest of sugarcane and during one year, with different initial amounts of straw added as mulch on soil, 4 (4S), 8 (8S) and 12 Mg DM  $\text{ha}^{-1}$  (12S). Fertilizer-N (urea) was applied on day 52. Vertical bar represents standard deviation. The data are the mean between treatments with and without fertilizer N and of four replicates per treatment and per date of sampling ..... 68

**Figure 3.** Soil  $\text{NH}_4^+$  (a) and  $\text{NO}_3^-$  (b) in the 0-10-m soil layer after 100 kg urea-N  $\text{ha}^{-1}$  (N) application over the different straw (S) rates (0, 4, 8 and 12  $\text{Mg ha}^{-1}$ ) in the first ratoon cane ..... 69

**Figure 4.**  $\text{N}_2\text{O}$ -N flux (b) and  $\text{CO}_2$ -C flux (c) in the first ratoon sugarcane, with or without application of 100 kg urea-N  $\text{ha}^{-1}$  (+N) over the different straw (S) rates (0, 4, 8 e 12  $\text{Mg ha}^{-1}$ ) at day 52. Vertical bar represents the least significant difference (LSD) between treatments ( $P < 0.05$ )..... 70

**Figure 5.** Cumulative  $\text{N}_2\text{O}$  emission during the first ratoon sugarcane (365 days) after application of different straw (S) amounts (0, 4, 8 and 12  $\text{Mg ha}^{-1}$ ) with and without 100 kg urea-N  $\text{ha}^{-1}$  (+N). Vertical bar represents the least significant difference (LSD) between treatments ( $P < 0.05$ ) ..... 71

**Figure 6.** Principal component analysis (PCA) of 0-65-day period in treatments without urea-N application (a) and 52-120-day period in treatments with urea-N application (b) for  $\text{N}_2\text{O}$  fluxes from soil and soil-straw variables: nitrate –  $\text{NO}_3^-$ , ammonium –  $\text{NH}_4^+$ , water-filled pore space – WFPS, soil  $\text{CO}_2$  fluxes, soil temperature –  $^{\circ}\text{C}$  and straw-C content in the first ratoon sugarcane, with or without application of 100 kg urea-N  $\text{ha}^{-1}$  over the different straw (S) rates (0, 4, 8 and 12  $\text{Mg ha}^{-1}$ ) ..... 72

## LISTA DE TABELAS

### ARTIGO I

**Table 1.** A three-way ANOVA for the effects of straw level (S), nitrogen fertilizer (N) and year (Y) on cumulative NH<sub>3</sub> losses ..... 34

**Table 2.** Soil ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) in the 0.10-m soil layer after 100 kg urea-N ha<sup>-1</sup> (N) application over the different straw (S) quantities (0, 4, 8 e 12 Mg ha<sup>-1</sup>) in the first ratoon cane (2016 and 2017) ..... 35

**Table 3.** Straw ammonium (NH<sub>4</sub><sup>+</sup>), water-soluble total N concentration in straw and straw moisture after 100 kg urea-N ha<sup>-1</sup> (N) application for different straw (S) quantities (4, 8 and 12 Mg ha<sup>-1</sup>) in the first ratoon cane (2017)..... 36

**Table S1.** Soil ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) in the 0.10-cm soil layer over the different straw (S) quantities (0, 4, 8, and 12 Mg ha<sup>-1</sup>) without N applied (0S, 4S, 8S, and 12S treatments) in the first ratoon cane (2016 and 2017)..... 41

**Table S2.** Straw ammonium (NH<sub>4</sub><sup>+</sup>) and water-soluble total N concentration in straw for different straw (S) quantities (4, 8 and 12 Mg ha<sup>-1</sup>) with no fertilizer in the first ratoon cane (2017) (4S, 8S and 12S treatments)..... 42

**Table S3.** Straw ammonium (NH<sub>4</sub><sup>+</sup>) and water-soluble total N concentration in straw after 100 kg urea-N ha<sup>-1</sup> (N) application for different straw (S) quantities (4, 8 and 12 Mg ha<sup>-1</sup>) in the first ratoon cane (2017)..... 43

### ARTIGO II

**Table 1.** Cumulative N<sub>2</sub>O-N emission in the first ratoon sugarcane with and without urea-N for the different straw (S) rates (0, 4, 8 and 12 Mg ha<sup>-1</sup>) and emission factor. Emission factor was calculated as a function of total straw N added (a) and straw N released during decomposition (b) ..... 66

## SUMÁRIO

1	<b>INTRODUÇÃO GERAL</b> .....	12
2	<b>HIPÓTESE E OBJETIVOS</b> .....	15
2.1	HIPÓTESE.....	15
2.2	OBJETIVO GERAL.....	15
2.3	OBJETIVOS ESPECÍFICOS.....	15
2.3.1	Volatilização de NH <sub>3</sub> :.....	15
2.3.2	Emissão de N <sub>2</sub> O:.....	15
3	<b>ARTIGO I - STRAW REMOVAL REDUCES THE MULCH PHYSICAL BARRIER AND AMMONIA VOLATILIZATION AFTER UREA APPLICATION IN SUGARCANE</b> .....	16
3.1	<b>Abstract</b> .....	16
3.2	<b>Introduction</b> .....	16
3.3	<b>Materials and Methods</b> .....	18
3.3.1	Experimental site.....	18
3.3.2	Treatments and experimental design.....	19
3.3.3	Ammonia volatilization measurement.....	20
3.3.4	Collection and analysis of soil and straw samples.....	20
3.3.5	Calculations and statistical analysis.....	21
3.4	<b>Results</b> .....	22
3.4.1	Climatic and soil environmental conditions.....	22
3.4.2	Dynamics of inorganic N in the 0-10-cm soil layer.....	22
3.4.3	NH <sub>4</sub> <sup>+</sup> -N and water-soluble total N in straw.....	23
3.4.4	Ammonia volatilization.....	23
3.5	<b>Discussion</b> .....	24
3.5.1	Effect of the amount of straw on NH <sub>3</sub> volatilization.....	25
3.5.2	Interannual variations in volatilization.....	26
3.6	<b>Conclusions</b> .....	27
3.7	<b>References</b> .....	28
4	<b>ARTIGO II - MULCH AND NITROGEN FERTILIZER CONTRIBUTION TO N<sub>2</sub>O EMISSIONS IN A SUGARCANE CROP WITH INCREASING RATE OF STRAW REMOVAL</b> .....	44
4.1	<b>Abstract</b> .....	44
4.2	<b>Introduction</b> .....	45
4.3	<b>Materials and Methods</b> .....	46

4.3.1	Experimental site .....	46
4.3.2	Treatments and experimental design .....	46
4.3.3	Straw C and N measurement .....	47
4.3.4	N <sub>2</sub> O and CO <sub>2</sub> measurement and analyses .....	48
4.3.5	Soil measurements .....	48
4.3.6	Calculation and statistical analysis .....	49
4.4	<b>Results</b> .....	50
4.4.1	Soil environmental conditions and WFPS .....	50
4.4.2	Dynamics of straw-C and N .....	50
4.4.3	Soil mineral N .....	51
4.4.4	Soil N <sub>2</sub> O and CO <sub>2</sub> emissions .....	51
4.4.5	Drivers of N <sub>2</sub> O emissions .....	52
4.4.6	Cumulative N <sub>2</sub> O emission and Emission factor (EF) .....	53
4.5	<b>Discussion</b> .....	53
4.5.1	Effects of straw on N <sub>2</sub> O emissions .....	53
4.5.2	N <sub>2</sub> O emissions from fertilizer and interaction with straw .....	55
4.5.3	Emission factors for fertilizer N and straw N .....	56
4.5.4	Consequences for crop residue management in sugarcane areas .....	57
4.6	<b>Conclusion</b> .....	58
4.7	<b>References</b> .....	58
5	<b>DISCUSSÃO GERAL</b> .....	73
6	<b>CONCLUSÕES GERAIS</b> .....	76
7	<b>REFERÊNCIAS BIBLIOGRÁFICAS</b> .....	77

## 1 INTRODUÇÃO GERAL

O Brasil é o maior produtor mundial de cana-de-açúcar com uma produção de 635.6 milhões de toneladas em 8.7 milhões de hectares na safra 2017 (CONAB, 2017), podendo a área de cultivo atingir 11,5 milhões de hectares até 2024 (OECD/FAO, 2015; OTTO et al., 2016). Tradicionalmente a colheita da cana-de-açúcar era realizada com a queima prévia do canavial, entretanto, restrições legais (SÃO PAULO, 2003) que visam atender demandas sociais e ambientais tem resultado na mudança para a colheita mecanizada sem despalha a fogo. Atualmente, cerca de 90,2% das áreas de cana-de-açúcar no Brasil são colhidas mecanicamente (CONAB, 2017) o que resulta em grandes quantidades de resíduo cultural (ponteiras, folhas e fragmentos de colmos) depositados na superfície do solo, variando de 7 a 25 Mg MS ha<sup>-1</sup> (LEAL et al., 2013). O resíduo depositado na superfície do solo promove o controle da erosão (VALIM et al., 2016), manutenção da umidade (NG CHEONG; TEELUCK, 2016), ciclagem de nutrientes (TRIVELIN et al., 2013) e a longo prazo aumenta os estoques de C no solo (CERRI et al., 2011). Apesar disso, a permanência de grandes quantidades de palha na lavoura tem provocado redução na taxa de brotação (DE CAMPOS et al., 2010), aumento no aparecimento de pragas (DINARDO-MIRANDA; FRACASSO, 2013) e modificação no manejo da adubação em soqueiras (VITTI et al., 2008).

Desde a “revolução verde”, o manejo da adubação é uma das práticas agrícolas mais importantes que eleva o rendimento das culturas e a fertilidade do solo. O nitrogênio (N) é o fertilizante mais aplicado nas áreas agrícolas o que representa um consumo mundial de 107,6 Tg N ano<sup>-1</sup> (LU; TIAN, 2017), sendo a ureia a fonte de N mais utilizada devido a sua melhor relação custo-benefício (FAO, 2018). O N possui diferentes vias de perda para a atmosfera, sendo as com maior impacto negativo para o meio ambiente, a volatilização de amônia (NH<sub>3</sub>) e a emissão de óxido nitroso (N<sub>2</sub>O) (IPCC, 2014). A volatilização de NH<sub>3</sub> é a primeira e principal forma de perda de N do solo que pode ocorrer após a aplicação de ureia e fertilizantes a base de ureia (DATTAMUDI et al., 2016; XU et al., 2012; CANTARELLA et al., 2008), representa globalmente uma perda de 10,76 Tg N ano<sup>-1</sup> (IPCC, 2014) e pode provocar impactos indiretos ao meio ambiente, como acidificação da atmosfera e emissão de N<sub>2</sub>O (BEHERA et al., 2013). Além disso, as áreas agrícolas são a principal fonte de N<sub>2</sub>O para a atmosfera, cujas emissões aumentaram 73% entre 1970 e 2010 (IPCC, 2014), como resposta ao uso de fertilizantes sintéticos e adição de resíduos orgânicos (BUTTERBACH-BAHL et al., 2013; SMEETS et al., 2009). O N<sub>2</sub>O é um importante gás do efeito estufa (GEE) com uma meia-vida

de 131 anos (HARTMANN et al., 2014), um potencial de aquecimento global (PAG) 265 vezes maior que o CO<sub>2</sub> (IPCC, 2014) e participa diretamente da depleção do ozônio estratosférico (RAVISHANKARA; DANIEL; PORTMANN, 2009).

A ureia é o fertilizante nitrogenado mais utilizado na cultura da cana-de-açúcar (MEGDA et al., 2012; RECH; POLIDORO; PAVINATO, 2017). A dificuldade e o elevado custo para a aplicação da ureia incorporada em cana soca devido à grande quantidade de palha que permanece sobre o solo após a colheita mecanizada tem provocado a aplicação do fertilizante nitrogenado em faixas ou em área total sobre a palha (VITTI et al., 2007). Nesse sistema, observa-se altas perdas de N por volatilização de NH<sub>3</sub> que podem atingir valores que variam de 10 a 50% do ureia-N aplicado sobre a palha (CANTARELLA et al., 2008; NASCIMENTO et al., 2013; OTTO et al., 2017; SOARES; CANTARELLA; MENEGALE, 2012). O aumento das perdas de N-NH<sub>3</sub> com a aplicação da ureia na superfície da palha pode estar relacionado a combinação de três fatores principais: i) a alta atividade da enzima urease promovida pela camada de palha (FRENEY et al., 1992); ii) a camada de palha na superfície do solo forma uma barreira física que reduz a transferência da ureia para o solo (VITTI et al., 2007); e iii) retenção de água pela palha e a manutenção da umidade no solo (ROCHETTE et al., 2009).

Além de facilitar as perdas de N-NH<sub>3</sub>, a presença dos resíduos culturais de cana-de-açúcar sobre o solo pode influenciar os dois principais processos responsáveis pelas emissões de N<sub>2</sub>O do solo, i.e., nitrificação e desnitrificação. Os resíduos culturais deixados na superfície do solo após a colheita mecanizada são uma fonte prontamente disponível de C e N, alteram a atividade microbiana e a mineralização-imobilização durante a decomposição e modificam a aeração, umidade e temperatura do solo (STAVI; BEL; ZAADY, 2016). Entretanto, as diferentes formas (e às vezes antagônicas) que os resíduos culturais podem influenciar a emissão de N<sub>2</sub>O do solo refletem em incertezas sobre seu impacto nas emissões de N<sub>2</sub>O na cultura da cana-de-açúcar (SIQUEIRA NETO et al., 2016; VASCONCELOS et al., 2018), sobretudo após a aplicação de fertilizantes nitrogenados (CARMO et al., 2013; PITOMBO et al., 2017).

Nos últimos anos, aumentou o potencial no uso de resíduos culturais para a produção de bioenergia aumentou e grandes investimentos têm sido realizados nessa área a fim de desenvolver tecnologias capazes de utilizar os resíduos culturais como matéria prima para este fim (GRAHAM-ROWE, 2011). Devido a isso, a remoção da palha de cana-de-açúcar no Brasil para fins energéticos é uma realidade e poderá ser intensificada nos próximos anos (FRANCO

et al., 2013). Entretanto, os resíduos culturais possuem papel fundamental na sustentabilidade do solo e a remoção indiscriminada pode gerar impactos agronômicos e ambientais indesejados, particularmente no cultivo da cana-de-açúcar (CARVALHO et al., 2017; CHERUBIN et al., 2018). Portanto, a remoção parcial da palha da lavoura para uso na geração de energia através da queima ou da produção de etanol de segunda geração (SANTOS et al., 2012; SORDI; MANECHINI, 2013) apresenta-se como uma alternativa viável. Essa situação levanta a importante questão dos “trade-offs” entre reciclagem e remoção da palha da superfície do solo, evidenciando a necessidade de pesquisas para quantificar as consequências agronômicas e ambientais no manejo de resíduos culturais para a produção de bioenergia.

Neste contexto, as incertezas sobre a interação entre os resíduos culturais de cana-de-açúcar e fertilizantes sintéticos nitrogenados e seus efeitos na volatilização do  $\text{NH}_3$  e emissões de  $\text{N}_2\text{O}$  aumentam ainda mais a necessidade de entender como a quantidade de resíduos deixados no solo, ou, a quantidade removida do campo afeta a volatilização de  $\text{NH}_3$  e as emissões de  $\text{N}_2\text{O}$ .

## 2 HIPÓTESE E OBJETIVOS

### 2.1 HIPÓTESE

A remoção parcial da palha de cana-de-açúcar após a colheita mecanizada reduz as perdas de N-ureia devido a redução das condições favoráveis para o processo de volatilização de  $\text{NH}_3$  e dos mecanismos que afetam os processos de nitrificação e desnitrificação do solo, responsáveis pela emissão de óxido nitroso ( $\text{N}_2\text{O}$ ).

### 2.2 OBJETIVO GERAL

Avaliar a interação entre diferentes níveis de remoção de palha e adubação nitrogenada nas perdas de N por volatilização de  $\text{NH}_3$  e a emissão de  $\text{N}_2\text{O}$  na cultura da cana-de-açúcar.

### 2.3 OBJETIVOS ESPECÍFICOS

#### 2.3.1 Volatilização de $\text{NH}_3$ :

- a) Avaliar que a barreira física formada pela palha dificulta a chegada até o solo do fertilizante nitrogenado aplicado sobre a palha;
- b) Avaliar como diferentes níveis de remoção de palha de cana-de-açúcar alteram a umidade do solo e a concentração de amônio ( $\text{NH}_4^+$ ) na camada superior do solo;
- c) Quantificar as perdas de  $\text{NH}_3$  após a aplicação de N-ureia sob diferentes níveis de remoção de palha.

#### 2.3.2 Emissão de $\text{N}_2\text{O}$ :

- a) Avaliar como diferentes níveis de palha de cana-de-açúcar afetam os mecanismos relacionados a produção de  $\text{N}_2\text{O}$  (conteúdo de água, temperatura do solo e disponibilidade de C e N);
- b) Quantificar as emissões de  $\text{N}_2\text{O}$  sob diferentes níveis de remoção de palha com e sem o uso de fertilizante nitrogenado.

### **3 ARTIGO I - STRAW REMOVAL REDUCES THE MULCH PHYSICAL BARRIER AND AMMONIA VOLATILIZATION AFTER UREA APPLICATION IN SUGARCANE<sup>1</sup>**

#### **3.1 ABSTRACT**

Crop residues left as mulch on the soil surface generally increase the risk of ammonia (NH<sub>3</sub>) volatilization from fertilizer-N, but the roles of mulch as a physical barrier and as a biological support of N transformation are not well known, particularly in response to straw removal. Thus, our goal was to assess how NH<sub>3</sub> volatilization from urea-N was affected by different amounts of residues left on the soil surface after harvest in the sugarcane crop by mimicking different rates of straw removal. We ran a replicated field experiment during two consecutive years in the first ratoon sugarcane with 4 amounts of straw (0, 4, 8 and 12 Mg dry matter ha<sup>-1</sup>) and with 0 or 100 kg urea-N ha<sup>-1</sup>. Over approximately 2 weeks, we measured the NH<sub>3</sub> emissions, levels of inorganic N in soil and water-soluble total N and NH<sub>4</sub><sup>+</sup> of straw. The dynamics of N in the soil and in straw supported the hypothesis that mulch acts as a physical barrier to the incorporation of urea in soil but also that NH<sub>3</sub> emissions occurred directly from the mulch. The NH<sub>3</sub> losses were different according to rain pattern of each year, but we showed that the emissions of NH<sub>3</sub> were higher with higher amounts of straw (12 > 8 > 4 > 0) for both years (9.2 to 27.6% in 2016 and 30.7 to 60.8% in 2017). These results suggest that straw removal contributes to a reduction in NH<sub>3</sub>-N losses, but since total straw removal is not a recommended practice, N fertilization strategies should be implemented in systems with residue mulches on the soil surface to prevent N loss and to improve the environmental footprint of these cropping systems.

Keywords: NH<sub>3</sub> volatilization; crop residue, mulch, N losses, straw removal

#### **3.2 INTRODUCTION**

Ammonia (NH<sub>3</sub>) volatilization poses the highest potential for loss among several pathways of N loss from synthetic N fertilizers in agricultural systems (IPCC, 2014). The IPCC estimates that 10% of the fertilizer-N applied in soil is lost by NH<sub>3</sub> volatilization (IPCC, 2014), which globally represents 10.76 Tg N y<sup>-1</sup>. However, NH<sub>3</sub> losses in agricultural lands range from 0 to

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<sup>1</sup> Artigo elaborado de acordo com as normas da Atmospheric Environment.

64% of N applied depending on the differences in sources, rates, places and times of fertilizers-N application (Pan et al., 2016). Thus, NH<sub>3</sub> volatilization in agricultural areas is a global issue that still must be solved, not only because volatilization represents a loss on investment in fertilizers (mineral or organic) for the farmer but also because of the direct and indirect environmental impacts (e.g., atmospheric acidification and N<sub>2</sub>O emission) associated with these emissions (Behera et al., 2013).

The maintenance of crop residues on the soil surface after crops are harvested, as in no-till agriculture, is a very important principle for sustainable soil management. The soil cover promotes soil erosion control (Valim et al., 2016), the maintenance of soil moisture (Ng Cheong and Teeluck, 2016), nutrient cycling (Trivelin et al., 2013), and, in the long term, increased soil C stocks (Cerri et al., 2011). The presence of mulch also modifies fertilizer-N management because the fertilizer is applied on crop residues instead of directly on the soil. It has been shown that the application of fertilizer-N on crop residue surfaces may affect the fate of N in mulch-cover systems. In a sugarcane field with mechanized harvesting, which is common in major sugarcane-producing areas of the world, the amount of straw (tops, leaves and stalks) remaining on the soil surface may be high, ranging from 7 to 25 Mg DM (Leal et al., 2013). In this sugarcane system, Cantarella et al. (2008) found that NH<sub>3</sub>-N losses represent approximately 25% of urea-N applied on the straw surface under the tropical conditions of southeast Brazil. Under similar conditions, Mira et al. (2017) found that NH<sub>3</sub>-N losses may reach 30% of urea-N applied. However, there are conflicting results that show reduced volatilization in the presence of residues at the soil surface (Su et al., 2014) or no difference between the presence of residues on the soil surface and bare soil (Da Ros et al., 2005). In a meta-analysis based on 43 studies in different cropping systems worldwide, Pan et al. (2016) observed that residue retention on the soil significantly increased NH<sub>3</sub> volatilization by an average of 25.5%. In a given situation, the intensity of NH<sub>3</sub> volatilization is strongly related to the ammonium (NH<sub>4</sub><sup>+</sup>) concentration, which is itself under the control of N transfer, diffusion, biological transformation, and temperature (Sommer et al., 2004). Thus, mulch has a complex - and sometimes antagonistic - effect on these parameters, both directly as a physical barrier, as suggested by Vitti et al. (2007) and Su et al. (2014), and indirectly by modifying physical conditions (temperature and moisture) at the soil-mulch interface (Rochette et al., 2009; Pinheiro et al., submitted).

In the last two decades, the use of crop residues for producing bioenergy by industry has become a reality worldwide (Graham-Rowe, 2011), and the situation is similar for Brazil

(Franco et al., 2013). This situation reinforces the need to quantify the impacts of mulch on soil surfaces, particularly environmental impacts, in order to (i) establish at a broad scale a global assessment of the substitution of fossil resources by plant-derived carbon (Cadoux et al., 2014) and (ii) manage at the scale of the cropping system the necessary trade-offs between different uses of crop residues. In this context, the uncertainties about the interaction between mulch derived from crop residues and synthetic fertilizers on  $\text{NH}_3$  volatilization raises the question about the mechanisms involved. Knowledge about this issue would help understand how different amounts of residues left on the soil surface by harvest affect these losses. To the best of our knowledge, this question has not been studied so far.

To address this issue, our objective was to assess how urea-N application on different amounts of sugarcane straw affects  $\text{NH}_3$  volatilization. This assessment was achieved using a replicated field experiment conducted during two consecutive years in a sugarcane cropping system under subtropical conditions. We investigated specifically how sugarcane mulch acted as a physical barrier between applied urea and soil and how it influenced both soil moisture and the dynamics of  $\text{NH}_4^+$  concentration in the top soil layer.

### 3.3 MATERIALS AND METHODS

#### 3.3.1 Experimental site

The field experiment was conducted at Federal University of Santa Maria (29°42'54" S, 53°42'23" W, 90 m above sea level) Rio Grande do Sul state, Brazil. The local climate according to the Köppen classification is a subtropical humid climate type Cfa (Alvares et al., 2013). The mean annual temperature is 19.3°C, with June being the coldest month with a mean minimum temperature of 9.3°C and January the warmest month with a mean maximum temperature of 30.4°C. The mean annual precipitation is 1660 mm, without a dry season. The soil is classified as a Typic Paleudalf (Soil Survey Staff, 2010), with 110 g kg<sup>-1</sup> clay, 630 g kg<sup>-1</sup> sand and a soil bulk density of 1.63 g dm<sup>-3</sup> in the 0-20-cm layer. Soil chemical properties at the beginning of the experiment were as follows: pH (water) = 5.4; CEC = 2.5 cmol<sub>c</sub> dm<sup>-3</sup>, Mehlich-I P = 33.4 mg dm<sup>-3</sup>, K = 40.0 mg dm<sup>-3</sup>, total C = 4.1 g kg<sup>-1</sup> and total N = 0.32 g kg<sup>-1</sup>. The climatic variables, i.e., wind speed, average air temperature and daily precipitation, were obtained from an automatic meteorological station located 1.6 km from the experimental site.

### 3.3.2 Treatments and experimental design

#### 3.3.2.1 Main experimental design

A replicated field experiment was conducted in January 2016 and in February 2017 in adjacent areas cultivated with sugarcane (RB95-6911) in the first-ratoon sugarcane. The two cycles of first-ratoon sugarcane began after cane plant harvest held on November 20, 2015, and November 22, 2016, for the two years. At that time, sugarcane was manually harvested, removing all aboveground biomass (stalks, tops and leaves). In both years, an area was demarcated with 32 plots of 22.4 m<sup>2</sup>, consisting of 4 lines with 1.4 m of spacing between rows and 4 m of length. Inside these plots, three microplots of 0.16 m<sup>2</sup> (0.4 x 0.4 m) were delimited and used for NH<sub>3</sub> volatilization chambers.

The experimental design was identical for the two years, laid out as a randomized block design with two factors and four replicates. The first factor was straw amount, with four straw quantities: 0 (0S), 4 (4S), 8 (8S) and 12 (12S) Mg of dry matter (DM) ha<sup>-1</sup>; the second factor was fertilizer N, with two doses of urea-N: 0 and 100 kg N ha<sup>-1</sup>. This arrangement resulted into 8 different treatments: 0S, 0S+N, 4S, 4S+N, 8S, 8S+N, 12S and 12S+N. The straw used in the study came from a mechanically harvested sugarcane crop at the Grandespe company in Salto do Jacuí, Rio Grande do Sul, Brazil (28° 59'S, 53° 14' W, 345 m above sea level). After harvest, straw was air-dried for 20 days and then distributed on the soil surface in the plots and microplots at rates equivalent to 4, 8 and 12 Mg DM ha<sup>-1</sup>, plus a treatment without straw.

Urea-N was applied on sugarcane plots and microplots as solid granules in a single dose on the soil (and mulch) surface at day 52 (2016) and day 60 (2017) after cane harvest following the straw application. At the time of urea application, the remaining amount of straw on the soil surface was 2.5, 4.9 and 7.1 Mg DM ha<sup>-1</sup> in 2016 and 2.7, 5.2, 7.1 Mg DM ha<sup>-1</sup> in 2017, for the 4S, 8S and 12S treatments, respectively. The average thickness of straw mulch was 0.87 cm (4S), 2.24 cm (8S) and 3.02 cm (12S).

#### 3.3.2.2 Additional experiment

To investigate the concentration of N in sugarcane straw shortly after urea-N application, five PVC rings with 0.2 m diameter and 0.05 m height were installed in the 2017 experiment at the soil surface. Sugarcane straw was laid out in the PVC rings at same dates and quantities as those

in the main experiment. Half of the rings received urea at a rate equivalent to  $100 \text{ kg N ha}^{-1}$ , while the other half received no N, resulting in 8 treatments as those in the main experiment.

### 3.3.3 Ammonia volatilization measurement

Ammonia ( $\text{NH}_3$ ) volatilization was measured during 16 days in 2016 (from January 15<sup>th</sup> to January 28<sup>th</sup>) and 14 days in 2017 (from February 21<sup>th</sup> to March 06<sup>th</sup>), immediately after urea-N application. A semi-open static chamber collector adapted from Jantalia et al. (2012) was used to quantify ammonia ( $\text{NH}_3$ ) volatilization. Briefly, the chambers consisted of transparent polyethylene terephthalate (PET) bottles with a capacity of 3 L and a base diameter of 0.114 m (area of  $0.0103 \text{ m}^2$ ). The  $\text{NH}_3$  absorber system remained inside the PET chamber and consisted of a polyurethane foam ( $0.017 \text{ g cm}^{-3}$ ), 0.5 cm thick, 2.5 cm wide and 25 cm length, vertically suspended inside the chamber. The foam absorbers were suspended inside the chamber with a 25-cm-long wire designed with a hook to support it from the top of the chamber and a wire basket on the bottom end to support a plastic jar (80 mL). Jantalia et al. (2012) provides more details about the apparatus used to collect volatilized  $\text{NH}_3$ . At each evaluation, the foam absorbers were soaked in 50 mL of  $\text{H}_2\text{SO}_4$  ( $1 \text{ mol dm}^{-3}$ ) + glycerol (4% v / v) acid solution. Plastic jars of 80 mL were used to carry the acid-immersed foam from the laboratory to the field and vice versa. Immediately after each sampling, a new foam and plastic jar were installed in the chamber. In 2016, foams were changed 14 times while 12 exchanges were performed in 2017. After each foam exchange, the chamber was installed in another microplot to minimize the chamber effect on the  $\text{NH}_3$  volatilization measurements. The chamber exchange among microplots was also performed after rainfall events, but with no foam changes. At the laboratory, the foams and acid solution excess were transferred to snap-caps glass flasks containing 20 mL of distilled water. The snap-cap flask was shaken for 30 minutes to extract the ammonium sulfate [ $(\text{NH}_4)_2\text{SO}_4$ ] formed in the foam by the reaction between sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and the captured ammonia ( $\text{NH}_3$ ). The  $\text{NH}_3$ -N content was determined by distilling 20 mL of the solution present in the snap-cap after the addition of 10 mL of 5 M NaOH followed by titration with  $\text{H}_2\text{SO}_4$  (Keeney and Nelson, 1982).

### 3.3.4 Collection and analysis of soil and straw samples

Soil samples were collected from the surface layer (0–10 cm) at days 3, 8, 14 and 19 (2016) and days 1, 2, 7, 13 and 15 (2017) after N application. The composite soil samples consisted of six randomly distributed sampling points collected using a stainless-steel auger (3 cm diameter).

Inorganic N ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) was extracted by shaking 20 g of field-moist soil in 80 mL of 1 M KCl solution for 30 minutes. After decantation for 30 minutes, the supernatant of the solution was filtered and kept frozen until analysis.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were quantified by distillation with sequential addition of MgO and Devarda's alloy, respectively, and titrated with  $\text{H}_2\text{SO}_4$  (Keeney & Nelson, 1982). Gravimetric soil moisture content was determined by oven drying ( $105^\circ\text{C}$  for 24 h). In the field, soil volumetric moisture was determined every 10 minutes by sensors (FDR CS 616-L, Campbell Scientific, Logan, Utah, USA) inserted 2.5 cm deep in the crop line (perpendicular to the line) and coupled to a datalogger (CR1000, Campbell Scientific, Logan, Utah, USA).

To determine the water-soluble total N and  $\text{NH}_4^+$  of straw (secondary experiment in year 2017), straw was collected from inside the PVC rings on days 1, 2, 7, 13 and 15 after N application and chopped into pieces of approximately 1 cm. Water-soluble total N and  $\text{NH}_4^+$  were extracted by shaking 4 g of chopped straw in 80 ml of ultrapure water for 30 minutes. Afterward, the solution was filtered (Whatman #5). Water-soluble total N concentration in the extract was analyzed using a total organic carbon (TOC) analyzer equipped with an N-kit (Shimadzu TOC-LCPH, Shimadzu, Kyoto, Japan). The  $\text{NH}_4^+$  content of the extract (this N form was also included in the water-soluble total N) was determined independently by distillation after addition of MgO followed by titration with  $\text{H}_2\text{SO}_4$  (Keeney & Nelson, 1982).

### 3.3.5 Calculations and statistical analysis

The  $\text{NH}_3\text{-N}$  volatilized ( $\text{kg N ha}^{-1}$ ) at each evaluation interval was calculated using the following equation:

$$\text{NH}_3 \text{ losses} = \left( \frac{N_{tf}}{A_c} \times 10 \right) / 0.74$$

where  $N_{tf}$  is the amount of N (mg) captured in the foam during the evaluation interval;  $A_c$  is the soil area ( $\text{m}^2$ ) covered by the chamber; 10 is the transformation factor of the values for  $\text{kg ha}^{-1}$ ; and 0.74 is the correction factor of the chamber (Jantalia et al., 2012).

The net cumulative  $\text{NH}_3\text{-N}$  lost in the treatments + N was calculated by summing the  $\text{NH}_3\text{-N}$  quantities measured in each evaluation period and subtracting the value measured in the respective treatment without N. The ratio of applied N that was lost via  $\text{NH}_3$  volatilization was calculated by dividing the cumulative net  $\text{NH}_3\text{-N}$  lost by the amount of N-urea applied ( $100 \text{ kg ha}^{-1}$ ). The results of soil inorganic N, water-soluble total N and  $\text{NH}_4^+$  of the straw represent the difference between the treatments with and without N.

All data were submitted to an analysis of variance (ANOVA), wherein the interactions among straw, N and year factors were tested. The means of each treatment were compared by the LSD test at the 5% probability level. For the cumulative  $\text{NH}_3$  volatilized at the different amounts of straw, a linear regression was fitted. The data were processed using the SISVAR software (version 5.3- Build 75).

### 3.4 RESULTS

#### 3.4.1 Climatic and soil environmental conditions

Rainfall distribution after urea application differed between the two years, although the cumulative amount of rain was similar. In 2016, urea-N application was followed by rainfall of 1.6 mm and a dry period of 10 days. Between the 11<sup>th</sup> and 13<sup>th</sup> day after N application, three rainfall events totaled 21 mm (Fig. 1a). In 2017, urea-N application was followed by rainfall events of 8.5 mm on the first day and 3 mm on the second day. On the 10<sup>th</sup> and 12<sup>th</sup> day after N application, rainfall events of 10 and 2.5 mm occurred, respectively (Fig. 2a).

The average air temperature ranged from 20.7 to 28.5°C in 2016 (Fig. 1a) and from 19.9 to 23.1°C in 2017 (Fig. 2a). The volumetric soil water content in the 0-5 cm layer varied according to the rainfall intensity and frequency during the experiments (Fig. 1b and 2b). In both years, a higher soil water content was observed in treatments with higher amounts of straw on the soil surface, particularly when the soil was drying.

#### 3.4.2 Dynamics of inorganic N in the 0-10-cm soil layer

In 2016, the inorganic N content in the 0-10-cm soil layer was low in treatments without N applied (0S, 4S, 8S and 12S); the content was, on average, 2.0 kg ( $\text{NH}_4^+$ -N) and 2.1 kg ( $\text{NO}_3^-$ -N)  $\text{ha}^{-1}$ , with no significant difference between treatments (Suppl. Table S1). The dynamics of  $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N in the 0-10-cm soil layer differed significantly between treatments (Table 2). We observed that  $\text{NH}_4^+$  appearance in the 0-10-cm soil layer was delayed by higher straw quantities on the soil surface. In treatments with straw, the  $\text{NH}_4^+$  content only peaked at day 14, with a fast decrease afterward. The soil  $\text{NO}_3^-$  content remained low for all treatments over the evaluation period.

In 2017, the soil inorganic N level (mean 5.7 kg  $\text{NH}_4^+$ -N; 5.3 kg  $\text{NO}_3^-$ -N) in the treatments without N was slightly higher than that in 2016, but there was no significant

difference between the treatments (Suppl. Table S1). Unlike 2016, in treatments that received urea-N, there was no delay in the accumulation of  $\text{NH}_4^+$  in the 0-10-cm soil layer, which was already very high in the first two days. We observed a range of 100 to 38 kg  $\text{NH}_4^+\text{-N ha}^{-1}$  for the 0S+N to 12S+N treatments. Thus, soil ammonium content was inversely related to straw quantities left on the soil surface ( $0\text{S+N} > 4\text{S+N} > 8\text{S+N} \geq 12\text{S+N}$ ). The soil  $\text{NH}_4^+$  content for the 4S+N, 8S+N and 12S+N treatments decreased rapidly within 7 days after N application, and in the 0S+N treatment, within 13 days. The soil  $\text{NH}_4^+$  decrease was followed by an increase in the soil  $\text{NO}_3^-$  content in the 0-10-cm layer, suggesting an active nitrification. The total soil inorganic N in the first 14 days ranged, on average, from 40 to 50 kg N  $\text{ha}^{-1}$  in 2016 and from 50 to 100 kg N  $\text{ha}^{-1}$  in 2017.

### 3.4.3 $\text{NH}_4^+\text{-N}$ and water-soluble total N in straw

The  $\text{NH}_4^+\text{-N}$  and water-soluble total N amounts extracted from straw were low in treatments that received no N (4S, 8S and 12S). The values ranged from 0.02 to 0.06 kg  $\text{ha}^{-1}$  of  $\text{NH}_4^+\text{-N}$  and from 0.34 to 0.98 kg  $\text{ha}^{-1}$  of water-soluble total N; the values were proportional to the straw quantities (Suppl. Table S2). By contrast, the  $\text{NH}_4^+\text{-N}$  and total N in soluble extracts from straw plus N-fertilizer treatments (expressed by the difference with the controls, for each treatment) differed significantly between the treatments ( $P < 0.05$ ) and were greater than the amount proportional to the amount of straw due to the higher N concentration in the straw with increasing amounts of straw (Suppl. Table S3). Approximately 6.5 times more N was observed at day 1 in the 12S+N treatment than that in the 4S+N treatment (Table 3). The difference between the total  $\text{NH}_4^+\text{-N}$  and total N in soluble extracts is attributable to urea-N remaining in the straw. From day 7, we observed a fast decrease in the  $\text{NH}_4^+\text{-N}$  and water-soluble total N for all treatments. In total, the amount of N retained by the mulch, which was directly related to the urea application, represented approximately 10 kg N  $\text{ha}^{-1}$  on day 1 in the 12S+N treatment. The straw moisture had the highest values at day 1 and decreased over time. The straw from the 12S+N treatment remained wetter throughout the period than that from the other treatments did.

### 3.4.4 Ammonia volatilization

In both years,  $\text{NH}_3$  losses were practically negligible in the treatments without N application (0S, 4S, 8S and 12S), regardless of the amount of the straw on the soil surface. In the treatments receiving urea, the  $\text{NH}_3$  volatilization dynamics differed between treatments and years (Fig. 1c and 2c). In 2016,  $\text{NH}_3$  volatilization increased immediately after N application and gradually

decreased until day 10 (Fig. 1c). During this period, the  $\text{NH}_3$  losses did not differ between 4S+N, 8S+N and 12S+N but exceeded the 0S+N treatment by a factor of 3 (mean of 1.3 vs 0.4 kg N ha<sup>-1</sup>). The highest  $\text{NH}_3$  losses were observed between day 10 and day 12 and ranked in the order 0S+N (2.3) < 4S+N (6.6) = 8S+N (8.4) < 12S+N (11.9 kg N ha<sup>-1</sup>). From day 14,  $\text{NH}_3$  volatilization decreased in all treatments but was significantly higher for the 4S+N, 8S+N and 12S+N treatments than for the 0S+N treatment.

In 2017, the highest  $\text{NH}_3$  losses were observed in the first two days after urea-N application (Fig. 2c). On day 1, the  $\text{NH}_3$  volatilization reached 29.6 kg of  $\text{NH}_3\text{-N}$  ha<sup>-1</sup> (29.6% of N applied) in the 12S+N treatment. On day 2,  $\text{NH}_3$  volatilization remained high and did not differ between the 12S+N and 8S+N treatments, with a mean  $\text{NH}_3\text{-N}$  loss of 26.5 kg N ha<sup>-1</sup>. Then, the  $\text{NH}_3$  volatilization decreased quickly. From day 5, the  $\text{NH}_3$  losses did not differ between the treatments with and without N addition.

Cumulative  $\text{NH}_3\text{-N}$  losses were significantly affected by climatic conditions, N addition and sugarcane straw (Table 1) and ranged from 9.2% to 27.6% and 30.7% to 60.8% of N applied in 2016 and 2017, respectively (Fig. 3). The  $\text{NH}_3\text{-N}$  losses in treatments receiving urea-N were 2.4 times higher in 2017 than those in 2016. In 2016, 90% of the  $\text{NH}_3\text{-N}$  losses occurred in the first 12 days after N application, while in 2017, this effect was observed in the first 2 days. The  $\text{NH}_3$  volatilization was directly proportional to the straw amount left on the soil surface (Fig. 4). In 2016, every 4 Mg ha<sup>-1</sup> of straw remaining on the soil surface resulted in an ammonia loss of +7.1 kg N ha<sup>-1</sup>; in 2017, this value was +12.0 kg N ha<sup>-1</sup> per 4 Mg ha<sup>-1</sup> straw left.

### 3.5 DISCUSSION

Conservation agriculture practices that encourage the return and maintenance of mulch on the soil surface (e.g., no-till system) are increasing in agricultural areas. The industrial valorization of crop residues for bioenergy production is also raising the importance of knowing how the disposal of crop residues on the soil surface and the partial or total removal of straw can affect the fate of fertilizer-N and particularly  $\text{NH}_3$  volatilization. While various studies have investigated  $\text{NH}_3$  volatilization after application of fertilizer-N on the straw surface, particularly in sugarcane fields (Cantarella et al., 2008; Nascimento et al., 2013; Otto et al., 2017; Mira et al., 2017), there are few studies comparing  $\text{NH}_3$  volatilization between situations with a straw layer and without straw (bare soil) in sugarcane fields (Dattamudi et al., 2016) and with other crops such as wheat, maize, soybean and barley (Meyer et al., 1961; Barreto and Westerman,

1989; Rochette et al., 2009). Thus far, there is no clear evidence for the processes that are involved.

### 3.5.1 Effect of the amount of straw on $\text{NH}_3$ volatilization

For the two years of the experiment, the striking finding is the increase in the amount of  $\text{NH}_3$  emitted when the amount of mulch increased, which is in a quasi-linear relationship under our environmental conditions and range of straw amounts. The cumulative  $\text{NH}_3$ -N losses varied greatly from 9.2% in 2016 (0S + N) to 60.8% in 2017 (12S + N). These values are in the range of the  $\text{NH}_3$ -N losses observed in other studies with sugarcane fields (Cantarella et al., 2008; Nascimento et al., 2013; Soares et al., 2015; Otto et al., 2017). These results are consistent with those of Pan et al. (2016) indicating an increase in volatilization when crop residues are retained at the soil surface, which is a common situation, for example, in conservation agriculture. In the meta-analysis of Pan et al. (2016), the mean increase in volatilization in the presence of straw was 25.5% compared to that of bare soil. Our study goes one step further than existing data by describing a close relationship between the amount of straw and the  $\text{NH}_3$  loss by volatilization.

Several processes have been mentioned to explain the effect of the presence of straw layer on volatilization after surface application of fertilizer-N: direct effects related to the presence of urea in the straw mulch and indirect effects related to the effect of mulch on the environmental and biological conditions at the mulch-soil interface (Dawar et al., 2011; Otto et al., 2013). Most likely, both types of processes take place simultaneously. Our results showed that the amount of straw greatly influenced the concentration in  $\text{NH}_4^+$  of the top soil layer. A higher concentration of  $\text{NH}_4^+$  was observed with a lower amount of straw (0S and 4S) than that for a higher amount of straw (8S and 12S), but with different patterns depending on the year. In 2016, the  $\text{NH}_4^+$  accumulation was clearly delayed with a higher amount of straw (8S and 12S), suggesting a retention of urea in the mulch, which we explained by the lack of rain after fertilization. In 2017, urea-derived N was immediately recovered in the soil (day 1) at increasing concentrations with decreasing straw rate. For the control treatment in particular (0S+N), the  $\text{NH}_4^+$ -N content was equivalent to the urea application (approximately  $100 \text{ kg N ha}^{-1}$ ), which signifies that a fast dissolution of urea granules and hydrolysis occurred. Actually, the dissolution of granules associated with rain was observed visually within less than one day. Le Cadre et al. (2004) showed that the concentration of  $\text{NH}_4^+$  in the vicinity of fertilizer granules is much higher than that suggested by the mean concentration measured in the top 0-10 cm soil

layer. A very high concentration could explain the high emission observed immediately from the first day after application in 2017. Nevertheless, the  $\text{NH}_4^+$  concentration in soil was inversely related to the emission of  $\text{NH}_3$ , suggesting that differences in the soil  $\text{NH}_4^+$  concentration were not responsible for the differences in  $\text{NH}_3$  emission during the first days and that the retention of urea or  $\text{NH}_4^+$  in the straw layer was responsible for the increase in emitted  $\text{NH}_3$  for the straw treatments. This hypothesis is supported by the observed increase in  $\text{NH}_4^+$  and water-soluble total N in straw layer, measured on the secondary “ring” experiment in the second experimental year, with higher concentration of N in the straw when the straw layer was greater. This result suggests that the straw layer acted as a physical barrier to transport of urea down to the soil. The presence of a high amount of  $\text{NH}_4^+$  in the straw means that urea hydrolysis occurred directly on the straw. Freney et al. (1992) observed urease activity on sugarcane straw and correlated this activity to a higher  $\text{NH}_3$ -N loss after urea-N was applied. Similar results were observed by McInnes et al. (1986) with wheat straw, with 20 times more urease activity per kg of wheat straw compared to that of kg dry soil. We did not measure urease activity on straw, but the presence of high  $\text{NH}_4^+$ -N content is evidence for urease activity in each straw layer. In our experiment, the accumulation of  $\text{NH}_4^+$  and water-soluble N was transient, and  $\text{NH}_4^+$  disappeared rapidly, suggesting fast transport of urea down to the soil and an active nitrification on the one hand but also high losses by volatilization on the other hand.

Furthermore, urease activity is regulated by water availability (Rochette et al., 2009; Otto et al., 2017; Mira et al., 2017). Our study shows higher straw moisture when the amount of straw is higher. Mira et al. (2017) related the peak of  $\text{NH}_3$  volatilization after rain to a rise in straw moisture. Straw water absorption capacity and the maintenance of soil moisture (Peres et al., 2010; Silva et al., 2012) increases urease activity and favors  $\text{NH}_3$  emission after urea-N application in comparison to that for drier conditions (Ma et al., 2010). Therefore, our results show that the physical barrier formed by higher amounts of straw on soil surface prevents urea-N infiltration into soil. Combined with its role as a physical barrier, sugarcane straw, which has almost zero  $\text{NH}_4^+$  absorption capacity (Freney et al., 1992) and contains urease, facilitated N losses as  $\text{NH}_3$ .

### 3.5.2 Interannual variations in volatilization

Although  $\text{NH}_3$ -N loss was affected by straw level on the soil surface regardless of the experimental year, the dynamics and amount of volatilized N were strongly influenced by climatic conditions after urea-N application, especially the distribution and intensity of rainfall,

as temperature was not significantly different in the two years over the measurement period. A small volume of rainfall after urea-N was applied in 2016 was, however, sufficient to solubilize urea granules present on the surface of the straw (visual confirmation). However, the  $\text{NH}_3$  volatilization rates were low until day 10 after urea application. During this period,  $\text{NH}_3$  volatilization dynamics were similar to those reported by Ma et al. (2010), who observed low but persistent  $\text{NH}_3$  volatilization emissions when the N application was followed by a dry period. In our situation, 5.2 mm rain split into two events between day 10 and day 12 increased the  $\text{NH}_3$  volatilization, followed also by an increase in the soil  $\text{NH}_4^+$ -N content. This result indicates that part of N applied was still in the urea form or  $\text{NH}_4^+$  retained in straw and that the increased water availability due to rain increased the urease activity, which resulted in higher  $\text{NH}_3$  volatilization from the straw and soil.

In 2017,  $\text{NH}_3$  volatilization rates were already high in the first two days after urea-N application due to the occurrence of 11.5 mm rainfall. However, the threshold amount at which rain either intensifies or reduces  $\text{NH}_3$  volatilization seems to be narrow, since after 15.8 mm of rain at day 13 in 2016,  $\text{NH}_3$  volatilization decreased rapidly, and an increase in the soil  $\text{NH}_4^+$  content was observed. This result suggests that each amount of straw present on soil surface could be related with a quantity of rain or irrigation necessary to leach and incorporate urea-N in soil after being applied at the surface of the straw. Cantarella et al. (2008) found that a 13.8 mm amount of rainfall was not adequate to fully incorporate urea into soil but reduced the  $\text{NH}_3$  volatilization. In addition, Freney et al. (1994) reported that a 16 mm amount of rainfall reduced the  $\text{NH}_3$  volatilization and incorporated urea into soil. The reduction in  $\text{NH}_3$  volatilization due to increased precipitation occurs by distribution and urea infiltration into the soil and by  $\text{NH}_4^+$  immobilization at soil cation exchange sites (Holcomb et al., 2011; Sanz-Cobena et al., 2011).

### 3.6 CONCLUSIONS

Our results clearly show that increasing the amount of straw mulch increased the volatilization of  $\text{NH}_3$  after urea application on sugarcane. Analysis of the top soil and of the straw indicated a higher retention of urea and  $\text{NH}_4^+$  with thicker mulch and effective hydrolysis of the urea in the mulch. This result supports the hypothesis of a direct contribution from the mulch layer to the volatilization of urea-derived N, which more than counterbalanced a weaker contribution of the soil to the volatilization compared to that of the situation without mulch. In the context of increasing the use of crop residues for bioelectricity or second-generation ethanol, our results indicate that for every 4 Mg ha<sup>-1</sup> of sugarcane straw removed, the volatilization decreased on

average by 9.5 kg of N ha<sup>-1</sup>. Thus, in agricultural systems with mulch on the soil surface, straw removal for industrial uses contributes to a reduction in fertilizer-N losses as NH<sub>3</sub>. However, other environmental and agronomic impacts are associated with the management of crop residues, and the environmental assessment cannot rely only on fertilizer-N volatilization and on an annual scale. Reducing volatilization in such agricultural systems would imply managing fertilization differently, i.e., by placing fertilizer below the straw layer, which is already considered in other cropping systems, particularly with animal manure application. In the context of bioenergy use of sugarcane residues, our results contribute to decision making on how much straw may be removed from the soil surface to optimize the environmental sustainability of agricultural practices.

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### Figure captions

Fig. 1. Wind speed, air temperature and rainfall (a), soil water content (b) and  $\text{NH}_3\text{-N}$  losses (c) in the first ratoon cane (2016) after 100 kg urea-N  $\text{ha}^{-1}$  (N) application over the different straw (S) quantities (0, 4, 8 and 12  $\text{Mg ha}^{-1}$ ). The vertical bars represent the least significant difference (LSD) between the treatments ( $P < 0.05$ ).

Fig. 2. Wind speed, air temperature and rainfall (a), soil water content (b) and  $\text{NH}_3\text{-N}$  losses (c) in the first ratoon cane (2017) after 100 kg urea-N  $\text{ha}^{-1}$  (N) application over the different straw (S) quantities (0, 4, 8 and 12  $\text{Mg ha}^{-1}$ ). The vertical bars represent the least significant difference (LSD) between the treatments ( $P < 0.05$ ).

Fig. 3. Net cumulative  $\text{NH}_3\text{-N}$  losses in the first ratoon sugarcane (2016 and 2017) after 100 kg urea-N  $\text{ha}^{-1}$  (N) application over the different straw (S) quantities (0, 4, 8 e 12  $\text{Mg ha}^{-1}$ ). The vertical bar represents the least significant difference (LSD) between the treatments ( $P < 0.05$ ).

Fig. 4. Relationship between straw quantities (0, 4, 8 e 12  $\text{Mg ha}^{-1}$ ) and  $\text{NH}_3\text{-N}$  losses in the first ratoon sugarcane (2016 and 2017) after 100 kg urea-N  $\text{ha}^{-1}$  (N) application. Vertical error bars indicate the standard mean deviation. \*significant difference with t test ( $P < 0.05$ ).

Table 1. A three-way ANOVA for the effects of straw level (S), nitrogen fertilizer (N) and year (Y) on cumulative NH<sub>3</sub> losses.

Source	Df	SS	<i>F</i>	<i>P</i> value
S	3	683.51	15.55	<0.001
N	1	9572.91	653.56	<0.001
Y	1	1333.98	91.07	<0.001
S x N	3	718.64	16.35	<0.001
S x Y	3	62.66	1.43	0.248
N x Y	1	1596.90	109.02	<0.001
S x N x Y	3	66.79	1.52	0.222
Error	45	659.12		

Table 2. Soil ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) in the 0.10-m soil layer after 100 kg urea-N  $\text{ha}^{-1}$  (N) application over the different straw (S) quantities (0, 4, 8 e 12  $\text{Mg ha}^{-1}$ ) in the first ratoon cane (2016 and 2017).

Treatments	2016				2017				
	3d <sup>1</sup>	8d	14d	19d	1d	2d	7d	13d	15d
$\text{NH}_4^+$ -N ( $\text{kg ha}^{-1}$ )									
0S+N	20.6 a <sup>2</sup>	27.4 a	5.1 b	12.2 a	94.8 a	99.9 a	38.2 a	3.2	7.0
4S+N	10.0 b	15.1 b	41.7 a	7.5 ab	77.7 ab	77.9 a	6.6 b	1.9	1.7
8S+N	4.0 b	3.1 c	32.0 a	2.8 b	55.0 b	38.0 b	8.5 b	1.9	4.1
12S+N	4.9 b	4.4 bc	33.4 a	1.3 b	54.8 b	42.0 b	6.0 b	2.7	5.8
$\text{NO}_3^-$ -N ( $\text{kg ha}^{-1}$ )									
0S+N	0.3 b	2.3	3.7 c	3.1	2.8	2.5	40.2	24.1 ab	22.7
4S+N	2.2 a	2.4	7.2 b	5.3	3.7	2.2	36.6	36.5 a	22.3
8S+N	2.5 a	2.9	6.0 b	5.2	2.8	2.2	52.5	24.9 ab	12.9
12S+N	1.6 ab	2.7	11.5 a	6.0	3.8	2.2	43.0	17.1 b	15.1

<sup>1</sup> Days after N-urea applied;

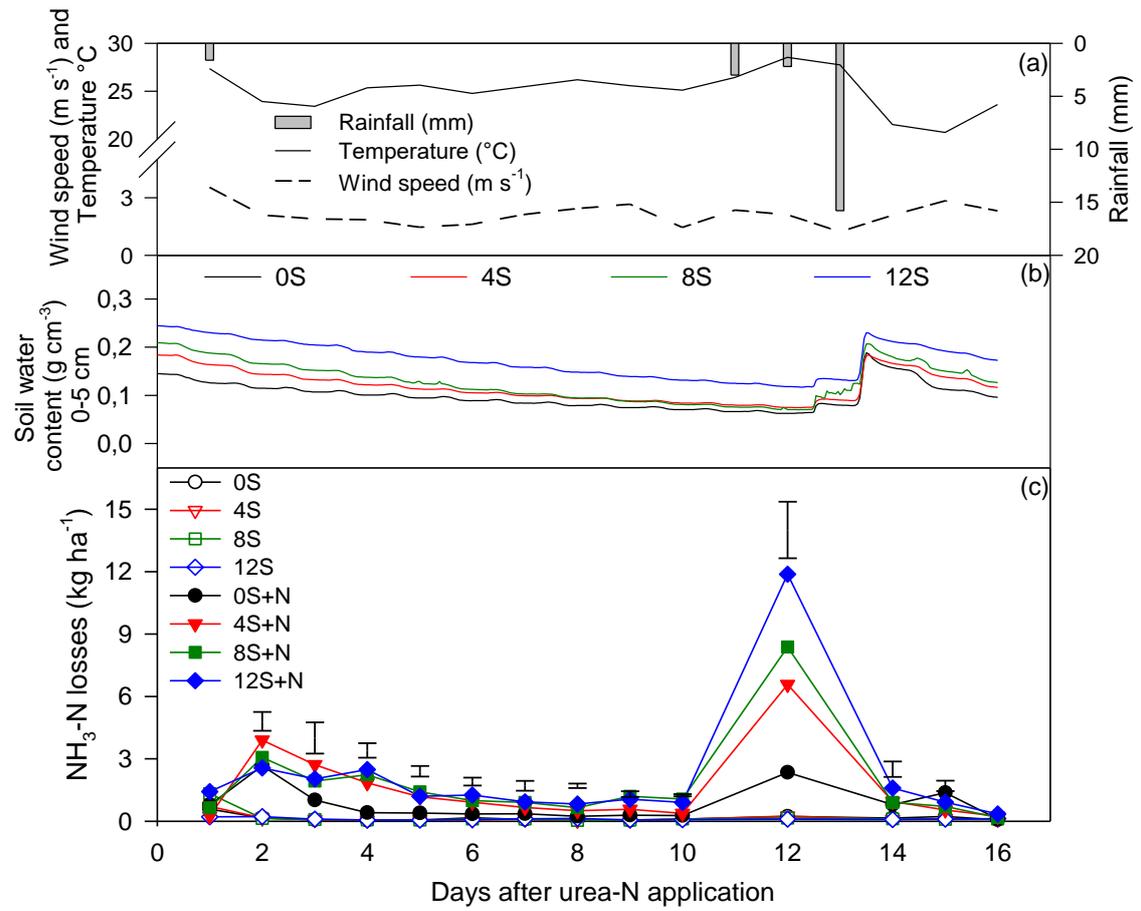
<sup>2</sup> Results followed by different letters in columns differ significantly according to the LSD test ( $P < 0.05$ ).

Table 3. Straw ammonium ( $\text{NH}_4^+$ ), water-soluble total N concentration in straw and straw moisture after 100 kg urea-N  $\text{ha}^{-1}$  (N) application for different straw (S) quantities (4, 8 and 12 Mg  $\text{ha}^{-1}$ ) in the first ratoon cane (2017).

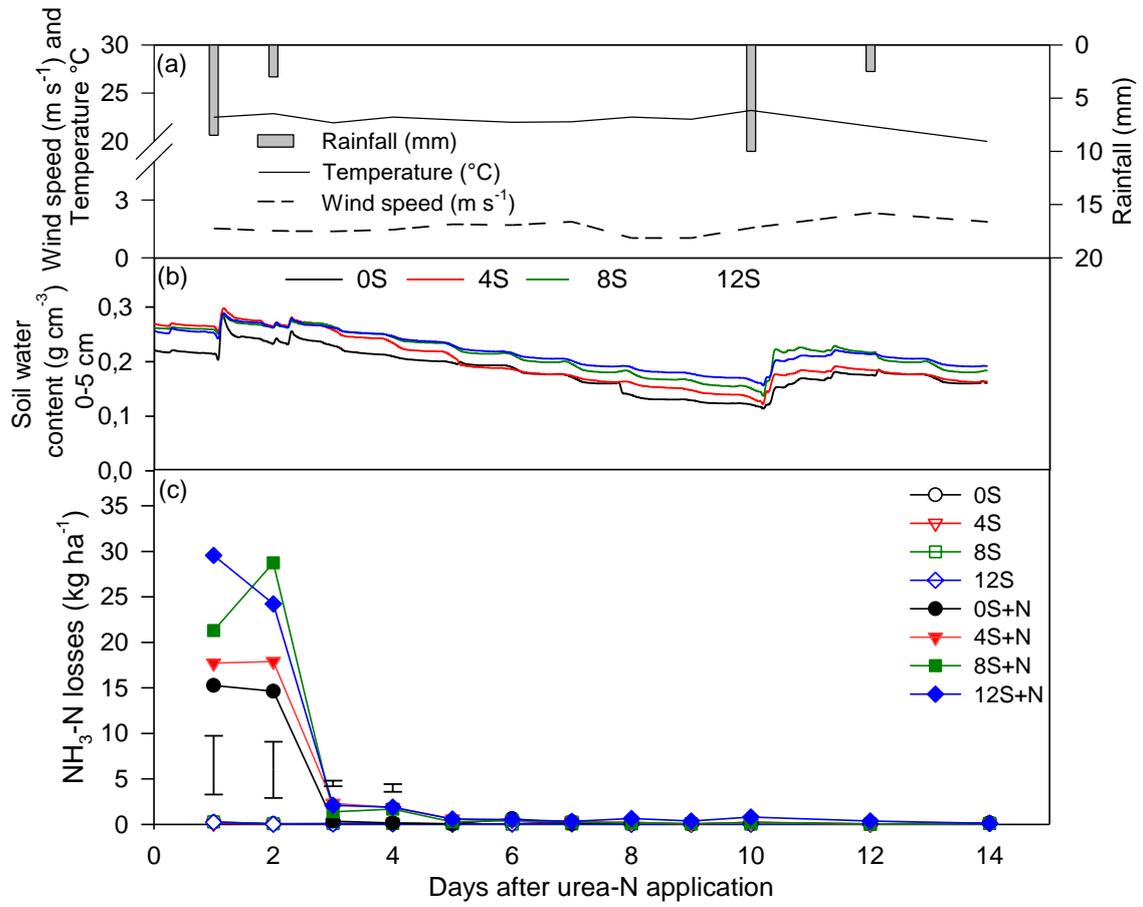
Treatments	2017				
	1d <sup>1</sup>	2d	7d	13d	15d
	----- kg $\text{NH}_4^+\text{-N ha}^{-1}$ -----				
4S+N	0.72 C a	0.70 C a	0.75 B a	0.02 B b	0.01 b
8S+N	2.70 B a	1.70 B b	1.40 A b	0.09 B c	0.02 c
12S+N	4.72 A a	2.21 A b	1.41 A bc	0.29 A c	0.01 c
	----- kg water-soluble total N $\text{ha}^{-1}$ -----				
4S+N	1.37 B a	1.20 B a	1.54 a	0.23 b	0.19 b
8S+N	4.62 B a	3.07 AB a	2.78 ab	0.76 bc	0.19 c
12S+N	9.21 A a	4.45 A b	2.79 bc	0.53 c	0.21 c
	----- Straw moisture % -----				
4S+N	52.0 B a	21.0 C b	25.4 B b	12.8 B c	5.5 B d
8S+N	60.7 A a	32.6 B b	28.7 B bc	19.2 B c	7.4 A d
12S+N	64.0 A a	48.6 A b	34.0 A c	34.1 A c	8.9 A d

<sup>1</sup> Days after N-urea applied;

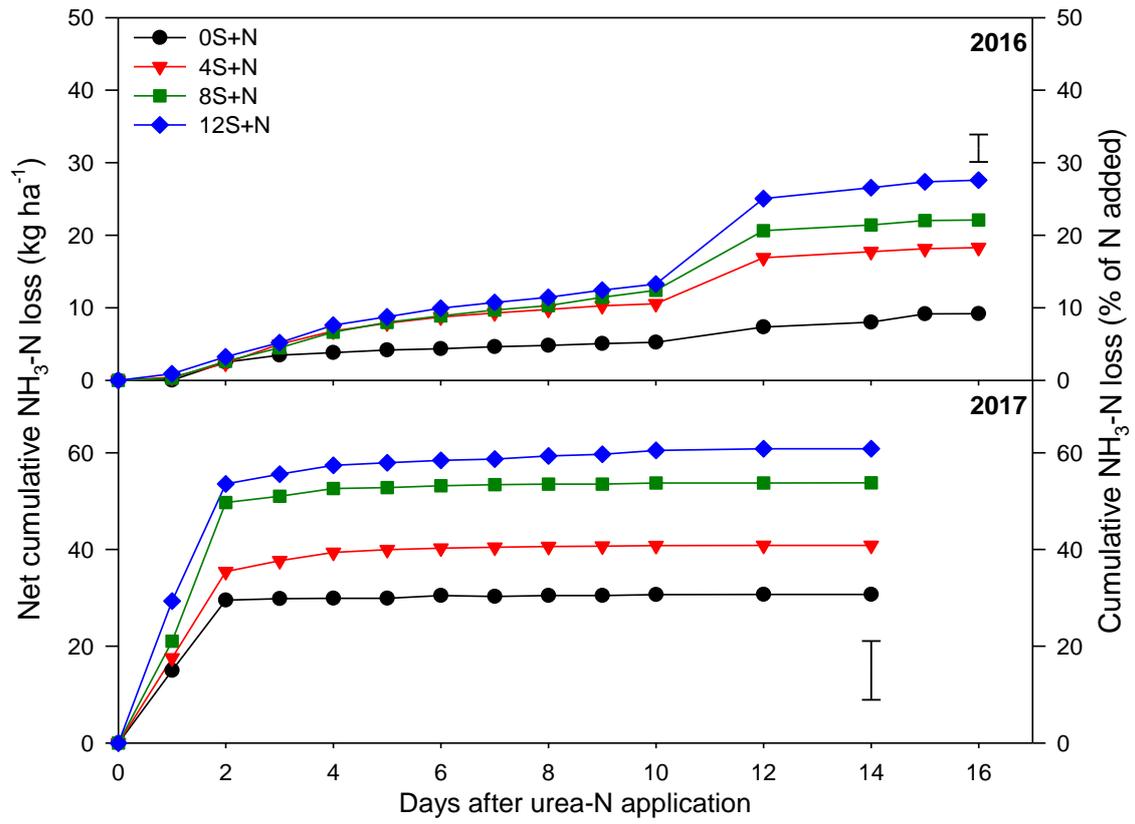
<sup>2</sup> Results followed by different capital letters in columns and small letters in lines differ significantly according to the LSD test ( $P < 0.05$ ).



**Fig 1.**



**Fig 2**



**Fig 3**

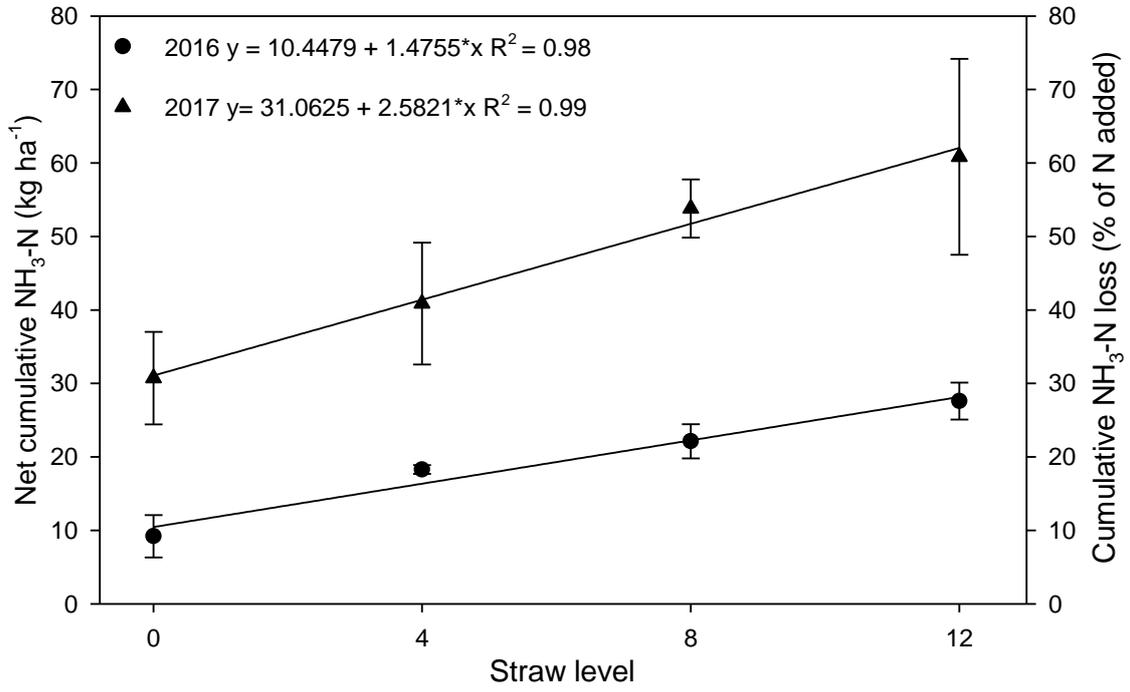


Fig 4

### Supplementary files

Table S1. Soil ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) in the 0.10-cm soil layer over the different straw (S) quantities (0, 4, 8, and 12  $\text{Mg ha}^{-1}$ ) without N applied (0S, 4S, 8S, and 12S treatments) in the first ratoon cane (2016 and 2017).

Treatments	2016				2017				
	3d <sup>1</sup>	8d	14d	19d	1d	2d	7d	13d	15d
	----- kg $\text{NH}_4^+$ -N $\text{ha}^{-1}$ -----								
0S	1.7	1.3	2.1	3.5	3.8	4.2	6.5	7.9	7.8
4S	3.2	2.9	1.8	2.0	3.8	4.9	4.4	7.5	6.9
8S	2.8	2.9	0.8	1.8	3.5	7.1	4.6	7.2	3.5
12S	1.0	0.7	2.7	1.9	3.9	5.0	3.5	9.7	9.3
	----- kg $\text{NO}_3^-$ -N $\text{ha}^{-1}$ -----								
0S	2.2	3.1	2.9	1.9	6.3	5.1	6.7	5.2	1.0
4S	1.7	4.3	3.7	0.5	6.1	4.9	7.5	6.6	0.3
8S	1.0	1.9	2.4	0.2	5.7	5	8.9	7.6	1.4
12S	2.8	3.1	2.5	0.6	6.4	5.5	7.6	6.9	2.1

Table S2. Straw ammonium ( $\text{NH}_4^+$ ) and water-soluble total N concentration in straw for different straw (S) quantities (4, 8 and 12  $\text{Mg ha}^{-1}$ ) with no fertilizer in the first ratoon cane (2017) (4S, 8S and 12S treatments).

Treatments	2017				
	1d <sup>1</sup>	2d	7d	13d	15d
	----- kg $\text{NH}_4^+$ -N $\text{ha}^{-1}$ -----				
4S	0.03	0.03	0.02	0.01	0.01
8S	0.06	0.05	0.05	0.03	0.02
12S	0.08	0.07	0.07	0.04	0.03
	----- kg water-soluble total N $\text{ha}^{-1}$ -----				
4S	0.49	0.41	0.33	0.27	0.21
8S	0.95	0.84	0.69	0.57	0.46
12S	1.31	1.17	1.02	0.75	0.64

Table S3. Straw ammonium ( $\text{NH}_4^+$ ) and water-soluble total N concentration in straw after 100 kg urea-N  $\text{ha}^{-1}$  (N) application for different straw (S) quantities (4, 8 and 12 Mg  $\text{ha}^{-1}$ ) in the first ratoon cane (2017).

Treatments	2017				
	1d <sup>1</sup>	2d	7d	13d	15d
	----- mg $\text{NH}_4^+$ -N $\text{kg}^{-1}$ straw -----				
4S+N	265 B a <sup>2</sup>	259 a	279 a	6 B b	4 b
8S+N	519 AB a	327 b	270 b	17 B c	3 c
12S+N	665 A a	311 b	199 bc	41 A c	1 c
	----- mg water-soluble total N $\text{kg}^{-1}$ straw -----				
4S+N	508 B a	446 a	570 a	85 b	70 b
8S+N	888 AB a	590 a	535 ab	146 bc	37 c
12S+N	1297 A a	627 a	393 bc	75 c	29 c

<sup>1</sup> Days after N-urea applied;

<sup>2</sup> Results followed by different capital letters in columns and small letters in lines differ significantly according to the LSD test ( $P < 0.05$ ).

## 4 ARTIGO II - MULCH AND NITROGEN FERTILIZER CONTRIBUTION TO N<sub>2</sub>O EMISSIONS IN A SUGARCANE CROP WITH INCREASING RATE OF STRAW REMOVAL<sup>2</sup>

### 4.1 ABSTRACT

Crop residues harvest for bioenergy production became a common practice in the past few years. This has motivated an intense discussion about how much straw could be removed from soil surface, particularly about the uncertainties between the interactions straw mulch and nitrogen (N), and their effects on nitrous oxide (N<sub>2</sub>O) emissions. Therefore, we investigated the effect of the sugarcane straw removal and the impact on the mechanisms that make the mulch a “hot spot” of N<sub>2</sub>O emissions under subtropical conditions. We ran a field experiment in the first ratoon sugarcane with four quantity of straw (0, 4, 8 and 12 Mg ha<sup>-1</sup>) at soil surface combined with 0 or 100 kg urea-N ha<sup>-1</sup>. The urea-N was applied 52 days after straw application. Over one year, we measured N<sub>2</sub>O and carbon dioxide (CO<sub>2</sub>) emissions, inorganic N, soil moisture and temperature, and remaining straw carbon (C) and N in the mulch. We observed two “hot moments” for N<sub>2</sub>O emissions, the first one just after sugarcane straw application to soil, and the second one after fertilizer N application. Lower rates of straw removal raised the water filled pore space (WFPS), and both WFPS and straw-C had a strong correlation with N<sub>2</sub>O fluxes. Cumulative N<sub>2</sub>O increased from 510 (0 Mg + N) to 1055 (12 Mg + N) g N<sub>2</sub>O-N ha<sup>-1</sup> for the straw treatments fertilized. Over 70% of cumulative N<sub>2</sub>O emissions measured in straw + fertilizer-N treatments during one year were attributed to the presence of straw mulch, underlining the importance of straw layer at the soil surface as hot spot of N<sub>2</sub>O emissions. Therefore, emission factors (EF) increased with lower straw removal rate, in the range 0.16 % (4 Mg) to 0.34% (12 Mg) for straw-N source and 0.07 % (0 Mg + N) to 0.29% (12 Mg + N) for urea-N source. These results showed the direct and indirect effects of the quantity of straw left as mulch on the soil surface on the mechanisms involved in N<sub>2</sub>O emissions. This study demonstrates that the rate of removal and the presence of the straw at the soil surface is an important issue as it affects greatly N<sub>2</sub>O emissions and therefore the global greenhouse gas emissions balance of sugarcane cropping system.

Keywords: crop residue removal, decomposition, emission factor, mulch, nitrous oxide

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<sup>2</sup> Artigo elaborado de acordo com as normas da Agriculture, Ecosystems & Environment.

## 4.2 INTRODUCTION

Agricultural lands are the main source of nitrous oxide ( $N_2O$ ) to the atmosphere due to two major processes that occur in soil, i.e. nitrification and denitrification, as a response of synthetic-N fertilizer application and organic matter mineralization (Butterbach-Bahl et al., 2013; Smeets et al., 2009). In particular, crop residues recycled to soil influence these processes by different ways, i.e., by providing a source of readily available C and N in the soil, modifying microbial activity and mineralization-immobilization turnover during decomposition, modifying soil aeration, soil moisture and temperature (Stavi et al., 2016). The very different (and sometimes antagonistic) ways that crop residue can influence  $N_2O$  emission reflect in uncertainties about their impact on  $N_2O$  emission from soil. Whereas some studies reported an increase  $N_2O$  emissions with crop residue (Shan and Yan, 2013), others showed a decrease on emission (Basche et al., 2014) or no difference between crop residue on soil surface and bare soil (van Kessel et al., 2013). The effect of biological factors, soil type, agricultural systems and environmental conditions on  $N_2O$  emissions results in a large range of uncertainty (0.3% to 3%) in emission factor (EF) from Intergovernmental Panel on Climate Change (IPCC) that has a default value of 1% (IPCC, 2014).

Management of plant residues is also recognized as an important factor affecting  $N_2O$  emissions (Mutegi et al., 2010), and could lead to “hot moments” and “hot spots” of  $N_2O$  emissions in soils (Kravchenko et al., 2017). Combined with reduced tillage or no-till, crop residues left as mulches after crop harvest in conservation agriculture, or in semi-perennial cropping systems such as with sugarcane (Sousa Junior et al., 2018), or others bioenergy crops (e.g., Peyrard et al., 2016) allow to increase soil C sequestration in the long-term and  $CO_2$  mitigation potential (Lal, 2004). However, these practices can influence the emission of non- $CO_2$  gases, such as  $N_2O$ , which alter the global warming potential (GWP) and could reduce the “savings” promoted by C sequestration (Crutzen et al., 2008; Lugato et al., 2018). In this context, the shift of harvest with burn to mechanized harvest without burn in sugarcane areas such as in Brazil returns 7 to 25 Mg DM  $ha^{-1}$  year $^{-1}$  of sugarcane residue as mulch onto the soils (Leal et al., 2013), with a high potential for bioenergy use (Manochio et al., 2017; Sindhu et al., 2016). It raises the important question of trade-offs between recycling and removal, which led to an unprecedented research effort to quantify the agronomic and environmental consequences of managing plant biomasses, particularly in sugarcane sector (Bordonal et al., 2018; Carvalho et al., 2017), but not only (Cherubin et al., 2018). Particularly, uncertainties about the interactions between residue mulches and fertilization, and their effects on  $N_2O$  emissions

(Carmo et al., 2013; Pitombo et al., 2017; Siqueira Neto et al., 2016), further increases the need to understanding how the quantity of residues left on the soil (or the mirror question, the quantity removed from field) affect soil N<sub>2</sub>O emissions.

In this context, our scientific objectives were i) to assess the effect of the sugarcane mulch removal on N<sub>2</sub>O emissions from soil under subtropical conditions of southern Brazil, and ii) to understand the mechanisms that make the mulch a “hot spot” of N<sub>2</sub>O emissions during sugarcane growing cycle. By following N<sub>2</sub>O emissions during one year in a sugarcane crop with four scenarios of straw removal, with and without urea-N applied, we examined the effect of mulch of various thickness on residue decomposition and the soil environmental conditions, and quantified the respective effects of straw mulches and of fertilizer-N, and their interaction, on N<sub>2</sub>O emissions. We hypothesized that higher quantities of straw on soil surface increase the input of labile C and N from crop residue and favor the maintenance of soil moisture, which lead a higher N<sub>2</sub>O emissions from soil in both fertilizer and non-fertilized sugarcane situations.

### 4.3 MATERIALS AND METHODS

#### 4.3.1 Experimental site

The study was conducted at the Federal University of Santa Maria (29°42'54" S, 53°42'23" W, approximately 90 m elevation) in the state of Rio Grande do Sul, Brazil. The local climate according to the Köppen classification is sub-tropical humid climate type Cfa (Alvares et al., 2013). The mean temperature is 14°C during the coldest month (June) and 25°C during the hottest month (January). The mean annual precipitation is 1700 mm, without dry season. The soil is classified as Typic Paleudalf (Soil Survey Staff 2010) with 110 g kg<sup>-1</sup> clay, 630 g kg<sup>-1</sup> sand and soil bulk density of 1.63 g dm<sup>-3</sup> in 0-20 cm. The chemical properties of the soil at the beginning of the experiment were pH (water) 5.4, CEC 2.5 cmol<sub>c</sub> dm<sup>-3</sup>, Mehlich-I P 33.4 mg dm<sup>-3</sup>, K 40.0 mg dm<sup>-3</sup>, total C 4.1 g kg<sup>-1</sup> soil and total N 0.32 g kg<sup>-1</sup> soil. The climatic variables, i.e., average air temperature and daily precipitation, were obtained from an automatic meteorological station located 1.6 km from the experimental site.

#### 4.3.2 Treatments and experimental design

The experiment was carried out at the first sugarcane ratoon from November 2015 to November 2016 and began after the harvest of the cane plant held on November 20, 2015. The sugarcane variety was RB95-6911 and harvest was manual, removing all aboveground biomass (stalks,

tops and leaves) leaving the soil uncovered. An area was demarcated with 32 plots of 22.4 m<sup>2</sup>, consisting of 4 lines with 1.4 m of spacing between rows and 4 m of length.

Experimental design was of randomized blocks in a factorial scheme 4x2 with four replicates. The first factor were four straw levels: 0, 4, 8 and 12 Mg DM ha<sup>-1</sup> (0S, 4S, 8S, 12S). The second factor were two doses of urea-N: 0 and 100 kg N ha<sup>-1</sup>. This arrangement resulted into 8 different treatments: 0S, 0S+N, 4S, 4S+N, 8S, 8S+N, 12S and 12S+N. The quantity of straw (equivalent to 4, 8 and 12 Mg DM ha<sup>-1</sup>) was homogeneously distributed by hand on soil surface in each plot. The urea-N was applied in a single dose on the soil surface (0S) and on straw surface (4S, 8S, 12S), in tillering phase of sugarcane, at day 52 after the harvest of the plant cane in November 2015. At this moment, the remaining amount of straw at soil surface was 2.5, 4.9 and 7.1 Mg DM ha<sup>-1</sup> in treatments 4, 8 and 12 Mg ha<sup>-1</sup>, respectively.

The straw used in the study came from a mechanically harvested sugarcane crop at the Grandespe company in Salto do Jacuí, Rio Grande do Sul, Brazil (28 ° 59 'S, 53 ° 14' W, 345 m elevation). After collected, the straw was air-dried for 20 days. To determinate chemical composition, a straw sample was dried at 40°C for 48 h in a forced-air oven to a constant weight then ground in a ball mill. The soluble (SOL), cellulose (CEL), hemicellulose (HEM), and lignin (LIG) fractions of the straw were determined by proximate analysis using Van Soest method described by Redin et al. (2014). Another subsample was oven-dried at 65 °C for 48 h and finely ground in a ball mill for the determination of the C and N contents using an elemental analyzer (FlashEA 1112, ThermoFinnigan, Milan, Italy). The chemical composition of sugarcane straw at the beginning of experiment were SOL 228 g kg<sup>-1</sup>, CEL 372 g kg<sup>-1</sup>, HEM 335 g kg<sup>-1</sup>, LIG 65 g kg<sup>-1</sup>, C 425 g kg<sup>-1</sup>, N 8 g kg<sup>-1</sup> and C:N ratio 53.

#### 4.3.3 Straw C and N measurement

Microplots delineated by open-wooden frame (40 cm length, 40 cm width and 8 cm height) were installed between cane rows and the air-dried straw and urea-N calculated to be equivalent to the area of each microplot. The microplots were placed in the plots of six straw treatments: 4S, 4S+N, 8S, 8S+N, 12S and 12S+N. The bottoms of the wooden frames were delimited with 2-mm nylon mesh, while the tops of wooden frames were closed with 10-mm plastic screen mesh in order to prevent straw loss by wind and allow access for soil macrofauna, as described by Dietrich et al. (2017).

Straw dry matter, C and N measurements were made at 0, 15, 36, 51, 72, 103, 168, 238, 298 and 360 days after straw application. One microplot was destroyed by treatment at each measurement date, with 4 replicates. Straw sample was oven-dried at 65°C for 48 h and

separated from adhering soil by dry cleaning, then a sub-sample was finely grounded in a ball mill for the determination of the C and N content using an elemental analyzer (Flash EA 1112, Thermo Electron Corporation, Milan, Italy).

#### 4.3.4 N<sub>2</sub>O and CO<sub>2</sub> measurement and analyses

Soil N<sub>2</sub>O and CO<sub>2</sub> emitted were measured during 365 days after start of the experiment. Soil N<sub>2</sub>O and CO<sub>2</sub> were measured using a static chamber method (Mosier, 1998). In each experimental plots, prior to straw application, a galvanized steel rectangular base (70 cm length, 40 cm width and 10 cm height) was installed perpendicular to a cane row and inserted into the soil (5 cm) for gas measurements and the bases were left in place for the whole experimental period. For each treatment, the straw levels and urea dose were calculated to be equivalent to the area of each base. To measure soil-surface N<sub>2</sub>O and CO<sub>2</sub> flux an insulated, fan-mixed, non-flow-through and non-steady-state chamber (70 cm length, 40 cm width and 20 cm height) was placed on the base. In each measurement, the chamber was placed between 09:00 and 11:00 hours to represent the daily soil N<sub>2</sub>O and CO<sub>2</sub> flux. The measurements were performed before rainfall and the morning after rainfall in two to three times per week during the first month following straw and urea applications and less frequently thereafter. During chamber deployment, air samples were taken at 18-min intervals (t<sub>0</sub>, t<sub>18</sub> and t<sub>36</sub>) using a 20-mL polypropylene syringe fitted with a three-way stopcock and immediately transferred to 12-mL pre-evacuated glass vials. All samples were analyzed at the Federal University of Santa Maria, Rio Grande do Sul, Brazil, using gas chromatographer Shimadzu GC-2014 (Shimadzu Co., Columbia, MD, USA). Air samples were analyzed for N<sub>2</sub>O and CO<sub>2</sub> concentration within 7d. The chromatographer was equipped with a packed column, an electron capture detector to analyses N<sub>2</sub>O and CO<sub>2</sub> gas.

#### 4.3.5 Soil measurements

Soil water content was monitored using sensors with two 30-cm-long stainless steel rods (FDR CS 616-L, Campbell Scientific, Logan, Utah, USA) inserted horizontally at 2.5 and 7.5 cm depth. The type T copper-constantan thermocouple was installed on soil surface and at 2.5 and 7.5 cm depth to measure soil temperature. Both sensors were coupled to a datalogger (CR1000, Campbell Scientific, Logan, Utah, USA) and measurements were done at a 10 min sampling interval. The water-filled pore space (WFPS) in the 0-5 and 5-10 cm soil layer was estimated by dividing the volumetric water content by the total soil porosity determined from the bulk

density. Soil samples were collected from the surface layer (0–10 cm) 22 times during the experiment. Soil collection occurred frequently during the first month following straw and urea applications and less frequently thereafter, but were always collected on days that had a GHG measurement. Soil samples consisted of six randomly distributed sampling points in each 22.4 m<sup>2</sup> plots and were collected using a stainless steel auger (3 cm diameter). Inorganic N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) was extracted by shaking 20 g of field-moist soil in 80 mL of 1M KCl solution for 30 minutes. After decantation for 30 min, the supernatant of the solution was filtered and kept frozen until analysis. NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were quantified by distillation with sequential addition of MgO and Devarda's alloy, respectively, and titration with H<sub>2</sub>SO<sub>4</sub> (Keeney & Nelson, 1982). Gravimetric soil moisture content was determined by oven drying (105°C for 24 h).

#### 4.3.6 Calculation and statistical analysis

Soil N<sub>2</sub>O and CO<sub>2</sub> fluxes were calculated considering the variation of the gas concentrations inside the chamber during the period that stay closed, the volume of the chamber, the area of soil occupied by base and the molecular weight of the N<sub>2</sub>O and CO<sub>2</sub> gas (Jantalia et al., 2008). The molar volume of the gas was corrected for the temperature inside the chamber measured at the time of each sampling. The daily N<sub>2</sub>O and CO<sub>2</sub> flux was calculated by linear interpolation and the cumulative flux obtained by the integration of the daily averages. The N<sub>2</sub>O emission factor (EF) due to input of N from crop residue and the application of urea-N were calculated using methodology described in Guidelines for National Inventories of Greenhouse Gases (IPCC, 2006). EF from N released by crop residue decomposition was calculated by the difference in the cumulative N<sub>2</sub>O from the treatments with different amounts of straw after discounting the value for bare soil and divided by straw N released after one year of decomposition.

All data were submitted to analysis of variance (ANOVA) and the interactions among straw and N were tested. The means of each treatment were compared by the LSD test at the 5% probability level. For the cumulative N<sub>2</sub>O-N at the different levels of straw a linear regression was fitted. The data were processed using the SISVAR software (Ferreira et al, 2013).

The N<sub>2</sub>O emissions from each straw quantity, soil variables, CO<sub>2</sub> emission and straw C remaining were subjected to multivariate analysis (principal component analysis, PCA) using Statistica® software (version 7.0). PCA was performed to address the variables that drive N<sub>2</sub>O emissions. PCA was performed on the correlation matrix obtained from the results of soil temperature and WFPS (0-10 cm), soil NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> content, CO<sub>2</sub> and N<sub>2</sub>O fluxes and C

remaining in sugarcane straw. Only correlation coefficients ( $r$ ) above 0.50 between variables and ordination axes were considered significant. Correlation between  $N_2O$  and variable drivers of  $N_2O$  emission were considered significant at  $P < 0.05$ .

## 4.4 RESULTS

### 4.4.1 Soil environmental conditions and WFPS

The cumulative rainfall during the one-year experiment was 1487 mm and the mean daily air temperature was 18 °C. From time of straw application to date of fertilization (day 52), water-filled pore space (WFPS) varied between 25.9 and 68.9% in the 0-5 cm soil layer and, between 40.8 and 71.6% in the 5-10 cm soil layer. From day 52 to day 120, WFPS varied between 11.7 and 61.8% in the 0-5 cm soil layer and between 24.1 and 66.7% in the 5-10 cm soil layer. Our results showed that during the whole experimental period, WFPS was different for the different straw treatments (Fig. 1b-c): during the drying periods, soil with lower amounts of straw on surface (0S and 4S) dried significantly faster compared to other treatments ( $p < 0.05$ ), leading to an average higher WFPS with higher amount of straw. This tendency was observed until the end of experiment. Soil temperature varied between about 20.5 to 35°C in the 0-5 and 5-10 cm layers during the year. Treatments with lower amounts of straw had the highest soil temperatures at soil surface and in the 0-5 cm soil layer (0S = 4S > 8S = 12S), with a mean difference of 2.0 and 1.6°C, respectively during the 0-68-day period. After day 68, we did not observed differences in soil temperature between treatments, which we attribute to the development of the sugarcane canopy, which decreased the relative effect of mulch layer.

### 4.4.2 Dynamics of straw-C and N

At the start of experiment, straw-C left on the soil represented 1.56, 3.13 and 4.69 Mg C ha<sup>-1</sup> for 4, 8 and 12 Mg DM ha<sup>-1</sup> of straw (Fig. 2a), respectively, and a mulch thickness of 1.91, 3.62 and 4.69 cm. During the 0-52-day period, before fertilizer-N application, straw-C decreased quickly for 4S, 8S and 12S treatments, and C loss represented, on average,  $37.6 \pm 2.0$  % of initial C, without significant difference between straw levels, indicating that the loss of straw-C was proportional to the initial amount. At day 52, just before N application, the remaining straw-C on soil was 0.94, 1.99 and 2.98 Mg C ha<sup>-1</sup> in 4S, 8S and 12S treatments, respectively. Until the end of the experiment, we did not found any significant difference in C loss between treatments with and without N applied. After one year of experiment, C loss from mulch

represented  $72.1 \pm 2.2$ ,  $73.9 \pm 2.7$  and  $78.0 \pm 4.2$  % of initial straw-C for the 4S, 8S and 12S treatments, respectively.

Straw-N content at the beginning of experiment was 29.5, 59.0 and 88.4 kg N ha<sup>-1</sup> for 4, 8 and 12 Mg DM ha<sup>-1</sup> of straw, respectively (Fig. 2b). During the 0-36 days period, a fast decrease in straw N was observed, in parallel to straw C. In one year of experiment, straw-N loss differed significantly between straw levels with slightly slower loss with lower straw levels. Total straw-N loss represented  $50.2 \pm 6.1$ ,  $52.7 \pm 4.4$  and  $58.2 \pm 8.5$  % of initial straw N for the 4S, 8S and 12S treatments, respectively.

#### 4.4.3 Soil mineral N

Very little amount of mineral N was found into the soil in the treatments without N, on average, 1.9 kg NH<sub>4</sub><sup>+</sup>-N ha<sup>-1</sup> and 1.8 kg NO<sub>3</sub><sup>-</sup>-N ha<sup>-1</sup>, with no difference between straw levels (Fig. 3a, b). This low level persisted until the end of experimental year. In plots receiving N fertilization, a higher amount of mineral N was observed after urea application, as expected, with significant differences between straw treatments (Fig. 3a, b). The highest NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N content were observed in soil between day 52 and day 129, with significantly more NH<sub>4</sub><sup>+</sup>-N in the soil when the mulch was thinner. Even we observed an increase in NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N content in soil soon after N applied, the highest peak was observed at day 65 only. For 0+S treatment, NH<sub>4</sub><sup>+</sup>-N content in soil remained significantly higher compared to others treatments until day 129. Peak of NO<sub>3</sub><sup>-</sup>-N occurred also at day 65 and decreased rapidly afterwards for all fertilized treatments. After day 129, no difference in soil NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N content were found between treatments with N.

#### 4.4.4 Soil N<sub>2</sub>O and CO<sub>2</sub> emissions

##### 4.4.4.1 Without fertilizer-N application

From sugarcane harvest to date of fertilizer-N application (0-52-day period), the different amounts of straw influenced strongly the N<sub>2</sub>O and CO<sub>2</sub> emitted from soil (Fig. 4). During this period, N<sub>2</sub>O fluxes fluctuated from 0.84 to 14.6 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup> depending of the days and treatments (Fig. 4a). In general, we observed lower N<sub>2</sub>O emitted with lower amount of straw (0S < 4S < 8S < 12S), and this pattern persisted until day 65. The highest N<sub>2</sub>O fluxes occurred between day 9 and day 34 in the 8S and 12S treatments, corresponding to rainfall events and an increase in WFPS (Fig. 1) with differences between straw levels (Fig. 4). From day 65 until

day 365, N<sub>2</sub>O emissions remained low for the 0S, 4S, 8S and 12S treatments, with a mean of 0.8 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup>, and not significantly different whatever the amount of straw. The same pattern was observed for CO<sub>2</sub> emissions. During the 0-52-day period, CO<sub>2</sub> fluxes were immediately high, and ranked generally as 12S=8S > 4S=0S (Fig. 4b), but with quite large variations for each treatments between days of measurements.

#### 4.4.4.2 After fertilizer-N application

After application of urea on straw plots on day 52, N<sub>2</sub>O emitted became much higher compared to no-fertilized plots (Fig. 4). In fertilized-N treatments (0S+N, 4S+N, 8S+N, 12S+N), N<sub>2</sub>O emissions varied from 1.1 to 23.8 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup> between day 52 and day 80 and the different amounts of straw modified the N<sub>2</sub>O emissions, with 0S+N < 4S+N < 8S+N < 12S+N (Fig. 4a). We observed that the highest N<sub>2</sub>O flux after fertilizer-N application was triggered also by rainfall events. During twelve days after N application, rainfall did not occurred (Fig. 1), and our results showed the lowest N<sub>2</sub>O emission. A part of this period, overall higher N<sub>2</sub>O flux were well related to higher WFPS with 12S+N ≥ 8S+N > 4S+N ≥ 0S+N (Fig. 1b-c). After day 120, N<sub>2</sub>O flux returned to basal levels and did not differ significantly from 0S, 4S, 8S and 12S treatments. CO<sub>2</sub> emissions were lower after N applied and showed a high discrepancy between treatments (Fig. 4b).

#### 4.4.5 Drivers of N<sub>2</sub>O emissions

For the 0-65-day period in treatments without urea-N application, when the highest N<sub>2</sub>O fluxes occurred in the presence of straw, PCA showed that the first two principal components accounted for 58% of the variance in the data (Fig. 6a). The first component (PC1) was negatively related to soil temperature (-0.81) and positively related to N<sub>2</sub>O (0.79), WFPS (0.76) and straw-C (0.69). For the second component (PC2), a positive relation of NH<sub>4</sub><sup>+</sup> (0.69) and NO<sub>3</sub><sup>-</sup> (0.62) was observed. The N<sub>2</sub>O emission was negatively related to soil temperature (-0.45) and positively related to WFPS (0.70) and straw-C (0.53). The 52-120-day period was meaningful for N<sub>2</sub>O emissions linked to N fertilization. Over this period, PCA showed that the first two principal components accounted for 69% of the variance in the data (Fig. 6b). The first component (PC1) was negatively related to N<sub>2</sub>O emission (-0.50), CO<sub>2</sub> emission (-0.84), soil temperature (-0.69), soil NH<sub>4</sub><sup>+</sup> (-0.63) and NO<sub>3</sub><sup>-</sup> (-0.79) content and positively related to WFPS (0.60). For the second component (PC2), a positive relation of N<sub>2</sub>O (0.64), WFPS (0.66) and straw-C (0.81) was observed. The N<sub>2</sub>O emission was positively related to CO<sub>2</sub> emission (0.37), straw-C (0.50) and NO<sub>3</sub><sup>-</sup> content (0.54).

#### 4.4.6 Cumulative N<sub>2</sub>O emission and Emission factor (EF)

Cumulative N<sub>2</sub>O emission differed significantly between straw treatments with 12S > 8S > 4S > 0S (Fig. 5). For these treatments, cumulative N<sub>2</sub>O varied from 436.9 (0S) to 766.8 (12S) g N<sub>2</sub>O-N ha<sup>-1</sup> and was linearly correlated to the initial amount of straw at the soil surface (Table 1). Similar response was observed for treatments + N, which cumulative N<sub>2</sub>O emission increased from 510 (0S+N) to 1055 (12S+N) g N<sub>2</sub>O-N ha<sup>-1</sup>, again with 12S+N > 8S+N > 4S+N > 0S+N (Fig. 5) and were strongly linearly correlated to the initial straw levels on soil surface (Table 1). On average, straw contribution to total N<sub>2</sub>O emitted by fertilized treatments, represented 70% of the emitted N<sub>2</sub>O during the year.

Although the effect of increased straw quantity on increased N<sub>2</sub>O emission was not statistically different with and without fertilizer (i.e., no interaction between straw and N fertilizer), due to large variability in N<sub>2</sub>O measurements, a clear trend was observed of a greater relative increase in N<sub>2</sub>O emissions with urea-N application for the largest straw quantities (12S+N and 8S+N). Taking the mean of the 0N and 100N treatments, the relationships between straw level and N<sub>2</sub>O emitted ( $y = 450.19 + 37.48x$ ,  $R^2 = 0.97$ ) indicated that for each extra Mg straw DM, 37.5 g N<sub>2</sub>O-N ha<sup>-1</sup> extra N<sub>2</sub>O emitted.

Emission factor (EF) from crop residue-N and urea-N varied according to straw levels and increase proportionally to straw quantity left on the soil surface. When crop residue EF was calculated as a function of actual residue-N released over one year, using the observed kinetics of remaining straw-N, EF values increased compared to standard IPCC calculation, as expected. On average, EF values differed for urea and straw N sources with lower EF from urea-N compared to total straw N or released straw N.

## 4.5 DISCUSSION

Crop residues are essential to maintain the sustainability of soils. However, the benefits of keeping crop residue as mulch after crop harvest can be lost with indiscriminate harvest of residue to produce bioenergy (Cherubin et al., 2018; Stavi et al., 2016). The balance between recycling and removal of crop residues and their impact on GHG balance is not fully understood, especially for sugarcane production system (Carvalho et al., 2017).

### 4.5.1 Effects of straw on N<sub>2</sub>O emissions

The presence of sugarcane straw had a major impact on N<sub>2</sub>O emissions from soil. Our study showed, in a quasi-linear relationship, a direct correlation between N<sub>2</sub>O emissions from soil

and the amount of straw on soil surface with a striking fact that increasing quantity of mulch raised N<sub>2</sub>O emissions. These results were especially observed in the period following immediately sugarcane harvest and recycling of sugarcane straw, without N fertilizer and while the mineral N concentration in the top soil was low. In this period, N<sub>2</sub>O emissions were closely correlated to WFPS and straw-C availability. First our study showed a strong relationship between the different amounts of straw on soil surface and soil moisture and WFPS, mainly during periods with lack of rain, where the straw layer limited evaporation and therefore slowed down soil drying (Hu et al., 2018). Similar results were obtained by Vargas et al., (2014) with sugarcane straw under laboratory conditions and Schaufler et al., (2010) in European soils under different land use which observed a positive correlation of N<sub>2</sub>O emission and soil moisture. Many studies (e.g., Bateman and Baggs, 2005; Davidson et al., 2000) observed that higher N<sub>2</sub>O emissions from soil occurred at WFPS between 50 to 70%, which influence O<sub>2</sub> availability to microbial activity in soil. Furthermore, one indirect effect of mulch on water dynamics in soil is the impact on soil temperature, which modified evaporation rates between straw levels (Fu et al., 2018). In general, our results showed a widely temperature range (between 09:00 and 11:00, time of N<sub>2</sub>O measurements) in soil with lower amounts of straw (0S and 4S) which varied from 21 to 35°C, whereas for the 8S and 12S treatments, the maximum temperature did not exceed 30°C while to 8S and 12S, confirming the role of the mulch as a buffer against climate fluctuations in soil. In addition, lower straw quantity (0S and 4S) had less soil coverage (visual confirmation), which implies in a higher quantity of soil became exposed. This allied to highly temperature range for 0S and 4S could lead to an increase of evaporation rates which reflected in lower soil water content in these treatments. Thus, our results suggest that straw acted as a buffer for temperature changes and preserved soil moisture, especially after higher rainfall events followed by drying periods, which contributed to N<sub>2</sub>O emissions from soil.

The presence of straw not only affected soil water and temperature dynamics, and the major impact was probably related to the recycling of C and N in the soil, although the contributions of the various drivers cannot be quantified separately. The release of labile straw-C and N from straw become a substrate for growing aerobic microorganisms, which results in a fast consumption of O<sub>2</sub>, and raise “hot moments” and “hot spots” of N<sub>2</sub>O emissions in soils, particularly in straw mulches or at the soil-straw interface (Kravchenko et al., 2017; Pugesgaard et al., 2017). C availability raises heterotrophic microbial activity that leads to increased denitrification potential, fast consumption of O<sub>2</sub> and favor denitrification process (Butterbach-Bahl et al., 2013; Chen et al., 2013). Several authors recently highlighted the importance of N<sub>2</sub>O losses directly linked to crop residues management and in the absence of fertilization

(Chen et al., 2013; Guzman et al., 2015; Pugesgaard et al., 2017; Shan and Yan, 2013). The conditions of this scenario had been met in the treatments without N applied, resulting in an increase in emissions proportional to the amount of straw back to the soil. A fast release of straw-N and C was observed during the first 7 weeks of experiment, with almost 35% of initial straw-N and C lost prior to fertilizer-N application, which can be explained by the initial composition of the straw. The impact of the amount of crop residues or of their chemical quality on N<sub>2</sub>O emissions has not been systematically observed. In their meta-analysis, Shan and Yan (2013) showed a negatively correlation between emissions of N<sub>2</sub>O from soil with crop residues in mulch at the soil surface and the C:N ratio of these residues, confirming that the N richness of crop residues influences N<sub>2</sub>O emissions. In sugarcane systems with a straw C:N ratio similar to that of this study, Siqueira Neto et al., (2016) and Vasconcelos et al., (2018) did not observed significant difference in N<sub>2</sub>O emissions with different quantities of sugarcane straw. However, as discussed previously, favorable conditions of moisture and temperature allied to the fast decomposition observed in our study could explain the response observed. Overall our study, showing that 70% of the N<sub>2</sub>O emitted over one year with fertilized sugarcane was attributed to the crop residues, confirmed recent studies underlying the importance of post-harvest periods for high N<sub>2</sub>O emissions and the role of crop residue management (e.g., Peyrard et al., 2017; Rezaei Rashti et al., 2017; Tongwane et al., 2016). This is particularly true in situations with perennial or semi-perennial crops and no-tilled arable systems, where crop residues are left at the soil surface, enhancing favorable conditions of emissions at the soil-straw interface (Peyrard et al., 2017; Shan and Yan, 2013; Vasconcelos et al., 2018).

#### 4.5.2 N<sub>2</sub>O emissions from fertilizer and interaction with straw

The input of synthetic N fertilizers is recognized as the main source in N<sub>2</sub>O emissions from agricultural soils (Smeets et al., 2009), which can be enhanced by the presence of crop residues on soil surface (Jin et al., 2014), however, the linkage between synthetic-N fertilizer and crop residues are not fully understood (Chen et al., 2013). Our results showed clearly that an increasing amount of straw on soil surface combined with a single quantity of fertilizer-N applied (100 kg N ha<sup>-1</sup>) raised fertilizer-derived N<sub>2</sub>O emission. However, all peaks of N<sub>2</sub>O observed were lower compared to other studies with sugarcane (Carmo et al., 2013; Siqueira Neto et al., 2016) and other crops (Basche et al., 2014; Muhammad et al., 2011) and at the end of the year, only 30% of the total N<sub>2</sub>O emitted could be attributed to the application of the fertilizer.

The lower emissions observed in our study could be explained by several factors. First, we observed that the mulch layer of crop residues acted as a physical barrier at time of urea application, and prevented fertilizer-N from reaching the soil (Pinheiro et al., 2018, submitted). In our study, this effect was enhanced by increasing thickness of the mulch and by the lack of rain observed during twelve days after N application. Secondly,  $\text{NH}_3$  losses were higher after urea application and raised with increasing amount of straw (Pinheiro et al., 2018, submitted), reducing the quantity of N recovered in soil and susceptible to be lost as  $\text{N}_2\text{O}$ . Lastly, the straw-C loss after N fertilization were almost four times less than what was observed before N applied, and C availability is one of the most limiting factor for denitrification process (Vargas et al., 2014). Despite the lower input of straw-C after N fertilization, a correlation between straw-C and soil  $\text{N}_2\text{O}$  emissions ( $r = +0.5$ ) were still observed and confirmed by PCA analysis.

$\text{N}_2\text{O}$  emissions are the result of microbial processes such as nitrification and denitrification (Domeignoz-Horta et al., 2018) which are enhanced, principally, by N application (Fracetto et al., 2017; Miller et al., 2008).  $\text{N}_2\text{O}$  production in soil during nitrification is traditionally considered to be minor in comparison with denitrification, however in WFPS below 60% nitrification became the major process in  $\text{N}_2\text{O}$  emissions from soil (Bateman and Baggs, 2005). Our results showed an increase in  $\text{N}_2\text{O}$  fluxes after N application followed by an increase of soil  $\text{NO}_3^-$  content at low WFPS (<60%) suggesting that nitrification in soil during this period was the main process involved in the  $\text{N}_2\text{O}$  production. This hypothesis is supported by PCA analyses, which showed a positive correlation between soil  $\text{NO}_3^-$  content and  $\text{N}_2\text{O}$  emissions after N fertilization ( $r = +0.54$ ). At the first rainfalls after N application,  $\text{N}_2\text{O}$  fluxes increased again even with WFPS remaining below 60%, reinforcing that nitrification was the main  $\text{N}_2\text{O}$  producing process. However, the presence of C through the straw also contributed to a decrease in soil  $\text{O}_2$  availability by increased microbial activity. Therefore, the combination of WFPS around 60% after rain events and microbial activity during straw decomposition may have favoured  $\text{N}_2\text{O}$  production by denitrification due to appearance of anoxic spots, mainly present at the soil-straw interface. In summary, our findings indicate that mulching provided favorable soil conditions for both nitrification and denitrification process which could happen simultaneously. The denitrifying community were favored by the reactive-N supply ( $\text{NO}_3^-$ ) resulting from nitrification and  $\text{O}_2$  consumption from microorganisms after N fertilization.

#### 4.5.3 Emission factors for fertilizer N and straw N

As a consequence of the cumulative  $\text{N}_2\text{O}$  emissions calculated over the full year of sugarcane growing cycle, the quantity of sugarcane straw on soil surface had a strong effect on the

emission factors calculated in our study, regardless the N source concerned. However, the EF from urea N and crop residue N inputs calculated in our study were lower than the IPCC default value of 1% (IPCC, 2014). Our results showed that the emission factor from crop residue is highly influenced by management (12S > 8S > 4S > 0S) in both residue-N added and residue-N released EF calculated, suggesting the limits of a standard IPCC default value based only on total N inputs. In addition, we showed a higher contribution from crop residue in N<sub>2</sub>O emissions from soil that compared to N fertilizer.

Several studies brought a wide range of “regional” EF in sugarcane fields for fertilizer N that is influenced by the presence of sugarcane straw at the time of N fertilization. The EF from fertilizer-N range from 0.07-0.29 % in our study, to 21% in sugarcane fields in Australia (Allen et al., 2010; Carmo et al., 2013; Denmead et al., 2010; Siqueira Neto et al., 2016). These large variations probably is a result from the difficulty to distinguish the contribution of crop residue and of mineral N to N<sub>2</sub>O emissions from soil which reflects the actual effects of biological factors, soil type, agricultural systems and environmental conditions on soil N<sub>2</sub>O emissions. Our results can help to reduce the variance of the values from IPCC indicating effect of mulch presence and the amount of straw on crop residue EF.

#### 4.5.4 Consequences for crop residue management in sugarcane areas

To analyze the favorable and unfavorable agricultural and environmental effects of straw removal in agricultural areas and to balance them, it is necessary to have a full view of the impacts resulting from this practice. Our study showed clearly that in our experimental conditions, N<sub>2</sub>O emissions increased with increasing amount of straw left on the soil, in other words, N<sub>2</sub>O emissions from soil could be reduced by straw removal in such cropping systems, even if in this study, overall, N<sub>2</sub>O emissions were low. However, extensive removal of straw for bioenergy production could lead also to strong impact in the long term, accelerating the depletion of C and N stocks, and therefore organic matter in the soil, reducing both the fertility of soils, and the mitigation of climate change promoted by soil C sequestration (Bordonal et al., 2018; Cherubin et al., 2018; Stavi et al., 2016). In addition, the recycling of straw returns considerable amount of N which becomes available to the plants after direct decomposition or via mineralization of soil organic matter, and by turn reduce the needs of N inputs via synthetic fertilizer (Meier and Thorburn, 2016), the main source of N<sub>2</sub>O emissions in agriculture (Smith et al., 2007; Guzman et al., 2015). Our results bring a new point of view that helps in the decision-making of how much sugarcane straw could be removed from the field without affect the balance between recycling or removal of crop residues and the impact on GHG balance.

#### 4.6 CONCLUSION

This study showed a strong effect of leaving crop residues as mulch at the soil surface after sugarcane harvest, via an enhancement of N<sub>2</sub>O emissions, with two “hot moments” for emissions, after sugarcane harvest and after fertilizer urea application. Mulches of increasing masses favored environmental conditions for emissions, through nitrification and denitrification which could happen simultaneously, although microbial processes were not measured directly in this study. The differences in N<sub>2</sub>O emissions were fostered by the placement of crop residues as mulch at the soil surface, which modified physical processes, indicating that not only total N inputs but also agricultural management should be considered when estimating GHG emissions. In such experimental and climatic conditions, the crop residues were by far the main source of emitted N<sub>2</sub>O over the year, indicating the need for better understanding and accurate quantification of this N source in GHG national inventories. Our results combining the C and N dynamics of crop residues and the measurement of N<sub>2</sub>O losses, brings an understanding about the various impacts of crop residue removal and could help establish an overall of GHG that raise the sustainability of sugarcane scenario.

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### Figure captions

Figure 1. Mean daily air temperature and rainfall (a), WFPS in 0-5 cm soil layer (b), WFPS in 5-10 cm soil layer (c), temperature on soil surface (d), soil temperature in 0-5 cm soil layer (e) and soil temperature in 5-10 cm soil layer (f) in first sugarcane ratoon.

Figure 2. Dynamics of straw-C (a) straw-N (b) on soil from harvest of sugarcane and during one year, with different initial amounts of straw added as mulch on soil, 4 (4S), 8 (8S) and 12 Mg DM ha<sup>-1</sup> (12S). Fertilizer-N (urea) was applied on day 52. Vertical bar represents standard deviation. The data are the mean between treatments with and without fertilizer N and of four replicates per treatment and per date of sampling.

Figure 3. Soil NH<sub>4</sub><sup>+</sup> (a) and NO<sub>3</sub><sup>-</sup> (b) in the 0-10-m soil layer after 100 kg urea-N ha<sup>-1</sup> (N) application over the different straw (S) rates (0, 4, 8 and 12 Mg ha<sup>-1</sup>) in the first ratoon cane.

Figure 4. N<sub>2</sub>O-N flux (b) and CO<sub>2</sub>-C flux (c) in the first ratoon sugarcane, with or without application of 100 kg urea-N ha<sup>-1</sup> (+N) over the different straw (S) rates (0, 4, 8 e 12 Mg ha<sup>-1</sup>) at day 52. Vertical bar represents the least significant difference (LSD) between treatments (P < 0.05).

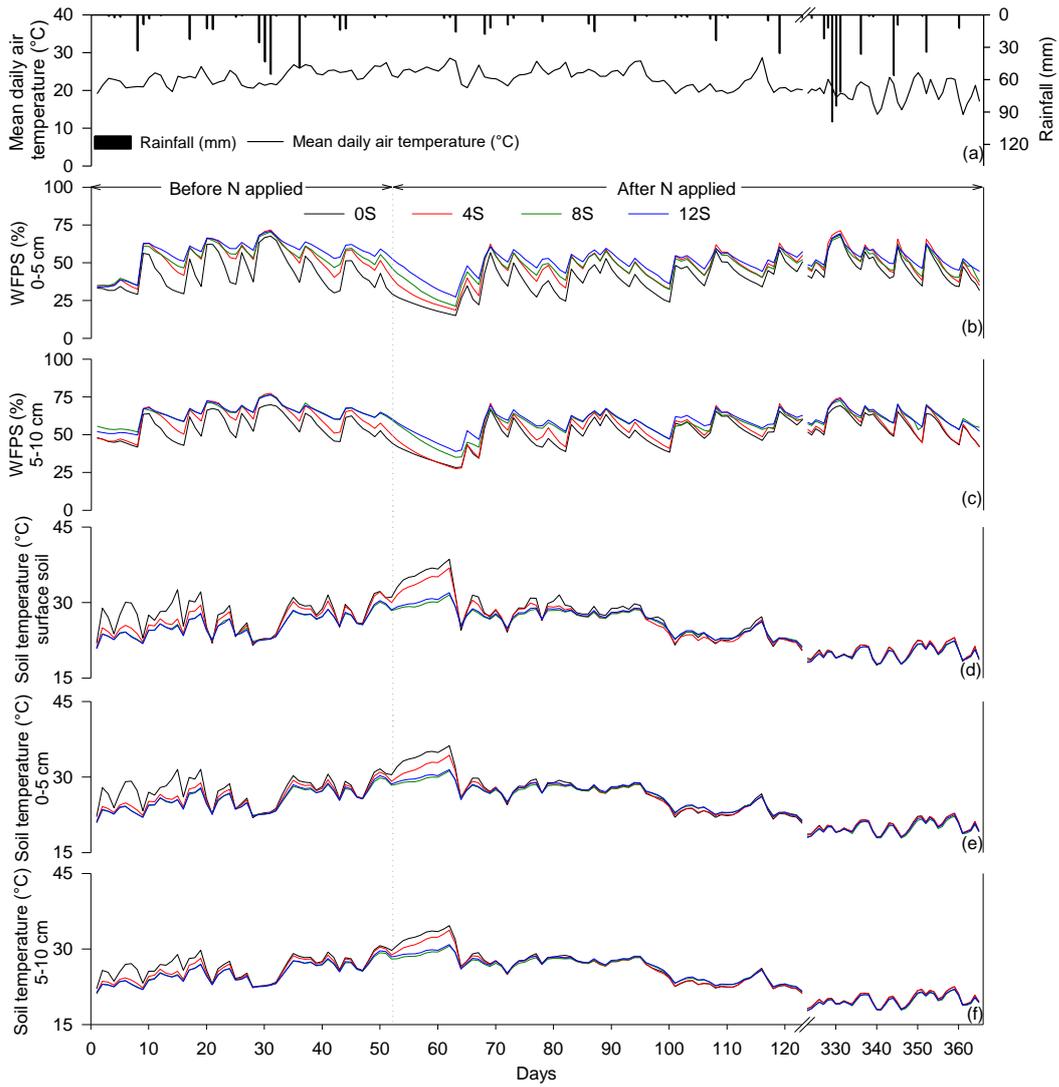
Figure 5. Cumulative N<sub>2</sub>O emission during the first ratoon sugarcane (365 days) after application of different straw (S) amounts (0, 4, 8 and 12 Mg ha<sup>-1</sup>) with and without 100 kg urea-N ha<sup>-1</sup> (+N). Vertical bar represents the least significant difference (LSD) between treatments (P < 0.05).

Figure 6. Principal component analysis (PCA) of 0-65-day period in treatments without urea-N application (a) and 52-120-day period in treatments with urea-N application (b) for N<sub>2</sub>O fluxes from soil and soil-straw variables: nitrate – NO<sub>3</sub><sup>-</sup>, ammonium – NH<sub>4</sub><sup>+</sup>, water-filled pore space – WFPS, soil CO<sub>2</sub> fluxes, soil temperature – T°C and straw-C content in the first ratoon sugarcane, with or without application of 100 kg urea-N ha<sup>-1</sup> over the different straw (S) rates (0, 4, 8 and 12 Mg ha<sup>-1</sup>).

Table 1. Cumulative N<sub>2</sub>O-N emission in the first ratoon sugarcane with and without urea-N for the different straw (S) rates (0, 4, 8 and 12 Mg ha<sup>-1</sup>) and emission factor. Emission factor was calculated as a function of total straw N added (a) and straw N released during decomposition (b).

	<b>Straw level (Mg ha<sup>-1</sup>)</b>				<b>Regression</b>
	0	4	8	12	
<b>Urea (kg N ha<sup>-1</sup>)</b>	<b>Cumulative N<sub>2</sub>O-N (g ha<sup>-1</sup>)</b>				
0	436.9	488.4	696.7	766.8	$y = 417.5 + 29.9 x$ , $R^2 = 0.94$
100	510.0	639.2	809.5	1054.7	$y = 482.7 + 45.1 x$ , $R^2 = 0.98$
	<b>Emission Factor (%)</b>				
Residue-N added <sup>a</sup>	-	0.16	0.28	0.34	$y = 0.0817 + 0.0225 x$ , $R^2 = 0.97$
Residue-N released <sup>b</sup>	-	0.33	0.54	0.60	$y = 0.2125 + 0.0347 x$ , $R^2 = 0.92$
Urea-N	0.07	0.15	0.19	0.29	$y = 0.0730 + 0.0170 x$ , $R^2 = 0.98$

\*significant differ with t test ( $p < 0.05$ ).



**Fig 1**

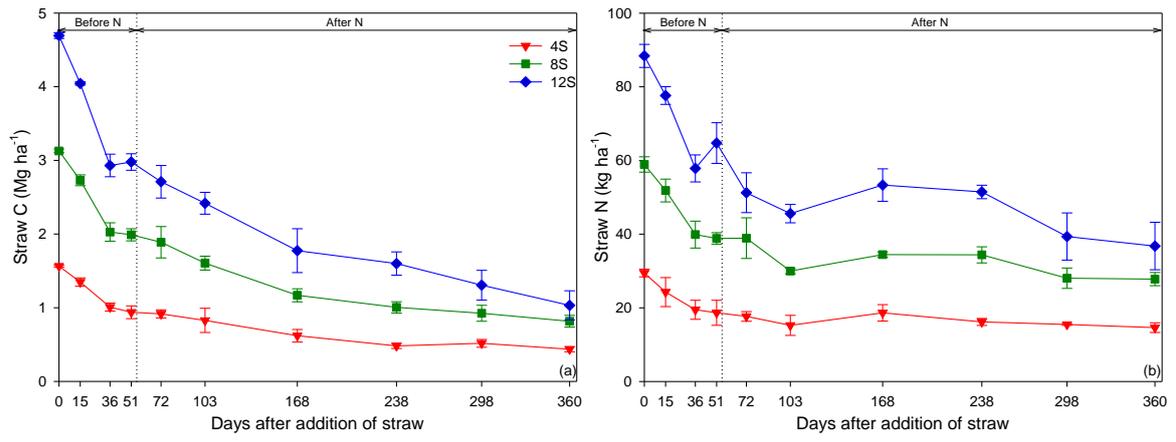
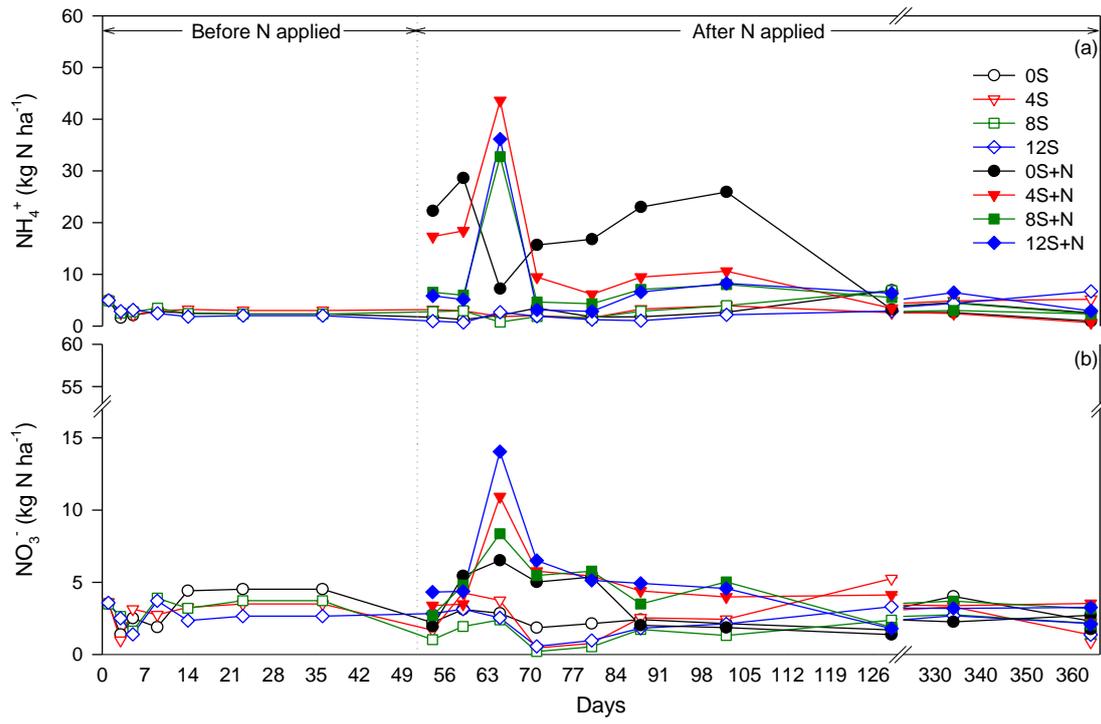
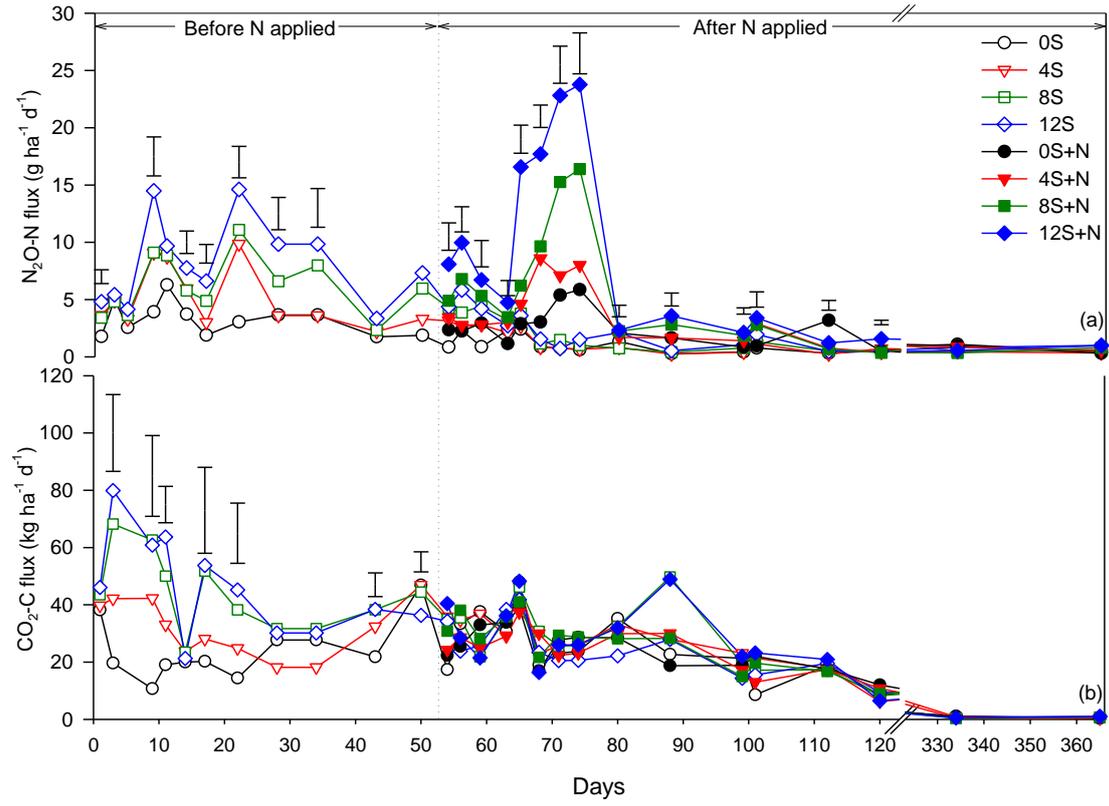


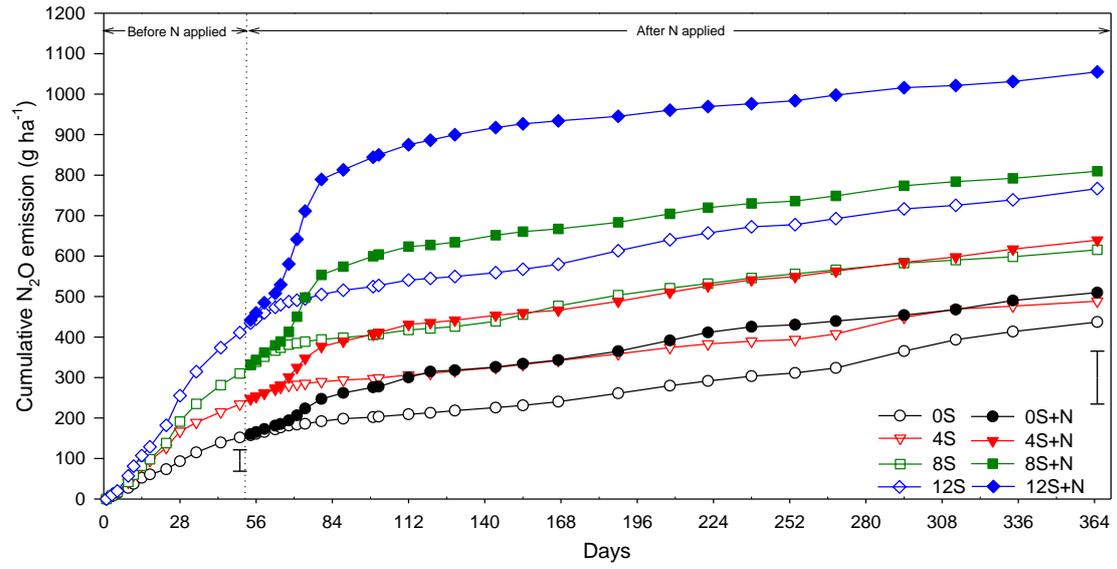
Fig 2



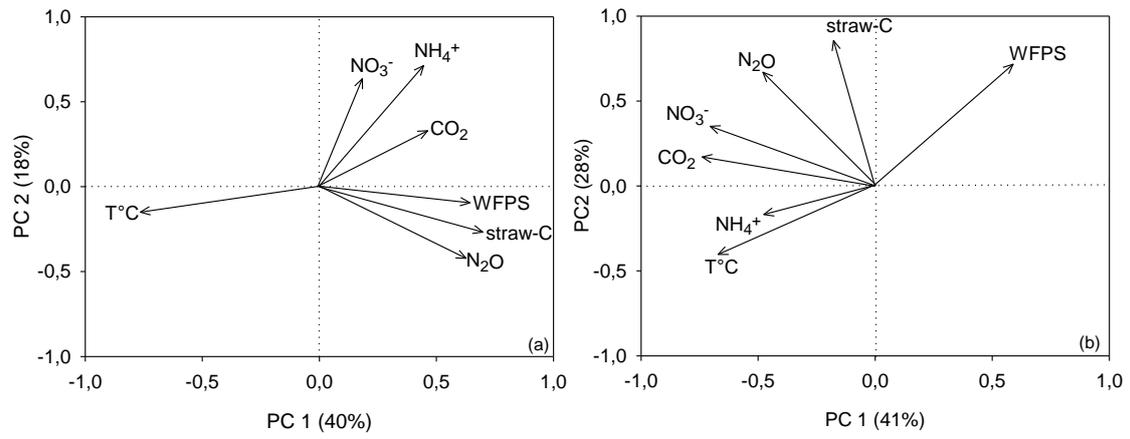
**Fig 3**



**Fig 4**



**Fig 5**

**Fig 6**

## 5 DISCUSSÃO GERAL

Os resultados apresentados nos artigos I e II evidenciam que a remoção parcial da palha de cana-de-açúcar após a colheita mecanizada reduz as perdas de N-ureia devido a redução das condições favoráveis para o processo de volatilização de amônia ( $\text{NH}_3$ ) e dos mecanismos que afetam os processos de nitrificação e desnitrificação do solo, responsáveis pela emissão de óxido nitroso ( $\text{N}_2\text{O}$ ).

A remoção da palha de cana-de-açúcar reduziu, quase linearmente, a perda de N- $\text{NH}_3$  ( $12 > 8\text{S} > 4\text{S} > 0\text{S}$ ), apesar da dinâmica e da quantidade de N volatilizado terem sido fortemente influenciadas pela distribuição e intensidade das chuvas após aplicação do N-ureia, nos dois anos de avaliação (27,6% para 9,2% em 2016 e 60,8% para 30,7% em 2017). A redução da volatilização de  $\text{NH}_3$  nas menores quantidades de palha foi diretamente relacionada a dois fatores: i) diminuição da barreira física criada pela palha; e ii) menor retenção de umidade pela palha e manutenção da umidade do solo; e indiretamente relacionada a um fator: diminuição na ação da enzima urease na palha.

A palha exerce uma barreira física que impede a percolação da ureia até o solo. A remoção da palha reduz essa barreira física e facilita a infiltração da ureia no solo. Essa hipótese foi comprovada nos dois anos de estudo. Em 2016, durante o período seco após aplicação do N-ureia, nas maiores quantidades de palha sobre o solo (12S e 8S) o conteúdo de  $\text{NH}_4^+$  na camada superficial do solo foi menor que nas menores quantidades de palha sobre o solo (4S e 0S), o que sugere a retenção da ureia na palha durante esse período. Em 2017, a chuva ocorreu no mesmo dia da aplicação do N-ureia, o que promoveu a imediata infiltração da ureia no solo. Entretanto, o conteúdo de  $\text{NH}_4^+$  na camada superficial do solo foi menor com o aumento da quantidade de palha sobre o solo. Além disso, o aumento dos conteúdos de  $\text{NH}_4^+$  e N solúvel em água da palha com o aumento das quantidades de palha sobre o solo, sugerem que a palha impediu a infiltração de parte da ureia no solo.

Além de impedir a infiltração da ureia, a capacidade de retenção de água pela palha e manutenção da umidade do solo (PERES; SOUZA; LAVORENTI, 2010; SILVA et al., 2012) são fatores fortemente ligados a volatilização de  $\text{NH}_3$  (MA et al., 2010). Isso se relaciona, principalmente, pela atividade da enzima urease ser regulada pela disponibilidade de água na palha e no solo (OTTO et al., 2017; ROCHETTE et al., 2009). Apesar de nesse estudo não ter sido realizada a análise de urease da palha, a presença de  $\text{NH}_4^+$  na palha indica a ação da enzima

urease em cada quantidade de palha. Portanto, fica evidente que parte da ureia foi hidrolisada na palha e resultou que parte da volatilização de  $\text{NH}_3$  ocorresse diretamente da palha. Dessa forma, a remoção da palha sobre o solo diminui a barreira física e a ação da enzima urease sobre a ureia, o que reduziu as perdas de  $\text{N-NH}_3$ . No contexto de uso da palha de cana-de-açúcar para a produção de bioenergia ou etanol de segunda geração, nossos resultados indicam que para cada  $4 \text{ Mg ha}^{-1}$  de palha de cana removida, a volatilização diminuiu em média  $9,5 \text{ kg de N ha}^{-1}$ .

As emissões de  $\text{N}_2\text{O}$  foram fortemente relacionadas com a presença de palha de cana-de-açúcar sobre o solo e ocorreram, principalmente, em dois “hot moments” de emissão de  $\text{N}_2\text{O}$ : i) após a colheita da cana-de-açúcar; e ii) após adubação nitrogenada. A remoção de palha de cana-de-açúcar reduziu as emissões acumuladas de  $\text{N}_2\text{O}$  nos tratamentos sem N de 766 (12S) para 437 (0S)  $\text{g N}_2\text{O-N ha}^{-1}$  ( $12\text{S} > 8\text{S} > 4\text{S} > 0\text{S}$ ) e nos tratamentos + N de 1055 (12S + N) para 510 (0S + N)  $\text{g N}_2\text{O-N ha}^{-1}$  ( $12\text{S}+\text{N} > 8\text{S}+\text{N} > 4\text{S}+\text{N} > 0\text{S}+\text{N}$ ). Em média, nos tratamentos + N, a palha contribuiu com 70% da emissão anual de  $\text{N}_2\text{O}$ . O fator de emissão (FE), independente da fonte de N utilizada para o cálculo, seguiu a mesma tendência que as emissões acumuladas de  $\text{N}_2\text{O}$ . De forma geral, a remoção da palha diminuiu o FE da palha de 0,34% em 12S para 0,16% em 4S e o FE do N-ureia de 0,29% em 12S + N para 0,07% em 0S + N. Além disso, as emissões indiretas de  $\text{N}_2\text{O}$  provocadas pela perda do N-ureia por volatilização de  $\text{NH}_3$  também reduzem com a remoção de palha apesar de quase dobrarem o FE do N-ureia (0,56% em 12S+N para 0,16% para 0S+N).

A presença da palha teve forte influência nos mecanismos que alteram os processos responsáveis pela emissão de  $\text{N}_2\text{O}$  do solo, i.e., nitrificação e desnitrificação. As maiores quantidades de palha (12S e 8S) apresentaram maior espaço poroso ocupado por água (EPSA) e umidade do solo comparado as menores quantidades de palha (4S e 0S). Essa resposta ficou mais evidente durante períodos com ausência de chuva. Hu et al. (2018) observaram que a presença de palha sobre o solo diminui as taxas de evaporação e preserva a umidade do solo. Além disso, maiores quantidades de palha no solo previniram grandes flutuações de temperatura no solo, o que diminui as taxas de evaporação do solo nas maiores quantidades de palha. Esses fatores resultaram em EPSA do solo em torno de 50 a 70%, valores em que pode ser observado as maiores emissões de  $\text{N}_2\text{O}$  do solo (BATEMAN; BAGGS, 2005; DAVIDSON et al., 2000).

Além do EPSA e temperatura do solo, outro fator determinante para a produção de  $\text{N}_2\text{O}$  é a disponibilidade de C e N para o crescimento microbiano (BUTTERBACH-BAHL et al.,

2013). Apesar das diferentes quantidades de C liberado pela palha nos dois “hot moments” de emissão de  $N_2O$  do solo, a relação entre C liberado e a emissão de  $N_2O$  permaneceu estreita e foi confirmada pela análise de PCA. No primeiro “hot moment” de emissão de  $N_2O$ , a rápida decomposição da palha e liberação de C e N observadas foram proporcionais a quantidade de palha sobre o solo, o que determinou as diferentes taxas de emissão de  $N_2O$  entre os níveis de palha. No segundo “hot moment”, apesar da baixa taxa de liberação de C pela palha foram observadas maiores taxas de emissão de  $N_2O$ , provavelmente pela adição de N-ureia ao sistema. A produção de  $N_2O$  do solo durante o processo de nitrificação geralmente é considerado menor que no processo de desnitrificação (BATEMAN; BAGGS, 2005). Entretanto, em condições de EPSA até 60%, o processo responsável pelas emissões de  $N_2O$  é a nitrificação (DAVIDSON et al., 2000). Após a aplicação de N-ureia, ocorreu aumento nas emissões de  $N_2O$  seguido por um aumento do conteúdo de  $NO_3^-$  no solo, evidenciando a importância do processo de nitrificação nas emissões de  $N_2O$  do solo. Apesar disso, parte do  $N_2O$  pode ter sido originado do processo de desnitrificação do solo, principalmente após a adubação nitrogenada. A liberação de C pela palha pode favorecer o crescimento microbiano e, portanto, um rápido consumo do  $O_2$  do solo. O EPSA de 60% após as chuvas e a redução de  $O_2$  do solo possibilita o surgimento de pontos anóxicos no solo que aliado a presença de  $NO_3^-$  no solo promove o ambiente ideal para ocorrer o processo de desnitrificação. Dessa forma, a presença de palha sobre o solo cria condições ideais para os processos de nitrificação e desnitrificação no solo, que podem ocorrer simultaneamente.

A remoção da palha de cana-de-açúcar sobre o solo para a produção de bioenergia ou etanol de segunda geração reduziu a volatilização de  $NH_3$  e as emissões de  $N_2O$  do solo. Entretanto, a palha da cana-de-açúcar apresenta um papel fundamental na preservação e sustentabilidade do solo e se removida de maneira indiscriminada pode trazer prejuízos as propriedades químicas, físicas e biológicas do solo. Dessa forma, os “trade-offs” entre remoção e reciclagem da palha da cana-de-açúcar não podem ser subestimados e estudos que possam relacionar os impactos da remoção de diferentes quantidades de palha nos aspectos agronômicos e ambientais são de extrema importância. Assim, com o auxílio de vários estudos é possível determinar a quantidade ideal de palha que pode ser removida da lavoura para fins energéticos sem diminuir a sustentabilidade da cultura da cana-de-açúcar.

## 6 CONCLUSÕES GERAIS

A volatilização de amônia ( $\text{NH}_3$ ) diminui com o aumento das taxas de remoção de palha de cana-de-açúcar sobre o solo. A análise da camada superficial do solo e da palha indicou maior retenção de ureia e  $\text{NH}_4^+$  nas maiores quantidades de palha sobre o solo, além de efetiva hidrólise da ureia diretamente na palha. Estes resultados demonstram uma contribuição direta da camada de palha para a volatilização de  $\text{NH}_3$ . Apesar da redução da volatilização de  $\text{NH}_3$  com a remoção da palha da cana-de-açúcar, a escolha da quantidade de palha a ser removida não pode basear-se apenas na volatilização de  $\text{NH}_3$  do fertilizante nitrogenado.

As emissões de óxido nitroso ( $\text{N}_2\text{O}$ ) ocorreram principalmente em dois momentos: i) após a colheita da cana-de-açúcar; e ii) após adubação nitrogenada. A remoção de palha diminuiu as emissões acumuladas de  $\text{N}_2\text{O}$  com e sem adubação nitrogenada. O efeito direto da palha sobre as emissões de  $\text{N}_2\text{O}$  está relacionado aos mecanismos que alteram os processos de nitrificação e desnitrificação, os quais podem ocorrer simultaneamente. Além disso, a palha foi responsável por grande parte da emissão de  $\text{N}_2\text{O}$  do solo ao longo do ano, o que indica que mais estudos devem ser feitos para aprimorar o conhecimento da palha como fonte de N para as emissões de  $\text{N}_2\text{O}$  e, por consequência, aprimorar os inventários nacionais de gases do efeito estufa (GEE).

Apesar da diminuição da volatilização de  $\text{NH}_3$  e emissão de  $\text{N}_2\text{O}$  com o aumento das taxas de remoção de palha, a remoção indiscriminada não é recomendada. O papel fundamental do resíduo cultural na sustentabilidade da cultura da cana-de-açúcar não pode ser negligenciado. Portanto, diferentes aspectos ambientais e agrônômicos devem ser considerados para definir a quantidade ideal de palha a ser removida. Esses estudos aliados aos nossos resultados podem auxiliar para a tomada de decisão sobre o quanto de palha pode ser removida da superfície do solo para otimizar a sustentabilidade ambiental da cultura da cana-de-açúcar.

A remoção de parte dos resíduos culturais de cana-de-açúcar após a colheita mecanizada pode auxiliar em outros métodos utilizados na redução das perdas de N por volatilização de  $\text{NH}_3$  com o uso da ureia. A diminuição na quantidade de palha pode contribuir para aumentar a eficiência de inibidores de urease e da incorporação da ureia, métodos já conhecidos e com potencial para a redução nas perdas de N- $\text{NH}_3$ . A soma dessas práticas pode aumentar a eficiência no uso do N na cultura da cana-de-açúcar.

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