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Raquel Schmatz

DECOMPOSIÇÃO E EMISSÃO DE N2O EM FUNÇÃO DA QUALIDADE E QUANTIDADE DE RESÍDUOS CULTURAIS NA SUPERFÍCIE DO SOLO

Santa Maria, RS 2019 **Raquel Schmatz**

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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 Doutora em Ciência do Solo

Orientador: Dr. Sandro José Giacomini

Santa Maria, RS 2019

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Santa Maria, RS 2019.

Aos meus pais, Irineu e Jacinta

Dedico este trabalho!

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RESUMO

DECOMPOSIÇÃO E EMISSÃO DE N2O EM FUNÇÃO DA QUALIDADE E QUANTIDADE DE RESÍDUOS CULTURAIS NA SUPERFÍCIE DO SOLO

AUTORA: Raquel Schmatz ORIENTADOR: Sandro José Giacomini

O manejo dos resíduos culturais influencia vários processos na agricultura, como por exemplo, a proteção do solo, a dinâmica da água, a decomposição, o destino dos nutrientes e o balanço global dos gases de efeito estufa, principalmente o N₂O. Estes efeitos dependem da composição química e da quantidade inicial dos resíduos culturais. Assim, o presente trabalho teve como objetivo quantificar a decomposição e liberação de N, P e S de resíduos culturais com diferentes qualidades e quantidades depositados na superfície do solo e a emissão de N2O. Para atingir esses objetivos foi conduzido um experimento durante 360 dias na área experimental do Departamento de Solos da UFSM em solo Argissolo Vermelho distrófico arênico. O delineamento utilizado foi de blocos ao acaso, com quatro repetições. Os tratamentos consistiram de 3, 6 e 9 Mg ha⁻¹ de matéria seca (MS) de resíduos culturais de ervilhaca e trigo e um tratamento controle somente com o solo descoberto. Para avaliar a decomposição os resíduos foram acondicionados em quadros de madeira de $0,16 \text{ m}^2$. Os resíduos dos tratamentos com 6 e 9 Mg ha⁻¹ de MS foram divididos em duas (inferior e superior) e três (inferior, mediana e superior) camadas, respectivamente, com 3 Mg ha⁻¹ em cada camada. Em 9 coletas dos resíduos foram avaliadas a umidade do mulch e a MS, carbono, nitrogênio, fósforo e enxofre remanescentes. Os fluxos de N₂O e CO₂ foram medidos através do método da câmara estática fechada. No solo foi determinada continuamente a umidade e a temperatura nas profundidades de 2,5 e 7,5 cm e os teores de NH4⁺ e NO3⁻ em algumas datas que foram realizadas a avaliação da emissão de N2O. Não houve interação entre a qualidade e quantidade de C, N, P e S remanescentes nos resíduos de ervilhaca e trigo. A qualidade dos resíduos apresentou efeito significativo em todas as datas de avaliação, com rápida liberação dos nutrientes. A quantidade de resíduos não foi significativa para a liberação de nutrientes. A qualidade dos resíduos afetou as emissões de N2O, com maior emissão para o resíduo de ervilhaca quando comparado ao resíduo de trigo. Contudo a quantidade apresenta efeito apenas para os resíduos de maior qualidade até 6 Mg ha⁻¹. Para o resíduo de trigo, não houve diferença significativa entre as quantidades. Os resultados deste estudo evidenciam que a qualidade dos resíduos afeta a decomposição e liberação de nutrientes e consequentemente as emissões de N2O e que a quantidade de resíduos afeta apenas a emissão de N₂O quando o resíduo apresenta alta qualidade.

Palavras chaves: mulch, sistema de plantio direto, gases de efeito estufa, composição química.

ABSTRACT

DECOMPOSITION AND N₂O EMISSIONS AS AFFECTED BY THE QUALITY AND QUANTITY OF CROP RESIDUES ON THE SOIL SURFACE

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The management of crop residues influence several processes in agriculture, such as soil protection, water dynamics, decomposition, nutrient fluxes and the overall balance of greenhouse gases, mainly N₂O. These effects depend on the chemical composition and the initial quantity of the crop residues. Thus, the present work aimed to quantify the decomposition and release of nitrogen (N), phosphor (P) and sulfur (S) of crop residues with different qualities and quantities deposited in the soil surface and N₂O emission. The experiment was carried out during 360 days in a Typic Paluedalf, at Department of soil -UFSM, Rio Grande do Sul, Brazil. A randomized complete block design with four replications was used in the experiment. The treatments were composed of vetch (Vicia sativa L.) and wheat (Triticum aestivum) crop residues under quantities equivalent to 3, 6 and 9 Mg ha⁻¹ of dry matter plus a treatment with no crop residues (control). Crop residues were allocated in litter box of 0.16 m^2 to evaluate the decomposition. The mulch in 6 and 9 Mg ha⁻¹ treatments were spliced, respectively, in two (low and top) and three layers (low, middle and top) of 3 Mg ha⁻¹ each one. The moisture of the mulch, the DM, carbon, nitrogen, phosphorus and sulfur remaining were evaluated on nine sampling of the residues. The N₂O and CO₂ fluxes were periodically measured using closed static chambers. In the soil, soil moisture and temperature were continuously determined at depths of 2.5 and 7.5 cm. Soil NH_4^+ and NO_3^- contents were evaluated at some dates N_2O emission was performed. There was no interaction between the quality and quantity of C, N, P and S remaining in the residues of vetch and wheat. The quality of the residues had a significant effect on all the evaluation dates with a rapid release of the nutrients. The quantity of residues was not significant for the release of nutrients. The N₂O emission was higher for the vetch residue when compared to wheat residue, depending on the initial chemical composition. In contrast, the emission factor was higher for wheat than vetch residues. The quantity had an effect only for the residues of higher quality up to 6 Mg ha-¹. There was no significant difference between the quantities for the wheat residue. The results of this study show that the quality of the residues affects the decomposition and release of nutrients and consequently the N₂O emissions. In addition, the quantity of residues affects only the N₂O emission when the residue presents high quality.

Keywords: mulch, no-till, greenhouse gases, chemical composition

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1 INTRODUÇÃO GERAL

O plantio direto é um sistema de manejo de solo consolidado na agricultura que permite o controle da erosão e o aumento da fertilidade do solo (TIECHER et al., 2017). Esse sistema consiste na integração de três premissas básicas: mínimo revolvimento do solo, cobertura permanente do solo com resíduos e plantas e rotação de culturas. A deposição dos resíduos na superfície do solo em solos agrícolas, além de ser benéfica para o controle da erosão, permite através do processo de decomposição a ciclagem de nutrientes e o sequestro de carbono (C) no solo. Estima-se que a produção anual de resíduos culturais atinge quase 4 bilhões de toneladas no mundo (CHEN et al., 2013). Contudo, os resíduos culturais podem aumentar substancialmente as emissões de óxido nitroso (N₂O) no solo, devido as modificações provocadas nas propriedades físico-químicas do solo e na disponibilidade de nutrientes (KIM et al., 2017), principalmente de C e nitrogênio (N). O N₂O apresenta um potencial de aquecimento 265 vezes maior do que o dióxido de carbono (CO₂) e por isso o aumento de sua emissão em plantio direto pode contrabalancear o efeito positivo desse sistema no sequestro de C.

A decomposição dos resíduos culturais é influenciada por fatores bióticos e abióticos (SWIFT et al., 1979). Entre os fatores abióticos destaca-se a composição química (genericamente denominada de qualidade), umidade do mulch e contato dos resíduos com o solo. Esses dois últimos fatores dependem da morfologia dos resíduos e principalmente da quantidade de resíduos na superfície do solo. De acordo com Varela et al., (2017), a combinação de condições ambientais como umidade e temperatura do solo e a composição química inicial dos resíduos culturais devem controlar a decomposição e a liberação de nutrientes no sistema de plantio direto. Em geral, os resíduos culturais de alta qualidade (alto teor de N e fração solúvel) são decompostos e liberam os nutrientes mais rapidamente do que os resíduos de baixa qualidade (TRINSOUTROT et al., 2000; ABIVEN et al., 2005; REDIN et al., 2014; SCHMATZ et al., 2017).

Embora o efeito da composição química dos resíduos sobre a decomposição é amplamente conhecido (QUEMADA e CABRERA, 1995; COBO et al., 2002; REDIN et al., 2014; SCHMATZ et al., 2017), as informações do efeito de diferentes quantidades sobre a decomposição de resíduos são limitadas e divergentes. Alguns estudos relatam que maiores quantidades de resíduos apresentam menor decomposição devido a menor

proporção do mulch em contato com o solo (STOTT et al., 1990; STEINER et al., 1999). Esses resultados conduziram a inclusão do fator contato (F contact) em modelos que simulam a decomposição de resíduos na superfície do solo, como o APSIM Mulch (THORBURN et al., 2001) e PASTIS Mulch (FINDELING et al., 2007). Nesses modelos é considerado que a decomposição do mulch ocorre apenas na camada em contato com o solo, a qual é alimentada pela transferência de resíduos de camadas superiores que não sofrem o processo de decomposição. Assim, maiores quantidades de resíduos resultam em uma menor decomposição. Contudo, recentes estudos não encontraram efeito da quantidade de resíduos na decomposição, ou seja, independentemente da quantidade (espessura do mulch), o percentual de decomposição foi semelhante (ACOSTA et al., 2014; RAMOS et al., 2016; DIETRICH et al., 2017; PIMENTEL et al., 2019). Estes resultados contradizem os modelos iniciais que predizem a decomposição dos resíduos na superfície do solo. Portanto, é necessário melhorar nossa compreensão de como acontece a decomposição de diferentes quantidades de resíduos na superfície do solo.

Durante o processo de decomposição, os nutrientes são transformados e dependendo das características químicas do resíduo, eles podem ser liberados no solo (NOACK et al., 2012; VARELA et al., 2017). A maioria dos estudos sobre a liberação de nutrientes em resíduos culturais tem focado no N (COBO et al., 2002; AITA e GIACOMINI, 2003; ABIVEN et al., 2005) e no fósforo (P) (por exemplo, GIACOMINI e AITA et al., 2003; KWABIAH et al., 2003, VARELA ET AL., 2017). Por outro lado, pouca atenção tem sido dada ao estudo da liberação de enxofre (S) (JANZEN e KUCEY, 1988; GHARMAKHER et al., 2009) e principalmente como ocorre a liberação de N, P e S no mulch formado por diferentes quantidades de resíduos culturais (ACOSTA et al., 2014; DIETRICH et al., 2017). O efeito da quantidade de resíduos sobre o processo de decomposição e liberação dos nutrientes do mulch vem recebendo atenção principalmente pelo avanço dos sistemas dedicados a produção de energia a partir de biomassa, em que a remoção parcial da palha da lavoura provoca alterações nas quantidades de palha que formam o mulch na superfície do solo.

Da mesma forma que existe divergência sobre como ocorre a decomposição de diferentes quantidades de resíduos, ainda são limitadas as informações de como a manutenção dos resíduos culturais depositados na superfície do solo afetam a emissão de N₂O. Estudos relatam que a magnitude das emissões pode ser dependente da composição

química (MILLAR e BAGGS, 2004; GARCIA-RUIZ e BAGGS, 2007) e da quantidade de resíduos culturais adicionados ao solo (AULAKH et al., 2001, CHEN et al., 2013). No geral, maiores emissões de N₂O são observadas após a adição de resíduos culturais de leguminosas, caracterizadas pela menor relação C: N (BAGGS et al., 2003; HUANG et al., 2004; CHEN et al., 2013), alto teor de C e N solúvel em água (WEILER et al., 2018). No entanto, as emissões de N₂O nem sempre são diretamente relacionados com a composição química dos resíduos das culturas (BAGGS et al., 2006; MUHAMMAD et al., 2011).

Por outro lado, observou-se que os efeitos dos resíduos culturais nas emissões de N₂O do solo podem ser positivamente relacionados às quantidades de resíduos culturais depositados na superfície do solo. Isso ocorre porque diferentes quantidades podem alterar fatores como disponibilidade de C e N no solo, umidade do solo (EPSA), temperatura e teor de oxigênio (BARNARD et al., 2005) que altera os processos microbianos, isto é, nitrificação e desnitrificação responsáveis pelas emissões de N2O. No entanto, a maioria dos resultados sobre a quantidade de resíduos na superfície do solo sobre as emissões de N_2O foram obtidos em estudos conduzidos para avaliar o impacto da colheita de palha para a produção de bioenergia (por exemplo, cana de açúcar, palha de milho, etc.) Nesses estudos, como a quantidade de palha na superfície do solo é maior do que a quantidade de matéria seca produzida por outras culturas anuais (por exemplo, trigo e ervilhaca), observou-se que as emissões de N2O no solo podem aumentar (CARMO et al., 2013; PINHEIRO et al., 2019), diminuir (PITOMBO et al., 2017) ou permanecer inalterado (GUZMAN et al., 2015; VASCONCELOS et al., 2018). Assim, é necessário compreender como a interação da qualidade e da quantidade de resíduos culturais adicionados na superfície do solo podem influenciar as emissões de N2O. (CHEN et al., 2013; PEYRARD et al., 2016). Além disso, é necessário elucidar quais são os fatores que controlam a decomposição no interior do mulch, e como estes fatores afetam as emissões de N₂O. Por isso, a importância e a necessidade de intensificar os trabalhos de pesquisa nessa área, ainda carente de resultados.

Dentro deste contexto foi conduzido um experimento de campo com resíduos de ervilhaca e trigo com quantidades de 3, 6 e 9 Mg ha⁻¹ depositados na superfície do solo que deu origem a presente Tese, a qual foi organizada em dois artigos:

O artigo 1 engloba os dados de umidade, decomposição e liberação de C, N, P e S de diferentes camadas dos mulches de ervilhaca e trigo. O artigo 2 trata da emissão de N₂O e dos fatores controladores da produção desse gás na presença dos mulches de ervilhaca e trigo.

1.1 Hipóteses

- A decomposição dos resíduos culturais e a liberação de nutrientes (N, P e S) será maior na presença de resíduos com melhor qualidade química (ex. maior teor de N e fração solúvel).
- O aumento da quantidade de resíduos culturais na superfície do solo não afeta a taxa de decomposição dos resíduos de ervilhaca e trigo e a liberação de nutrientes (N, P e S).
- A emissão de N₂O aumenta com a adição de resíduos culturais com maior teor de N e fração solúvel. O aumento da quantidade de resíduos de culturas depositados na superfície do solo aumenta as emissões de N₂O.

1.2 Objetivo Geral

Compreender como ocorre a decomposição e liberação de N, P e S de resíduos culturais com diferentes qualidades e quantidades depositados na superfície do solo e a emissão de N₂O.

1.3 Objetivos Específicos

- Compreender como a qualidade e a quantidade dos resíduos culturais de ervilhaca e trigo depositados na superfície do solo afetam a decomposição e a liberação de C, N, P e S dos resíduos.
- Compreender quais fatores que controlam a decomposição e a liberação dos nutrientes no interior do mulch.
- Compreender o papel do contato entre o solo e o mulch formado por resíduos de diferentes qualidades.
- Investigar como as características e quantidades de diferentes resíduos culturais contrastantes como ervilhaca e trigo depositados na superfície do solo interagem e afetam as emissões de N₂O.

2 ARTIGO I DECOMPOSITION AND NUTRIENTS RELEASE OF DIFFERENT MULCH QUALITY AND QUANTITIES*

2.1 Abstract

The chemical composition of crop residues is the main factor driving the decomposition. However, there is limited information regarding the decomposition of different crop quantities residues and their interaction with quality. This study aimed to understand i) how the quality and quantity of vetch and wheat crop residues deposited on the soil surface affect the decomposition and release of C, N, P and S at different positions in the mulch, ii) the factors controlling the decomposition and release of nutrients in the mulch, and iii) the importance of contact between the soil and mulch. The experiment was carried out for 360 days in a Typic Paluedalf, at University Federal of Santa Maria, Rio Grande do Sul, Brazil. The treatments were composed of vetch and wheat crop residues with quantities equals to 3, 6 and 9 Mg ha⁻¹ of dry matter. The crop residues were allocated in a litter box of 0.16 m². The mulch for 6 and 9 Mg ha⁻¹ treatments was separated, in two and three layers of 3 Mg ha⁻¹, respectively. The amount of C, N, P and S remaining, thickness and moisture of the mulch were evaluated for each sampling. The soil moisture and soil temperature were continuously measured throughout the season. There was no interaction between the quality and quantity of C and N remaining for vetch and wheat residues. The P and S showed interaction, but it was transient. The quality of residues showed a significant effect with higher release of C, N, P, S for the vetch residue. There was no significant effect of quantity on decomposition. We observed some differences between mulch layers with higher nutrient release to 3 Mg ha⁻¹ treatment. In addition, we observed differences for the total water content of the mulch. For the layer positions, there was a greater maintenance of water content of the lower layers in the quantities of 6 and 9 Mg ha⁻¹. Thus, quality is the main factor that affects the decomposition and release C, N, P, S.

Keywords: crop residues, no-till, soil contact, moisture

*Artigo elaborado de acordo com as normas da Revista Biology and Fertility of Soils

2.2 Introduction

No-till system is characterized by minimum soil disturbance and the maintenance of crop residues on the soil surface (Amado et al. 2003). The success of no-till depends on crop rotation. This practice allows to grow different species resulting in the addition of crop residues with quantity and chemical composition varied to the soil (Campos et al., 2011; Freitas and Landers, 2014). Understand the dynamics of mulch decomposition is important once through this process occurs the nutrient cycling and the soil organic matter formation (Mitchell et al., 2016). The effect of the chemical composition of residues on the decomposition has been well studied (Cobo et al. 2002; Abiven et al. 2005; Redin et al. 2014; Schmatz et al. 2017). Crop residues with high nitrogen (N) content (low C: N) combined with high soluble fraction contents are rapidly decomposed (Abiven et al. 2005; Redin et al. 2014; Schmatz et al. 2017). On the other hand, crop residues that combine low N contents (high C: N) with higher contents of cellulose (CEL) and hemicellulose (HEM) exhibit slower decomposition (Redin et al. 2014). However, there is limited information on how different quantities of crop residues at soil surface affect the decomposition.

The first studies evaluating the decomposition of different quantities on the soil surface were carried out by Stott et al. (1990) and Steiner et al. (1999), which report that the increase of residues quantities causes reduction in the decomposition. This was attributed to the reduction of mulch proportion under direct contact with the soil with the increase of the quantities of residues in the soil surface. However, recent studies with sugarcane (Dietrich et al. 2017, 2019), oat, vetch and oil radish (Acosta et al. 2014) and rye crops residues (Williams et al. 2018) did not observe reduction in the decomposition with the increase on quantities, being the decomposition proportional to the added quantities of sugarcane straw promotes better moisture conditions for microbial activity at the soil-residue interface compensating the contact reduction with the soil. However, this fact has been not measured in mulches formed with annual crop residues. Therefore, limited information is available on factors controlling the decomposition of thicker mulches and their relationship to the chemical quality of the residues.

During the decomposition process, nutrients are transformed and may be released into the soil depending on the chemical characteristics of the residue (Noack et al., 2012;

Varela et al., 2017). The N release from crop residues was researched and conducted both under temperate (Trinsoutrot et al. 2000; Abiven et al. 2005) and subtropical (Aita and Giacomini, 2003; Giacomini et al. 2003) conditions. However, there are few studies about the dynamics of phosphor (P) release and sulfur (S) (Janzen and Kucey, 1988; Kwabiah et al. 2003; Varela et al. 2017;). In addition, a limited number of studies have shown release of these nutrients (N, P and S) under different quantities of residues deposited at the soil surface (Acosta et al. 2014; Dietrich et al. 2017).

Therefore, the objectives of this study were: i) to understand how the quality and quantity of vetch and wheat crop residues deposited on the soil surface affect the decomposition and release of C, N, P and S at different positions in the mulch, ii) understand the factors controlling the decomposition and release of nutrients in the mulch, and iii) understanding the importance of contact between the soil and mulch formed by different residues. Our hypotheses are 1) the decomposition of crop residues will be greater in the presence of higher quality residues (e.g. higher N content and soluble fraction), regardless of the quantities of crop residues deposited on the soil surface and 2) the increasing quantity of vetch and wheat crop residues on the soil surface does not affect the rate of decomposition.

2.3 Materials and methods

2.3.1. Study site

The field experiment was conducted at University Federal of Santa Maria (29°42'44" S, 53°42'74" W, approximately 90 m elevation) in Rio Grande do Sul state, Brazil. The local climate is humid subtropical Cfa. The mean historic annual temperature is 16.1 °C and precipitation is 1660 mm. The soil is a Typic Paleudalf (Soil Survey Staff, 2010) with 110 g kg⁻¹ clay, 260 g kg⁻¹ silt and 630 g kg⁻¹ sand in the 0-10 cm and following chemical properties: : pH_{H2O} of 4.8, 33.1 mg kg⁻¹ P extractable by Mehlich⁻¹, 66.0 mg kg⁻¹ K extractable by Mehlich⁻¹, 9.6 g kg⁻¹ total C and 0.9 g kg⁻¹ total N in the soil. The experimental area was previously conducted under no-tillage system with rotation of winter crops (oats (*Avena sativa*) or ryegrass (*Lolium multiflorum*) / summer [black bean (*Phaseolus vulgaris*) or soybean (*Glycine max*)] for 6 years.

The experiment was arranged in a randomized complete block design with four replications and plots with 2.0 x 2.5m from November 2016 to November 2017 . The treatments were composed of vetch (*Vicia sativa* L) and wheat (*Triticum aestivum* L.) by quantities of crop residues equivalent to 3, 6 and 9 Mg ha⁻¹ of dry matter (DM). The wheat aboveground crop residues was collected at the physiological maturation and vetch performed at the flowering stage. Vetch residues were spliced into 20 cm pieces to simulate the effect of passing a knife roller. Wheat residues were previously fragmented by the combine machine composed of pieces between 5 and 20 cm predominantly. Both crop residues were dried at 45°C for 48 hours in a forced-air oven to a constant weight. One subsample was taken and oven-dried at 65 °C for 48 h for DM correction. Then, the quantity of each dry residue at 45 °C equivalent to 3, 6, 9 Mg of DM ha⁻¹ was weighed and stored in bags until placed in the field.

The soluble fraction (SOL), cellulose (CEL), hemicellulose (HEM), and lignin (LIG) fractions of the straw were determined by proximate analysis using the Van Soest method described by Redin et al. (2014). The carbon (C) and N contents were determined using an elemental analyzer (FlashEA 1112; Thermo Finnigan, Milan, Italy). Determination of P and S the crop residues were through nitro-perchloric digestion (Carmo et al., 2000). P concentration was determined using the methodology of Murphy and Riley (1962), and S concentration was determined using the methodology of Tedesco (1995). For both, concentration was determined through the colorimetry in a spectrophotometer (SF325NM, Bel Engineering, Italy). The chemical characteristics of the residues are presented in Table 1.

2.3.3 Decomposition and C, N, P and S release from crop residues

The decomposition of vetch and wheat crop residues was evaluated using the litter box technique (Dietrich et al. 2019). The litter box was made of wood with the dimensions of 40 cm length x 40 cm width x 8 cm height and with a 5-mm nylon mesh in the bottom with a 10 mm plastic screen mesh in the top. The litterbox containing equivalent quantity of 3, 6 and 9 Mg ha⁻¹ of DM of vetch and wheat were installed for each field plots.

The mulch was divided into straw layers of 3 Mg ha⁻¹ each in order to evaluate the gradient of decomposition within 6 and 9 Mg ha⁻¹ treatments. We stacked two or three layers inside the litter box to reconstitute the two mulch quantities. The layers were separated by a maneable 5 mm nylon mesh the same use in the bottom, mesh with wide aperture so as to being able to sample every layer separately for analysis. Therefore, the 6 Mg ha⁻¹ treatment was composed of two layers, one in contact with the soil (low position: 6L) and the other in contact with the atmosphere (top position: 6T); the 9 Mg ha⁻¹ treatments were divided in three layers, a top (9T), a middle layer (9M) and a low layer (9L). The 3 Mg ha⁻¹ treatment had a single layer with soil and atmosphere (3L/T) contact at the same time.

Crop residues sampling was performed over a year at 15, 30, 45, 60, 90, 150, 210, 270 and 360 days after the field installation. For each sampling date, one litter box per plot was removed. The straw from each layer was sampled separately. After that, all vetch and wheat samples were taken to the laboratory, pre-cleaned, weighted, stored in paper bags and dried in an oven-dried at 65 °C for 48h. The straw was separated again from adhering soil. Samples were dry cleaned and weighted to determine the DM and water content. Crop residue ashes were measured by incinerating 0.2 g in a muffle furnace at 550 °C for 3 h. The sub-sample was finely grounded in a steel ball mill for the determination of C, N, P and S content as described above for the initial chemical characterization of the residues.

Mulch thickness was evaluated in four litter boxes (3, 6 and 9 Mg ha⁻¹), for the vetch and the wheat. In each litter box, nine non-destructive thickness measurements were performed using a graduate ruler. The measurements were performed at 0, 5, 15, 30, 45, 60, 90, 150, 210, 270 and 360 days after crop residue addition.

2.2.4 Soil water content and soil temperature

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 depths in the soil with 3 replicates in each treatment. The type T copper-constantan thermocouple was installed at the same depths to measure soil temperature. Both sensors were coupled to a data logger (CR1000; Campbell Scientific, Logan, Utah, USA) and measurements were performed at a 10 min sampling interval. Daily air temperature and

rainfall data were obtained from an automatic weather station located 1.7 km away from the experiment.

2.2.5 Calculations and statistical analysis

The remaining C, N, P and S of the straw at each sampling date were calculated as the remaining mass of each straw layer multiplied by its C, N, P and S concentrations (deduced from the ash content). In treatments 6 and 9 Mg ha⁻¹ for vetch and wheat residues, the amounts of C, N, P and S remaining were obtained by summing the amounts of nutrients in each straw layer.

The C remaining in each layer and in the total mulch over time was described with a simple one-compartment equation according to Plantae and Parton (2007):

C remaining = $C_0 e^{-kt}$

where C remaining is the mass of the remaining C (Mg C ha⁻¹), *C0* is the straw C pool at time 0 (Mg C ha⁻¹), *k* is the degradation rate constant (day⁻¹), and t is the time (days).

The mean residence time (t1/2) of the straw, which corresponds to the time necessary to degrade half of the initial quantity of mulch, was calculated from *k* according to Plantae and Parton (2007).

All data were subjected to analysis of variance (ANOVA). The effects of crop residue quantities and crop residue type and their interaction were tested in the total mulch for all parameters evaluated at each date (Table 2, 3). The C, N, P, S remaining for each layer of vetch and wheat crop residue were tested for quality and quantity. Differences between means were calculated using the Tukey test (P < 0.05). All data were analyzed using SISVAR® statistical software (version 5.6).

2.4 Results

2.4.1 Environmental conditions, soil water content and soil temperature

The cumulative rainfall during the experiment was 2337 mm and the daily mean air temperature was 20 °C with the minimum mean temperature of the 4.9 °C and the maximum mean temperature of the 29.3 °C (Fig. 1a). Considering that soil moisture and temperature at 2.5 and 7.5 cm showed similar trend for all treatments over the time only the data of the 2.5 cm layer are shown here. Soil moisture did not differ between vetch and wheat treatments for each quantity of crop residue. Although no significant effect of the crop residue was observed in dry periods (e.g., from day 10 to 20, day 115 to 140, day 200 to 250) there was a trend of higher soil moisture for wheat than vetch residue. We observed a significant effect of crop residue quantities on soil moisture. For both residues the higher water content was observed with highest quantities of residue at soil surface (9 Mg ha⁻¹ = 6 Mg ha⁻¹ > 3 Mg ha⁻¹ \ge soil). The crop residue and the quantity at the soil surface did not influence significantly soil temperature, however, there was a tendency of lower soil temperature values (average of -2 °C) with crop residues than bare soil during 360 days.

2.4.2 Thickness and water content of mulch

The thickness of the mulch did not differ between vetch and wheat at the beginning of the experiment. As we hypothesized, there was a decrease in the following order: 9 (7 cm) > 6 (5 cm) > 3 (3 cm) Mg ha⁻¹ (Fig. 2a, b). The mulch thickness was influenced by crop and quantities of residues. The mulch thickness was higher for wheat (Fig. 2b) than vetch (Fig. 2a). The evolution of mulch thickness was relatively similar between vetch and wheat which was characterized by a rapid decreased in the first five days (44% to 54% in vetch and 27 to 42% in the wheat), following the same trend for both residues and for the three quantities (3 < 6 < 9 Mg ha⁻¹). The mulch thickness values were relatively stable after 90 days for vetch and 150 days for wheat up to 360 days reaching 0.14, 0.27 and 0.54 cm in the vetch for 3, 6 and 9 Mg ha⁻¹, respectively, and 0.59, 1.09 and 1.73 cm in the wheat.

The water content of the mulch ranged from 5.4 and 78 g H₂O 100 g⁻¹ DM over the nine evaluations performed during one year of experiment. Overall, there was a significant effect of water content on the mulch for some dates of evaluation, being 4 dates for vetch and 2 dates for wheat residues under 3 than 6, 9 Mg ha⁻¹. For these dates there was an increasing or decreasing of soil moisture according to the precipitation regime (Fig. 2c, d). On average of all evaluations, there was no differences between types of residues. For the different layer, for the vetch residue, there were significant differences up to 210 days (Fig. S1a), being observed higher water content for the lower layers (6L and 9L) when compared to the top layer (6T and 9T) of the same treatment. In addition, the water content of each layer was similar when observed layers in the same position. For example at 30 days, the treatment 3L/T was similar to 6T and 9T, however, 3L/T treatment was also similar to the low 6L and the 9L (Fig. 2e). There were significant differences for wheat residue during 360 days (Fig. 2f). It was observed higher water content for lower layers such as 6L and 9L when compared to the top layers 6T and 9T. For some evaluated dates, the quantity of 3 L/T did not differ from the lower layers.

2.4.3 C, N, P and S remaining in the mulches

There was interaction for the P and S remaining between crop and quantity of residue on some dates. However, there was no interaction at the end of the experiment (Table 2). The effect of the quantity was observed for C (only two dates), P and S remaining with lower values for 3 Mg ha⁻¹ than 6 and 9 Mg ha⁻¹, however it did last at the final evaluation. The effect of the crop residues was observed for all nutrients. Vetch residues had a rapid and intense loss of the C, N, P and S compared to the wheat residues (Fig. 3). The C loss in the first 60 days was 84% for vetch residue (Fig. 3a) and 43% for wheat residue (Fig. 3b). At the end of 360 days, C remaining in vetch was than 10 times lower than measured in wheat (1.5 vs 16%).

The intensity and N, P and S losses were different between residues. For vetch, the loss of N (Fig. 3c) and P (Fig. 3e) reached 67% and 80% in the first 15 days, respectively. For wheat, the losses were only 41% for the N (Fig. 3d) and 33% for the P (Fig. 3f) during the same period. After that period, the amount of N and P remaining in vetch residues decreased up to 1% and 0.5% at the 360 days, respectively. The P also decreased for the wheat residue remaining 23.4% at the end of experiment. On the other

hand, the remaining N was relatively stable between 30 and 360 days (mean of 50%) for wheat residues. The loss of S at 60 days reached 70% in the vetch (Fig. 3g) and 15% in the wheat (Fig. 3h). At the end of the experiment, we observed differences between both residues, which only 5.4% remained in the vetch while 62% of S remained in the wheat.

The kinetics of C remaining was described using a one-compartment model (Table 4). There was no interaction between quality and quantity of residues for any of these parameters (Table 3). C₀ was not affected by the quality and quantity of the residues. For both residues, the *k* was significantly higher in the quantity of 3 Mg ha⁻¹ compared with the quantities 6 and 9 Mg ha⁻¹. The mean *k* of all quantities of crop residues was 5 times higher in vetch than wheat (0.028 vs 0.006) (Table 4). The $t_{1/2}$ differed only between 3 and 9 Mg ha⁻¹ for wheat residues. On average of the three quantities of crop residues, the $t_{1/2}$ was 123 days in wheat versus only 25 days in vetch.

The C: N, C: P and C: S ratio were not affected by the interaction between quality and quantity of crop residues (Table 2). These relationships were affected by the quality of residues. On the other hand, the effect of the quantity of crop residue only occurred in a few dates during the 360 days. The evolution of the C: N and C: P ratio was similar, however, they differ from C: S ratio. In the vetch, C: N and C: P ratio increased from 12 and 122 at time zero to 21 and 356 in the first 15 days, respectively, and remained relatively stable up to 360 days (C: N = 20 and C: P =358). In wheat, after a C: N ratio increase from 83 to 156 in the first 30 days and a C: P ratio increase from 780 to 1100 in the first 15 days, the values decrease until 360 days reaching 37 for C: N and 538 for C: P. Differently, for both crop residues the C: S ratio decreases over time (526 to 162 to vetch and 549 to 147 to wheat), with the exception of a 90 day increase observed with the vetch residues.

2.4.4 C, N, P and S remaining in the mulch layers

Overall, the C (Fig. 4), N (Fig. 5), P (Fig. 6) and S (Fig. 7) remaining kinetics followed the same pattern for each layer position with few exceptions. In the treatments of 9 Mg ha⁻¹ (9T, 9M, 9L) for vetch and wheat, the dynamics were characterized by a rapid decrease for all nutrients. We observed for vetch and wheat (Fig. 4 a, b) that the C remaining was similar among all layer positions. We observed for the N, P and S remaining little significant difference between the 3 layers for the vetch and wheat. In the

beginning N, P, S released in the T layer, demonstrating a transient difference that subsequently disappeared. Few differences were observed between the T and L layers for quantity of 6 Mg ha⁻¹. For some dates it was observed that the release of C, N, and P was 6 L> 6 T for both vetch and wheat. However, for P the 6T> 6L layer at 45 days. There was no effect for the S remaining in between layers of the quantity of 6 Mg ha⁻¹.

Few differences were observed para C, N, P, S comparing the top layers (3L/T, 6 T, 9T). However, there were significant differences on some dates, where the 3 L/T layer presented higher decomposition than 6T and 9T layers. The 3L/T layer had more nutrient release of N, P, S than layers 6L and 9L for all similar treatments. The C remaining of the vetch and wheat residue in the lower layers showed no differences. Similarly, the wheat residue showed few differences between the lower layers for all elements, with the tendency of higher decomposition of 3 L/T layer than 6L and 9L.

The decomposition parameters of the adjusted model (Table 4) were significant different between the mulch positions for vetch and wheat residues. The k was higher in the 6L and 9L layers when compared to the T layers for the both residues, however, did not differ from the 3 L/T. The $t_{1/2}$ varied as according for k.

The degradation rate (k) at day 360 in the L, M, T or L / T straw layers were significant and linearly related to the average moisture content of these layers sampled over the year for the wheat residue (Fig. 8 b) with 6T, 9T < 3L/T, 9M < 6L, 9L. For the vetch (Fig. 8 a), there was a tendency of increasing k for the lower layers and higher moisture.

2.5 Discussion

2.5.1 Effect of crop residue quality on mulch decomposition and N, P, S dynamics

The mulch decomposition was higher in vetch than wheat residues regardless of the quantity applied to the soil surface. The adjustment of the C remaining data to the one compartment model (Plantae and Parton, 2007) indicated that the *k* of vetch residues was 5 times greater than wheat residues and that the $t_{1/2}$ of the vetch mulch was only 25 days against the 123 days of the wheat mulch. These results agree with our first hypothesis that the decomposition will be higher with residues of better chemical quality (higher N soluble and low C: N). This is also in agreement with several other studies carried out

with incorporated residues (Abiven et al. 2005; Bertrand et al. 2006; Thippayarugs et al. 2008) or maintained on the soil surface (Quemada and Cabrera 1995; Cobo et al. 2002; Redin et al. 2014; Schmatz et al. 2017).

The rapid and greater decomposition of vetch residues is attributed to its characteristics. These residues present high N (low C: N) and soluble fraction combined with lower values of CEL and HEM compared to wheat residues. These characteristics of legume residues facilitate colonization and growth of the decomposing microbial population even for crop residues left on the soil surface (Redin et al. 2014). In addition, the rapid loss of matter for vetch residues may also be related to the loss of soluble compounds by rainfall especially in the initial phase of the decomposition process. In part, this may explain greater reduction in the thickness of the vetch mulch than in the wheat in the first five days after a precipitation of 58 mm.

Decomposition occurs at the same time to the transformation and release of the nutrients processes present in the crop residues (Noack et al. 2012). The amount of N, P and S released was higher in vetch than wheat residues, as well as also observed for C loss. The N and P initial contents were significantly higher in vetch than wheat residues with the exception of S. These characteristics explain the rapid and high losses of N and P of legume residues. In addition, a significant fraction of total N and P in legume residues must be in soluble forms (Aita e Giacomini 2003; Giacomini et al. 2003; Noack et al. 2012), which are easily removed from the mulch by the action of water. The loss of this nutrient fraction should be favored in residues that present high rates of decomposition. Although the initial S content in the tissue of the vetch and wheat residues were similar $(\pm 0.8 \text{ g kg}^{-1} \text{ MS})$, we also observed a rapid loss of S of legume residues indicating that possibly a significant proportion of S in these residues are present on soluble forms. According to Gharmakher et al. (2009) the S forms present in the residues may influence their rate of mineralization more than the initial concentration of S tissue. At the end of the experiment the averagequantity of N, P and S remaining in the wheat residues was 36%, 23% and 62% of the initial, respectively, and only 1%, 0.5% and 5.4% of the initial for the vetch residue.

In wheat residues after an initial period with rapid release of N (30 days), P (60 days) and S (90 days) relatively constant values were observed for these nutrients until the end of the experiment. This behavior, coupled with the decrease in the C: N, C: P and C: S ratios indicate the enrichment of the N, P and S residues, possibly by the microbial

immobilization that is decomposing the wheat residue. Frey et al. (2000) also verified the N enrichment of wheat residues during decomposition and demonstrated that part of the N present in the residues was taken up from the soil, probably by diffusion to the residue layer from colonizing fungal hyphae. In addition, during the first 60 days of the experiment, colonization of hyphae was observed between the residue layers. Considering that other nutrients such as P and S are also necessary for microbial growth, fungi were also responsible for the increase in the concentration of these elements in the wheat mulch.

2.5.2 Effect of crop residue quantity on mulch decomposition and N, P, S dynamics

Overall, the quantity of residues did not affect the mulch decomposition. This occurred even with increased initial thickness of the mulch, reducing the contact between soil and residue. However, some differences in loss of C between crop residues quantities were observed with higher losses determined for the 3 Mg ha⁻¹ quantity than 6 and 9 Mg ha⁻¹ quantities. These differences were important to show differences on kinetics of the decomposition between the treatments, with k for 3 > 6 (-8%) = 9 (-16%) Mg ha⁻¹. However, there was no significant difference between treatments for vetch in terms of values and the differences between 3 and 6 Mg ha⁻¹ for wheat was only of the 4% while comparing measured residual C after one year. This is contradictory to the results obtained by Stott et al. (1990) and Steiner et al. (1999) that verified a decrease in mulch decomposition due to the increase of the quantity of residues at the soil surface. The decrease was attributed to the lower proportion of the residues in contact with the soil (Thorburn et al.2001; Findeling et al. 2007).

On the other hand, the results of the present study are similar to those obtained by Willians et al. (2018) with rye straw (2-15 Mg ha⁻¹), Dietrich et al. (2017, 2019) with sugarcane straw (4-12 Mg ha⁻¹) and Acosta et al. (2014) with vetch, oil radish and oat straw (3-9 Mg ha⁻¹). Increasing the quantities of residues in the soil surface reduces the proportion of the mulch in contact with the soil. A thicker layer of residues maintains better moisture conditions for the microorganisms at the interface soil-residue compared to thinner mulch. These compensations determine the lack of effect regarding the quantity of residue on decomposition under certain conditions.

We observed a moisture gradient where lower values occur in the top layers (6T and 9T) and the higher values in the lower layers (6L and 9L) when we analyzed the different layers of 6 and 9 Mg ha⁻¹ of the both residues. The higher moisture of the lower layer is due to the reduction in the evaporation of water present in this layer, which is protected by the top layers that receive direct solar radiation and consequently present lower moisture (Fuchs and Hadas, 2011). This moisture gradient results in a decomposition gradient which the lower layers have higher decomposition rates than top layers. This is supported by the close relationship between the average moisture of the different layers of the mulch and the k for each layer. The fact that the lower and top layers of the mulches formed by the quantities of 6 and 9 Mg ha⁻¹ residues present similar water content dynamics and decomposition explain the lack of the effect of increasing the quantity of residues on the mulch decomposition. In addition, total mulch and soil moisture were similar between these two treatments for the two residues evaluated.

Although there was no interaction between quality and quantity of residues on the rates of decomposition of the total mulch and the different layers of the mulch, there was a strong tendency for the decomposition rates in wheat to be higher than vetch. The average increase of the decomposition rate of the lower layers relative to the rates of the top layers of the mulches with 6 and 9 Mg ha⁻¹ was 25% in the vetch and 50% in the wheat. These results indicate that the process of decomposition of lower quality residues, such as wheat, are more dependent on soil contact than better quality residues such as vetch.

The release of the nutrients in the total quantities did not show differences, except for the P for the wheat residue. For the S in some evaluations, there was a transient and small effect between the quantities for both residues. The similarity between the total quantities of the mulches was only observed due to the small differences found between the layers. Overall, we observed that all layers of vetch and wheat residues began to decompose at the same time. The N, P and S of the two residues, there was little significant difference between the 3 layers (T, M, L) of the quantity of 9 Mg ha⁻¹ for two residues. Initially greater release of N, P and S in the T layer was observed, after some evaluations this difference disappeared. This suggests that part of the initial fast N, P, and S losses could be due to the leaching of soluble compounds due to rainfall that occurred after the experiment was set up, of high intensity that first reached the top layer of the quantity of 9 Mg ha⁻¹ that provided greater release in the top layer. We observed that the top layers at some dates showed significant differences for N, P and S with 3L / T > 6T = 9T, but were transient. These results indicate that initially the top layers (6T and 9T) performed similarly, showing lower moisture and, releasing the same amount of nutrients, while the 3L / T layer had the effect of direct contact with the soil,. Likewise, the release of N, P and S from the lower layers presented similar trend as the top layers with the layer 3L / T being in some dates smaller than the lower layers. These results differ from Dietrich et al. (2019), who observed that the lower layers released more C and N than the single layer. These results may be related to the difference of the mulch formed by sugarcane, decomposition dynamics and maintenance of higher moisture in the lower layer, as well as the difference in the particle size of the residues.

2.6 Conclusion

This study confirms that the quality of crop residues affects the dynamics of decomposition and consequently influences the release of C, N, P and S, which was faster and greater for the vetch residue. On the other hand, there are no differences on decomposition and release of C, N, P, and S of the crop residues under different quantities regardless of the crop residues of residue. The similarity in the decomposition occurs because the lower layers of these residues present similar mulch moisture. These results are related to the close relationship between the moisture's layers of the residues and the rates of decomposition. The results of this study show the important role of the chemical quality of the residues on the decomposition and the release of nutrients from the mulch and that the effect of the quantity of residues mainly affects the water dynamics in the soil and the mulch.

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Tables

Table 1 Initial chemical composition of the vetch and wheat residues used in the field experiment.

| Residues | С | N | Р | S | SOL | CEL | HEM | LIG | C:N | LCI | |
|----------|--|----------|-----------|-----------|----------|----------|----------|--------|-----------|-----------|--|
| | | | | | - 1 | | | | | | |
| g kg -1 | | | | | | | | | | | |
| Vetch | 428±3.2 | 35.6±1.4 | 3.5±0.06 | 0.81±0.05 | 530±20 | 307±16.1 | 101±13.6 | 62±5.9 | 12.0±0.45 | 0.13±0.02 | |
| Wheat | 441±0.7 | 5.3±1.2 | 0.56±0.01 | 0.80±0.12 | 162±18.2 | 418±14.1 | 346±9.2 | 74±2.6 | 83.2±9.0 | 0.09±0.01 | |
| | C total C, N total N, P total P, S total S, SOL soluble fraction, CEL cellulose, HEM hemicellulose, LIG lignin, LCI lignocellulose index (LIG/CEL + HEM + LIG). Means ($n = 3$) ± standard deviation | | | | | | | | | | |

| Variables | 15 | | | 45 | | | 90 | | | 210 | | | | 360 | | | | | | |
|--|----------------|---------|---------|------------------|---------|---------|---------|------|---------|---------|---------|------|---------|---------|---------|------|---------|---------|---------|------------------|
| | R ^a | Qb | RxQ | CV | R | Q | RxQ | CV | R | Q | RxQ | CV | R | Q | RxQ | CV | R | Q | RxQ | CV |
| | | | | (%) ^c | | | | (%) | | | | (%) | | | | (%) | | | | (%) ^c |
| C remaining (%) | < 0.001 | 0.060 | 0.151 | 4.7 | < 0.001 | 0.361 | 0.123 | 6.2 | < 0.001 | 0.119 | 0.768 | 14.8 | < 0.001 | 0.408 | 0.959 | 20.4 | < 0.001 | 0.160 | 0.243 | 33.4 |
| N remaining (%) | < 0.001 | 0.204 | 0.067 | 10.5 | < 0.001 | 0.809 | 0.865 | 24.5 | < 0.001 | 0.134 | 0.199 | 19.3 | < 0.001 | 0.750 | 0.376 | 25.2 | < 0.001 | 0.739 | 0.976 | 25.4 |
| P remaining (%) | < 0.001 | 0.010 | 0.152 | 13.1 | < 0.001 | < 0.001 | 0.013 | 8.3 | < 0.001 | 0.141 | 0.405 | 17.6 | < 0.001 | 0.138 | 0.456 | 12.6 | < 0.001 | 0.598 | 0.854 | 30.5 |
| S remaining (%) | < 0.001 | < 0.001 | 0.003 | 5.3 | < 0.001 | < 0.001 | < 0.001 | 6.3 | < 0.001 | < 0.001 | 0.004 | 12.6 | < 0.001 | 0.011 | 0.639 | 18.4 | < 0.001 | 0.309 | 0.832 | 40.7 |
| Mulch thickness (cm) | < 0.001 | < 0.001 | < 0.001 | 7.3 | < 0.001 | < 0.001 | < 0.001 | 11.6 | < 0.001 | < 0.001 | < 0.001 | 12.0 | < 0.001 | < 0.001 | < 0.001 | 8.8 | < 0.001 | < 0.001 | < 0.001 | 11.8 |
| Water content in the mulch (%) | < 0.001 | < 0.001 | 0.07 | 10.3 | 0.760 | < 0.001 | 0.080 | 11.7 | 0.349 | 0.416 | 0.703 | 21.5 | < 0.001 | 0.497 | 0.620 | 18.4 | 0.092 | 0.911 | 0.444 | 22.6 |
| C:N ratio | < 0.001 | 0.132 | 0.068 | 10.9 | < 0.001 | 0.946 | 0.591 | 21.5 | < 0.001 | 0.419 | 0.052 | 16.1 | < 0.001 | 0.524 | 0.250 | 15.8 | < 0.001 | 0.028 | 0.200 | 9.7 |
| C:P ratio | < 0.001 | 0.009 | 0.062 | 11.6 | < 0.001 | < 0.001 | 0.577 | 10.1 | < 0.001 | 0.172 | 0.151 | 12.7 | < 0.001 | 0.030 | 0.110 | 16.1 | < 0.001 | 0.450 | 0.060 | 19.8 |
| C:S ratio | < 0.001 | 0.017 | 0.805 | 6.13 | < 0.001 | < 0.001 | 0.002 | 11.1 | 0.036 | 0.004 | 0.018 | 19.7 | < 0.001 | 0.334 | 0.463 | 12.9 | 0.416 | 0.358 | 0.378 | 28.1 |
| Soil water content*(cm ³ cm ³) | 0.585 | 0.006 | 0.600 | 7.0 | 0.522 | 0.008 | 0.839 | 7.4 | 0.113 | 0.239 | 0.884 | 10.0 | 0.134 | 0.666 | 0.995 | 10.0 | 0.165 | 0.862 | 0.988 | 15.4 |
| Soil temperature* (°C) | 0.765 | 0.279 | 0.725 | 2.5 | 0.686 | 0.164 | 0.793 | 2.3 | 0.669 | 0.107 | 0.813 | 1.06 | 0.308 | 0.145 | 0.678 | 0.9 | 0.648 | 0.214 | 0.655 | 1.6 |

Table 2 Results of analysis of variance (ANOVA) showing the effect of residues (R) and quantities (Q) and their interactions on measured variables.

^a vetch and wheat

^b quantities of crop residues (3, 6 9 Mg ha⁻¹) ^c coefficient of variation

*soil water content and temperature (intervals of soil: 0-15; 16-45; 46-90; 91-210; 211-360)

| Pool decomposition | | | | |
|--|--------|--------|-------|------|
| | R | Q | RxQ | CV |
| | | | | (%) |
| $C_0 (Mg ha^{-1})^a$ | 0.287 | 0.475 | 0.347 | 1.6 |
| k (days ⁻¹) ^b | <0.001 | <0.001 | 0.051 | 4.3 |
| t ½ (days ⁻¹) ^c | <0.001 | 0.040 | 0.099 | 11.2 |

Table 3 Results of analysis of variance (ANOVA) showing the effect of residues (R) and quantities (\mathbf{Q}) and their interactions for pool decomposition.

^a C_0 is straw C pool. ^b k is the degradation rate constant.

^c $t^{1/2}$ is the half-life of the mulch.

| Parameters | C re | emaining (Mg | ha ⁻¹) | | Mulch straw layers | | | | | | | | |
|---------------------------------------|--------------------|--------------|--------------------|----------|--------------------|---------|----------|----------|---------------------|--|--|--|--|
| | 3 | 6 | 9 | 3T/L | 6 T | 6 L | 9 T | 9 M | 9 L | | | | |
| Vetch | | | | | | | | | | | | | |
| $C_0(\%)^a$ | 96.6 ^{ns} | 98.0 | 99.0 | 96.6ab | 96.5c | 98.5abc | 96.3c | 99.8ab | 99.9ª | | | | |
| K (dias ⁻¹) ^b | 0.0298a | 0.0270b | 0.0280b | 0.0298ab | 0.0240c | 0.0314a | 0.0263bc | 0.0263bc | 0.0316 ^a | | | | |
| t ½ (dias-1) ^c | 23.3 ^{ns} | 26.0 | 25.0 | 23.3b | 3.3b 28.9a 22.2t | | 26.4a | 26.5a | 21.9b | | | | |
| Wheat | | | | | | | | | | | | | |
| C_0 (%) ^a | 97.1 ^{ns} | 97.0 | 97.0 | 97.1ab | 93.2b | 100.0a | 94.5b | 97.1ab | 100.1a | | | | |
| $K (\mathrm{days}^{-1})^{\mathrm{b}}$ | 0.0063a | 0.0056b | 0.0053b | 0.0063ab | 0.0045c | 0.0070a | 0.0048bc | 0.0047bc | 0.0070a | | | | |
| t ½ (days-1) ^c | 111.7b | 125.3ab | 132.3a | 111.7bc | 158.6a | 100.4c | 148.8ab | 151.1ab | 101.1c | | | | |

Table 4 Decomposition parameters for the mulch with different straw quantity 3, 6, 9 Mg ha⁻¹, and mulch straw layers (L: low, M: medium, T: top) for the vetch and wheat.

Values followed by the same letters are not significantly different (Tukey; P<0.05).

^aC₀ is straw C pool. ^bk is the degradation rate constant. ^c t1/2 is the half-life of the mulch



Fig. 1. Precipitation and air temperature (a) and soil water content in the depth of 0-5 in the vetch (b) and in the wheat (c) and soil temperature in the depth of 0-5 in the vetch (d) and in the wheat (e) treatments during the 360 days experiment.



Fig. 2. Evolution of the thickness for the vetch (a) and wheat (b) and water content of the mulch over the 360 days of the experiment for the vetch (c) and wheat (d) and water contents of the mulch layers at two sampling dates and on average for the year (e, f) 3, 6 and 9 Mg ha⁻¹ vetch and wheat and low (L), middle (M) and top positions (T), respectively, in the mulch. The vertical bars indicate the minimum significant difference between treatments (Tukey's test at P<0.05).



Fig. 3. Dynamics of total C remaining (a, b), total N remaining (c, d), total P remaining (e, f) and total S remaining (g, h) in the mulch particles for three quantities of straw (3, 6 and 9 Mg ha⁻¹) the vetch (a, c, e, g) and the wheat residues (b, d, f, h). The vertical bars in the graph indicate the minimum significant difference between treatments (Tukey's test at P<0.05).



Fig. 4. C remaining in the mulch straw layers for vetch (a, c, e, g) and for wheat (b,d, f, h) show different positions in the mulch (L: low, M: middle, T: top) for the 9 Mg ha⁻¹(a, b) and 6 Mg ha⁻¹ (c, d) and 3 L/T (3 Mg ha⁻¹). Crop residue layer is located on the top of the mulch (c, g) and on the low of the mulch (d, h). The vertical bars in the graph indicate the minimum significant difference between treatments (Tukey's test at P<0.05).



Fig. 5. N remaining in the mulch straw layers for vetch (a, c, e, g) and for wheat (b, d, f, h) show different positions in the mulch (L: low, M: middle, T: top) for the 9 Mg ha⁻¹(a, b) and 6 Mg ha⁻¹ (c, d) and 3 L/T (3 Mg ha⁻¹). Crop residue layer is located on the top of the mulch (e, f) and on the low of the mulch (g, h). The vertical bars in the graph indicate the minimum significant difference between treatments (Tukey's test at P<0.05).



Fig. 6. P remaining in the mulch straw layers for vetch (a, c, e, g) and for wheat (b, d, f, h) show different positions in the mulch (L: low, M: middle, T: top) for the 9 Mg ha⁻¹(a, b) and 6 Mg ha⁻¹ (c, d) and 3 L/T (3 Mg ha⁻¹). Crop residue layer is located on the top of the mulch (e, f) and on the low of the mulch in (g, h). The vertical bars in the graph indicate the minimum significant difference between treatments (Tukey's test at P<0.05).



Fig. 7. S remaining in the mulch straw layers for vetch (a, c, e, g) and for wheat (b, d, f, h) show different positions in the mulch (L: low, M: middle, T: top) for the 9 Mg ha⁻¹ (a, b) and 6 Mg ha⁻¹ (c, d) and 3 L/T (3 Mg ha⁻¹). Crop residue layer is located on the top of the mulch (e, f) and on the low of the mulch (g, h). The vertical bars in the graph indicate the minimum significant difference between treatments (Tukey's test at P<0.05).



Fig. 8. Relationships between k days⁻¹ and the average water content in the layers with different positions in the mulch (L: low, M: middle, T: top) for the three treatments (3 Mg ha⁻¹, 6 Mg ha⁻¹ and 9 Mg ha⁻¹) for the vetch (a) and wheat (b) over the 360 days of the experiment.



Supplementary material

Fig S1.Water content in the mulch straw layers in the vetch (a) and wheat (b) with different layers, (top, medium; low) of at 9 Mg ha⁻¹, top and low of 6 Mg ha⁻¹, and only layer of 3 Mg ha⁻¹ on the soil surface.



Fig.S2. Evolution of the C: N ratio (a, d), C: P ratio (b, e), C: S ratio (c, f) for 3, 6 and 9 Mg ha⁻¹ vetch (a, b, c,) and wheat (d, e, f) residues.

3 HOW THE MASS AND QUALITY OF WHEAT AND VETCH MULCHES AFFECT DRIVERS OF SOIL N₂O EMISSIONS *

3.1 Abstract

Crop residues management affects nitrous oxide (N_2O) emissions in no-tillage systems, but the magnitude of emissions depend on soil drivers which are directly influenced by crop residue management. We conducted a one-year study to investigate how mulch chemical characteristics and mass affect N₂O emissions during their decomposition in field under subtropical conditions. The mulch treatments consisted of vetch and wheat crop residues applied onto the soil at a rate of 0, 3, 6 and 9 Mg ha⁻¹ dry matter. We followed the kinetics of mulch carbon (C) and nitrogen (N), soil temperature, moisture and inorganic N, the denitrification end-product ratio [N₂O/(N₂O+N₂)] at days 15 and 30, and N₂O and carbon dioxide (CO₂) emissions by a static chamber method. Mulch decomposition and their C and N dynamics was very rapid for vetch and much more progressive for wheat, in accordance with their initial chemical composition, but for both residues there was no effect of the initial mulch mass on their decomposition rate. The presence of mulches decreased soil temperature and increased soil moisture in the 0-10cm layer under the mulches, with the water filled pore space (WFPS) as 0 = 3 < 6 = 9 Mg ha⁻¹. Vetch also increased significantly the inorganic N content in the soil, compared to wheat that caused net N immobilization. The highest N₂O fluxes were observed in the first 60 days with the vetch residues and increased as 0 < 3 < 6 = 9Mg ha-1, while for wheat the mean N₂O emitted was 50% lower than for vetch and not affected by mulch mass. Although the cumulative N₂O emitted was higher in vetch than in wheat, the N_2O emission factor (EF) was higher for the wheat than vetch residues (4.64% vs 1.75% of N applied) due to the physical effects of wheat mulches on soil N processes. We conclude that while mulch mass and quality influenced strongly soil drivers of N₂O emissions, not only the N input, but also the nature of the residue C, and the residue location must be taken into account to understand and predict N₂O emissions from soils.

Keywords: decomposition, nitrogen, greenhouse gas, no-tilled system, crop residue quality

^{*}Artigo elaborado de acordo com as normas da Revista Geoderma

3.2 Introduction

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Crop residue management is important for improving soil fertility through carbon (C) inputs to soil and nutrient cycling. In no-till systems, crop residues form a mulch on the soil surface that also promotes soil protection from erosion (Derpsch et al., 2014) and contributes to increased soil water storage (Govaerts et al., 2007). Despite these beneficial effects, crop residues can also enhance nitrous oxide (N₂O) emission to the atmosphere during their decomposition at the soil surface (Chen et al., 2013; Pinheiro et al., 2019). N₂O is the main non-CO₂ greenhouse gas emitted from agricultural soils and represents the largest source of anthropogenic N₂O emissions, contributing approximately 60% of total emissions (Lam et al., 2017). Nitrous oxide has a warming potential 265 times higher than that of CO₂ (IPCC, 2014); therefore, the increase of its emission in no-tillage systems can offset the positive effects of this system on C sequestration in soils.

Nitrous oxide is produced in soils mainly by the microbial processes of nitrification and denitrification (Bateman and Baggs, 2005), although this is a simplification of the numerous and complex microbial pathways that form or consume N₂O (Butterbach-Bahl et al. 2013). These processes are directly controlled by so-called proximal drivers: oxygen (O₂) availability, temperature, soil inorganic nitrogen (N) (NH_4^+ and NO_3^-) and labile C in soil (Weier et al. 1993; Davidson et al. 2000; Pimentel et al., 2015; Saggar et al., 2013). These drivers are themselves impacted by agroecosystem characteristics and cultural practices, such as crop type, tillage, crop residue management, and fertilization, also called distal drivers (Saggar et al., 2013). For example, crop residues in a no-till system can affect N₂O production directly by increasing the availability of C and N to microorganisms in the soil (Nadeem et al., 2012; Weiler et al., 2018) and indirectly by reducing the availability of O₂ by maintaining higher levels of soil moisture and by stimulating microbial activity (Baggs et al., 2003). In general, higher N₂O emissions are observed after the application of crop residues with a high N content (low C/N ratio) and a high soluble fraction content (Baggs et al. 2003; Shan and Yan, 2013; Weiler et al., 2018). However, most results have been obtained with buried residues in field or laboratory conditions, which considerably changes the conditions for their decomposition, the soil water dynamics and the net balance between N mineralization and N immobilization (Cosentino et al., 2017). In addition, the impacts of crop residues of different quality and quantity on N₂O emissions in no-till systems remain unclear (Chen et al., 2013). Most of the studies examining the effect of crop residue quantity on N₂O emissions were conducted to assess the impact of bioenergy production (i.e., sugarcane, maize stover, etc.). In a no-till situation, Dietrich et al. (2019) showed that an increase in the amount of sugarcane straw and the mulch thickness ensured better moisture conditions for microbial activity and a higher straw decomposition rate at the soil-residue interface for the thicker mulches, also inducing higher WFPS in soil and finally higher N₂O emissions (Pinheiro et al., 2019); these effects were also observed by Carmo et al., (2013) and Cosentino et al. (2017). However, in other studies, N₂O emissions decreased with increasing straw mass (Pitombo et al., 2017) or remained unchanged (Guzman et al., 2015; Vasconcelos et al., 2018). Therefore, the intensity of N₂O emissions cannot be directly related to the amount of crop residues left on the soil surface, confirming that the presence of residue mulch acts on both proximal and distal drivers of N2O emissions, sometimes in opposite directions (Chen et al., 2013; Peyrard et al., 2016). This is understandable given the number and complexity of the soil processes altered by the presence and decomposition of plant biomasses (Butterbach-Bahl et al., 2013). A common feature of most of these studies is the use of crop residues with low N (high C/N ratio) and low soluble fraction contents (Pinheiro et al., 2019; Carmo et al., 2013), which exhibit low decomposition rates and high potential for N microbial immobilization; the effect of mulch mass has not yet been investigated for cover crops, which are important components of no-till systems (Scopel et al., 2013).

Therefore, the main objective of this study was to clarify under field conditions how mulch chemical characteristics and quantities affect proximal drivers of N_2O emissions and the N_2O emitted. This was achieved by using two different types of crop residue, wheat residues collected at crop maturity and vetch residues collected at the vegetative stage as a cover crop, that were left as mulch on the soil in four quantities, ranging from 0 to 9 Mg of dry mass per hectare. The focus was on characterizing the kinetics of mulch C and N degradation and measuring N availability, water content and water-filled pore space (WFPS) in the soil layer underlying the mulch. We hypothesized that i) crop residue quality (N content and chemical composition, particularly the soluble fraction) affects the timing and magnitude of N_2O emissions due to its role in the dynamics of C degradation and N inputs and ii) emissions increase with increasing mass of mulch, regardless of the crop residue type, due to C and N inputs and the indirect effects of the presence of mulch on soil temperature and moisture.

3.3 Material and Methods

3.3.1 Site Characteristics

The experimental field site was located at the Federal University of Santa Maria (29°42'54" S, 53°42'23" W, approximately 90 m of elevation), state of Rio Grande do Sul, Brazil. The climate is classified as humid subtropical (type Cfa2 in Köppen's classification) with an annual rainfall of 1660 mm and average air temperature ranging from 14°C in June to 25°C in January (30-year average). Air temperature and daily rainfall were obtained from an automatic meteorological station located 1.6 km away from the experimental site. The soil is classified as Typic Paleudalf (Soil Survey Staff, 2010) with 110 g kg⁻¹ clay, 260 g kg⁻¹ silt, 630 g kg⁻¹ sand and soil bulk density of 1.60 g dm⁻³ in 0-10 cm layer. Prior the beginning of the study, the 0-10 cm soil layer had a pH_{H2O} of 4.8, 33.1 mg Mehlich-I P extractable kg⁻¹, 66.0 mg Mehlich K kg⁻¹, 9.6 g total C kg⁻¹ and 0.9 g total N kg⁻¹soil. As previous crop management, the area was grown under no-tillage with rotation of winter [oats (*Avena sativa*) or ryegrass (*Lolium multiflorum*)] and summer [black bean (*Phaseolus vulgaris*) or soybean (*Glycine max*)] crops for 6 years.

3.3.2 Treatments and experimental design

On 18 November 2016, one week before the experiment was sat up, an area of 12 x $20 \text{ m} (240 \text{ m}^2)$ was delimited and all residues were manually removed from the soil surface. The experiment was conducted in factorial scheme $2 \times 3 + 1$ and a randomized complete block with 4 replicates. Plots were $2 \times 2.5 \text{ m}$. The treatments consisted of vetch (*Vicia sativa* L) and wheat (*Triticum aestivum* L.) crop residues. Both crop residues were equivalent to 3, 6 and 9 Mg ha⁻¹ of dry matter (DM) plus a treatment without crop residues (control). These treatments were named vetch 3, vetch 6, vetch 9 and wheat 3 wheat 6, and wheat 9 and soil for the control. Crop residues were manually distributed on the soil surface for each plot.

The aboveground plant residues of vetch and wheat used in this study were on farmcollected. Vetch shoots were cut at the flowering time and wheat residues were collected immediately after the crop harvest. The plant residues were placed in bags and transported to the laboratory. Vetch residues were cut into 20 cm pieces to simulate the effect of passing a knife roller and wheat residues were previously fragmented by the combine and were composed predominantly of pieces between 5 and 20 cm. The crop residues were dried at 45°C for 48 hours in a forced-air oven to a constant weight. One crop residue subsample was oven-dried at 65 °C for 48 h for DM correction. Then, the amount of each dry residue at 45 °C equivalent to 3, 6, 9 Mg ha⁻¹ of dry matter (DM) was weighed and stored in bags until placed in the field.

The plant residue dried at 65°C was finely ground in a ball mill for the determination of C and N contents using an elemental analyzer (FlashEA 1112, Thermo Finnigan, Milan, Italy). Another sub-sample dried at 45°C was ground in 1 mm particles for analysis of soluble fraction (SOL), cellulose (CEL), hemicellulose (HEM), and lignin (LIG) fractions of the plant residues using the Van Soest method, as described by Redin et al. (2014). The water-soluble organic C (Csw) and water-soluble total N (Nsw) were extracted and analyzed from crop residue according to Schmatz et al. (2017). The chemical characteristics of the residues are given in Table 1. Vetch residue had 3.3 times more soluble fraction than the wheat residue (530.4 vs 161.7 g kg⁻¹). The C content was close in both residues but the N content was approximately 7 times higher in the vetch than wheat. The mulch-C added was similar between vetch (1.31, 2.62, and 3.94 Mg C ha⁻¹) and wheat (1.29, 2.58, 3.87 Mg C ha⁻¹). Due to differences in N content between the two residues the amount of N added to soil was much higher with the vetch (109, 218, 328 kg ha⁻¹) than wheat (15, 31 and 46 kg ha⁻¹).

3.3.3 Mulch decomposition

The vetch and wheat crop residues dried at 45 °C were placed in a litter box (Dietrich et al., 2017) delineated by open-wooden frames (40 cm length, 40 cm width and 8 cm height). The bottoms of the wooden frames were delimited with 5-mm nylon mesh, whereas the tops of wooden frames were closed with 10-mm plastic screen mesh to prevent straw loss by wind to allow access by soil macrofauna. The amount of crop residues added in each litter box was equivalent to 3, 6, and 9 Mg DM ha⁻¹. The initial thickness of the mulches measured initially was similar for vetch and wheat in each quantity (data not showed) and was 3, 5 and 7 cm thick for 3, 6 and 9 Mg residue ha⁻¹, respectively.

Samples for DM, C and N measurements were collected at 0, 15, 30, 45, 60, 90, 150, 210, 270 and 360 days after crop residues application. One litter box per plot was destroyed at each measurement date. Samples of vetch and wheat crop residues were collected in the field and oven-dried at 65°C for 48 h in the laboratory. After that, samples were gently

separated from adhering soil manually with a brush to determine DM. Sub-samples were finely grounded in a ball mill for the determination of C and N content using an elemental analyzer (Flash EA 1112; Thermo Electron Corporation, Milan, Italy). The Csw and Nsw in the remaining residues were determined according to Schmatz et al. (2017).

3.3.4 N₂O and CO₂ fluxes

Fluxes of N₂O and CO₂ were measured using insulated, fan-mixed, non-flow-through non-steady-state chambers (Rochette and Bertrand, 2008) from 26 November 2016 to 21 November 2017. The apparatus consisted of a galvanized steel collar inserted to 5-cm soil depth and a removable galvanized steel chamber measuring 40 x 70 x 20 cm (length x width x height), averaging 56 L of air volume per chamber. During the experiment 62 air-sampling events were performed. The air sampling was performed before rainfall and the morning after rainfall in two to three times per week during the first two months following crop residue application and less frequently thereafter. Air samples were manually taken between 9 and 11 a.m., a period that the N₂O concentration in the samples represents the average daily emission (Reeves et al., 2016). In a sampling event, samples were taken from each chamber 0, 15 and 30 min after chamber was placed on collar. Before air sampling, the headspace air was homogenized for 30s with an electric fan mounted on the chamber wall, and internal temperature was measured. The air samples were taken using a 20-mL polypropylene syringe fitted with a three-way stopcock and immediately transferred to 12mL pre-evacuated glass vials (Labco, Lampeter, UK). Air samples were analyzed for N₂O and CO₂ concentration within one week using gas chromatograph (GC-2014, Shimadzu Corp., Kyoto, Japan).

3.3.5 Soil measurements

Soil water content in all treatments was determined using FDR (frequency domain reflectometry) sensors (model CS616-L, Campbell Scientific, Logan, Utah, USA), coupled to a data logger (CR1000, Campbell Scientific, Logan, Utah, USA). The FDR sensors were placed horizontally at 2.5 cm (0-5 cm) and 7.5 cm (5-10 cm) in the soil profile and readings were recorded every 10 min. Soil samples were eventually taken to determine gravimetric moisture content (105°C for 24 h), thus each sample was then compared to FDR probe

readings, which allowed the development of calibration curves for each probe through regression analysis, and correct the FDR sensors measurements. For the temperature evaluation ($^{\circ}$ C), the T-type sensors were installed and 2.5 (0-5 cm) 7.5 (5 -10 cm) deep in the soil. The temperature sensors followed the same reading time as the moisture sensors.

Soil samples were collected from 0-10 cm depth from each plot on selected gas sampling dates to determine inorganic N content (NH₄⁺ and NO₃⁻). Inorganic N was extracted by shaking 20 g of field-moist soil in 80 mL of a 1 M KCl solution for 30 min. After decantation for 30 min, the supernatant of the solution was filtered (paper filter Unifil C42, particle size retention 1-2 μ m), and kept frozen until analysis. NH₄⁺ and NO₃⁻ were quantified an automated colorimeter (SAN plus, Skalar, Breda, Netherlands). Gravimetric soil moisture content was determined by oven drying soil samples at 105°C for 24 h.

To determine the denitrification end-product ratio $[N_2O/(N_2O + N_2)]$, the potential denitrification activity (PDA = N_2O+N_2) and potential N_2O production (N_2O) were measured using acetylene inhibition technique (Tiedje, 1982; 1994). The analysis was performed in soil samples from 0-5 cm layer depth collected at day 15 and day 30 after crop residues addition, period during which the highest frequency and intensity of N_2O fluxes were observed in the field. Briefly, 10g of fresh weight soil was placed in a 125 mL flask containing 1 mM glucose, 1 mM KNO₃, and 1 g L⁻¹ chloramphenicol. The flasks were capped with rubber caps and anaerobic conditions were created by evacuating the flask completely and after saturating the environment with N_2 . Soil slurries were incubated either with or without acetylene (10%, vol/vol). After, flasks were placed in a horizontal shaker at 25°C and gas sample were taken 20, 40 and 60 min. At each gas sampling, 15 ml of headspace was removed and placed in an evacuated glass vials (Labco, Lampeter, UK). An equal volume of N_2 was immediately injected into the flask. The N_2O concentration was measured in gas chromatograph as previously described.

3.3.6 Calculations and Statistical Analyses

The residue remaining total and soluble C and N was calculated at each sampling date as the product of remaining dry mass and its C and N concentrations. Soil-surface N_2O and CO_2 fluxes were calculated according to Rochette and Bertrand (2008). Cumulative N_2O emissions were obtained by linear interpolation of fluxes between consecutive sampling dates. The N₂O-N emission factor (EF) was calculated by subtracting the cumulative N_2O -

N emissions of the control plots from cumulative N₂O-N emissions of amended crop residues plots, divided by the amount of residue total N added. The inorganic N (kg N ha⁻¹) in the 0-10 cm depth soil layer was calculated as the product of inorganic N concentration (mg N kg⁻ ¹ dry soil) and the soil dry mass determined from bulk density (1.6 Mg m⁻³). Net mineralization of N in the 0-10 cm layer was calculated at each date, as the sum of NH4⁺-N and NO_3 N content and the difference with the control treatment. The water-filled pore space (WFPS) in the 0-5 and 5-10 cm soil layers was estimated by dividing the volumetric water content by the total soil porosity determined from the bulk density. The PDA measured with acetylene $(N_2O + N_2)$ and potential N₂O production measured without acetylene (N_2O) at 15 and 30 days were expressed as µg N₂O-N kg⁻¹ soil hr⁻¹ for each treatment. The ratio of potential N₂O production and PDA results provides the $[N_2O/(N_2O+N_2)]$. The available Csw to NO₃⁻-N ratio (Csw/NO₃⁻) was calculated at day 15 and day 30 from Csw loss from mulch and the average amounts of NO₃⁻N in the 0-10cm soil layer. The Csw on each date represents the Csw loss from mulches between 0-15 and 0-30 days. The amount of NO₃-N was calculated as the average NO₃⁻N content in the 0-10 cm soil layer between day 0 and day 15, then between day 0 and day 30.

All data were subjected to analysis of variance (ANOVA). When ANOVA showed significant (P<0.05), the differences between means of treatments were compared by the Tukey test (P<0.05). For the N₂O-N cumulative and EF data, the effects of crop residue quantities and crop residue type and their interaction were tested. All data were analyzed using the SISVAR® statistical software (version 5.6). Pearson's correlation coefficient was used to measure the relationship between the daily N₂O fluxes and CO₂ fluxes, WFPS, soil temperature and NO₃⁻-N and NH₄⁺-N soil content (0-10 cm), total C and N remaining in the mulches. The dataset includes only the observations (24 dates) that were performed on the same day as the N₂O fluxes and the listed variables. Only correlations coefficients with P < 0.05 were considered significant. The relationships between [N₂O/(N₂O + N₂)] and Csw/NO₃⁻ at day 15 and day 30 was fitted.

3.4 Results

3.4.1 Environmental conditions and WFPS

The total rainfall was 2337 mm, higher than the 30-yr normal of 1660 mm, with a heterogeneous distribution over the year. For example, while cumulative rainfall was 417 mm during the first 60 days, only 97 mm fell down during the first 30 days after crop residue addition. The mean daily air temperature was 20°C, close to the 30-yr normal (Fig 1a). Water-filled pore space (WFPS) varied from 30% to 74% in the 0-5 cm soil layer (Fig 1b) and from 42% to 79% in the 5-10 cm soil layer (Fig S1a, b). During the 360-day experiment, the WFPS was significantly affected by rainfall and straw quantities. Overall, regardless of the type of crop residue, the WFPS decreases in the following order: 9 Mg $ha^{-1} = 6$ Mg ha^{-1} > 3 Mg ha⁻¹ = 0 Mg ha⁻¹ (Supplementary Table S1). The effect of residue type on the WFPS was observed mainly in the periods with low rainfall and only after day 50. In general, but not significantly, WFPS of wheat residue treatments were 1.1 times higher than for vetch treatments. The soil temperature differ neither between crop residue types nor between residue quantities. Soil temperature only differed between the mulched and the bare soils in the 0-5 cm (Fig. 1 d e) and 5-10 cm soil layers (Fig. S2a, b) during the first 30 days of the experiment. In that case, the presence of the mulch decreased the daily soil temperature by 1 to 2 °C compared to the bare soil.

3.4.2 Dynamics of mulch-C and -N

The dynamics of mulch total C and N differed significantly between wheat and vetch, but for the two residues the loss of total C and N was proportional to the initial amount. For vetch, a fast and concomitant loss of C and N was observed, representing a mean loss of $-75\pm 2.0\%$ initial C and $-87\pm 1.0\%$ initial N at day 45. Conversely for wheat, the mulch-C and N losses were slower, representing on average $-25\pm 1.2\%$ initial C and $-45\pm 1.0\%$ initial N at day 45. After one year, the mulches have lost $96\pm 1.0\%$ added C and $98\pm 0.8\%$ added N for vetch, and $84\pm 3.0\%$ added C and $64\pm 0.8\%$ added N for wheat , irrespective of the initial amount of mulch. The mulch Csw and Nsw were initially 3 and 11 times higher in vech than wheat residues, respectively, and their overall dynamics followed the same pattern than for total C and N, except for a significant rapid loss during the first 15 days.

3.4.3 Evolution of inorganic N in the 0-10 cm soil layer

Soil NH₄⁺-N and NO₃⁻-N contents were affected by the crop residue addition only in the first 68 days (Fig 3). While NH₄⁺-N remained below 20 kg N ha⁻¹ in all treatments throughout the 360-day experiment, initial higher accumulation was observed in vetch 6 and vetch 9 at day 4 with 26 and 45 kg NH₄⁺-N ha⁻¹, respectively (Fig 3a). Compared to control, high NO₃⁻-N contents were measured between days 8 and 35 with vetch plots, ranking as control < vetch 3 < vetch 6 < vetch 9 (Fig. 3b). In contrast, over the same period, NO₃⁻-N content was lower in the three wheat treatments than in control soil, but did not differ whatever the quantity of wheat mulch. As a consequence, wheat mulches caused a net N immobilization peaking at about -23 kg N ha⁻¹ at day 27, irrespective of the mulch quantity, while vetch mulches caused net mineralization (in the range +10 to +40 kg N ha⁻¹) depending on the mulch quantity over the same period (Fig. 3c).

3.4.4 N₂O and CO₂ emissions

Crop residues increased N₂O fluxes (Fig 4a), especially during the first 60 days, ranging from -4.0 to 3259 μ g N m⁻² h⁻¹ with vetch residues and from -51 to 327 μ g N m⁻² h⁻¹ with wheat residues. As expected, the highest daily N₂O emissions were observed after rainfalls. For vetch, N₂O fluxes ranked as vetch 9 = vetch 6 > vetch 3. For wheat, N₂O emissions did not vary significantly between the three mulch quantities. After day 105, N₂O fluxes reduced to levels close to background in all treatments. The daily N₂O fluxes (n=672) were best correlated to CO₂ (r = 0.83), WFPS (r= 0.51) and mulch N remaining (0.50). They were poorly correlated to soil temperature (r = 0.15), soil NO₃⁺-N (r=0, 22), soil NH₄⁻-N (r=0.31) and mulch total C remaining (0.24).

The high CO₂ peaks were well synchronized with those measured for N₂O. Until day 45, CO₂ fluxes showed different magnitudes among the treatments (Fig 4 b), with vetch > wheat, vetch 9 > vetch 6 > vetch 3, and wheat 9 > wheat 6 = wheat 3. After day 82, CO₂ fluxes did no differ significantly between treatments.

Cumulative N₂O emissions calculated over one year were significantly affected by crop residue, quantities and their interaction (Table 2). Cumulative N₂O emissions was two

times higher with vetch mulches than wheat mulches (on average, $3.19 vs. 1.59 \text{ kg N ha}^{-1}$), and was significantly increased compared with bare soil only with the vetch mulches. For vetch treatments, the highest cumulative N₂O was observed for vetch 6 while vetch 9 showed intermediate behavior (Fig 5 and Table 2). For wheat, no significant difference in cumulative N₂O was observed between wheat 3, wheat 6 and wheat 9. The emission factor (EF) was higher for wheat mulch (on average 4.64% added N) than vetch mulches (on average 1.75% added N) (Table 2). Although there was no statistically different response of EF to the amount of mulch applied, there is a downward trend in EF for 9 Mg ha⁻¹ compared to 3 and 6 Mg ha⁻¹ treatments which were rather stable for each residue: a 49% and 40% relative reduction in EF value for vetch 9 and wheat 9 compared to the mean (vetch 6, vetch 3) and (wheat 6, wheat 3), respectively. For the two residues, EF exceeded the value of 1% proposed by the IPCC (2014), with the exception of EF measured for the 9 Mg vetch residue.

3.4.5 PDA and potential N₂O production

At day 15, PDA (N₂O+N₂) did not vary significantly between treatments, except for vetch 9 for which the N₂O produced was lower (Table 3). PDA significantly decreased at day 30, with no significant differences between treatments. The potential N₂O production (N₂O) was significantly lower for vetch 9 compared to other treatments, both at day 15 and at day 30. The [N₂O/(N₂O+N₂)] was also significantly lower for vetch 9 compared to all other treatments for which this ratio was relatively constant, increasing from on average 0.75 on day 15 to 0.92 on day 30 (Table 3). The Csw/NO₃⁻ in the 0-10cm layer varied greatly between wheat and vetch at days 15 and 30, due mainly to the high initial input of available soluble Csw with vetch (vetch 9> vetch 6> vetch 3). The [N₂O/(N₂O+N₂)] varied according to Csw/NO₃⁻ (Fig 6, Table 3) with lower ratio for the vetch 9 having high Csw/NO₃⁻ ratio, at both dates.

3.5 Discussion

3.5.1 Mulch quality and mass effects on mulch decomposition

The residues used in this study showed large differences in their initial chemical composition, with the vetch combining high N (low C/N ratio) and a high soluble fraction content, while wheat residues had a low N content (high C/N ratio) and a greater proportion of structural carbohydrates. As expected, the characteristics of vetch resulted in faster and higher decomposition when compared to that of wheat residues, which agrees well with numerous studies on this topic (Jensen et al., 2005; Redin et al., 2014). A large soluble fraction (SOL and Csw) combined with high N content (N and Nsw) in crop residues is recognized for promoting high microbial activity and respiration, especially in the early stages of decomposition (Cobo et al. 2002; Thippayarugs et al., 2008; Redin et al., 2014). Furthermore, microorganisms involved in the degradation of these compounds (Sylvia et al., 1998). The pattern of mulch N dynamics for vetch and wheat also reflected the differences in their initial chemical compositions, with higher rates of mulch N loss for vetch compared to wheat residues.

Regardless of the type of residue, the decomposition was not affected by the initial mass of mulch on the soil surface (in the range of 3 to 9 Mg ha⁻¹), which agrees with results obtained in recent studies with rye (Willians et al., 2018) and sugarcane (Dietrich et al., 2017; 2019). The fact that decomposition remained proportional to the initial amount (i.e., a similar degradation rate, k) means that there was no factor limiting the decomposition of the mulchs related to their mass in the range explored such as mulch moisture or mineral N availability to decomposers, particularly for the high C/N wheat mulch in the present study. As observed for C, the amount of mulch N remaining after one year was also proportional to the initial amount of residue N added. In fact, Dietrich et al. (2019), investigating gradients of decomposition within sugarcane mulches of various masses and thicknesses (in the range of 4 to 12 Mg ha⁻¹) under subtropical conditions in Brazil, showed that in thicker mulches, the fraction at the bottom of the mulch, which was in contact with the soil, had high moisture and a high rate of degradation, which compensated for the lower moisture and lower degradation rate of the upper part of the mulch that was in contact with the atmosphere. Our results suggest that these conclusions obtained with sugarcane can be extrapolated to mulches as different as vetch and wheat that are decomposing under the similar climate conditions in the area.

3.5.2 Effects of mulch dynamics on soil drivers of N₂O production

The difference in the nature of wheat and vetch mulches did not affect the soil temperature and had little effect on the soil moisture, expressed as WFPS. When differences in WFPS occurred, they were not significant, only appeared after day 50 and, on average, were at most 10% higher in soil covered with wheat than in soil covered with vetch. The lack of effect of the residue type on WFPS at the beginning of the experiment is attributed to the absence of a difference in mulch thickness between vetch and wheat for each quantity and possibly on the rate of soil surface coverage, which was similar for the two residues, based on visual observation. This condition changed over time with the rapid decomposition of the vetch residues, which led to a reduction in the soil coverage compared to the soil coverage under the wheat residues and could explain the differences that appeared later.

Conversely, the mass of residues showed a significant effect on soil WFPS. The presence of mulch maintained high WFPS after precipitation and reduced water evaporation mainly in periods where precipitation did not occur. In this study, the average WFPS was 25% higher with vetch 9 and wheat 9 than in the control during the first 105 days and 12% higher over the whole year. Gonzaga et al. (2018) also showed that soil WFPS was approximately 17 to 22% higher in treatments with 5 and 10 Mg ha⁻¹ of sugarcane mulch than in the bare soil treatment in the dry season. Pinheiro et al. (2019) also obtained a 23% difference in WFPS with sugarcane mulches and showed that despite the thick mulches preventing some fraction of the rain from reaching the soil, compared to bare soils (control), the main effect was the limitation of evaporation, allowing mulched soils to maintain higher moisture during dry periods. Likewise, other studies have reported that crop residues deposited on the soil surface maintain soil moisture for a longer period (Basche et al., 2016; Domeignoz-Horta et al., 2015, Peyrard et al., 2016; Peyrard et al., 2017). The range of WFPS values together with the possible depletion of O_2 at the soil-mulch interface during decomposition indicate that the presence of the mulch may favor the shift from nitrification to denitrification at a high amount of residues (6 and 9 Mg ha⁻¹). Mulch presence also significantly decreased the temperature in the underlying soil (average - 2°C compared to bare soil), which can increase or decrease microbial activity depending on the period considered. Therefore, the physical properties of increased mass and thickness of mulch at the soil surface might promote suitable conditions for microbial activity by preserving soil moisture and reducing temperatures under conditions of high heat and/or drought in the subtropical conditions of the study. Differences in crop residue quality (C/N vetch = 12; C/N

wheat = 83) translated into significant differences in the availability of mineral N in the soil under the mulch, notably during the initial decomposition phase of the residues. Compared to the decomposition of the control, wheat mulch decomposition resulted in a net immobilization of inorganic N in the 0-10 cm layer, while vetch residues first caused a transient accumulation of ammonium, which disappeared, and a net accumulation of inorganic N (ammonium + nitrate), i.e., a net mineralization of N. These results are in agreement with what we know about the effect of the C/N ratio of crop residues on the net balance between microbial N mineralization and N immobilization under field (Aita et al., 2004) and laboratory conditions (Jensen et al., 2005; Redin et al., 2014). Redin et al. (2014) found that during the decomposition of leaves, stems and mixtures of stems + leaves of 25 species left on the soil surface, the net mineralization of N in the soil was observed in residues with a C/N ratio below 36. However, the accumulation of mineral N in the 0-10 cm layer of soil under the vetch residues was low (at most 40-60 kg N ha⁻¹) compared to the amount added (100-300 kg N ha⁻¹) and was only transient. Several processes combined could explain this relatively low accumulation of inorganic N in the 0-10 cm layer for vetch and the erasure of the differences among vetch treatments. Part of the N released from residue probably migrated to deeper layers, while residue layers of different masses and thicknesses had an effect on the water infiltration into the soil, translating into effects on soil NO₃⁻ dynamics. A loss of N by volatilization of ammonia (NH₃) could also have occurred, as shown by Larsson et al. (1998), with 17% added residue N being lost through NH₃ volatilization with alfalfa (Medicago sativa). The lack of difference between vetch 6 and vetch 9 might also result from increased soil N microbial immobilization with increased addition of soluble C (Said-Pullicino et al., 2014), resulting in intensified competition between heterotrophic and nitrifying microorganisms (Bengtsson et al. 2003). Last, denitrification probably occurred and contributed to the loss of N, particularly under the observed favorable conditions for biological activity created by vetch mulches. Nevertheless, the early C and N dynamics of the wheat and vetch mulches created a large range in the amount of available C (not measured in soil but deduced from the initial amount and rapid loss of soluble C from mulches) and NO₃⁻-N in soil and in their ratio (varying from 0.8 to 12.9 at days 15 and 30), which has been shown to influence potential denitrification and the molar ratio of N₂O to N₂ produced (Saggar et al., 2013).

3.5.3 Consequences on N_2O emission and crop residue emission factor (EF)

As hypothesized, the presence of crop residue mulches increased N₂O emissions soon after mulch application, as shown by other authors, when soil properties and microbial processes were modified (Shan and Yan, 2013; Li et al., 2016). Regardless of the amount of mulch, the emission of N₂O was higher in the treatments with vetch than in those with wheat residues, whose results did not differ significantly from those of the bare soil most of the time. This result supports our first hypothesis that crop residue with higher N and soluble C contents increases N_2O emissions. Similar results were obtained by Davis et al. (2019) in a 3-year field study with vetch (C/N = 17) and rye (C/N = 78). We observed that the effect of vetch residues on N₂O emissions took place mainly in the first 60 days, representing approximately 82% of the total N₂O emissions during 1 year, which corresponds with the observed fast release of mulch C and N in vetch mulches, confirmed by the correlation we obtained between the N and N₂O fluxes in the remaining mulch. This was also observed in subtropical (Bayer et al., 2015; Weiler et al., 2018) and temperate (Peyrard et al. 2016) conditions and was attributed to the increase in the concentration of available C and mineral N in soil during the initial stage of cover crop residue decomposition. Wheat mulches added much less N to the system, showed slower decomposition and induced net N immobilization in the soil. Together, this explains the lower total N₂O emitted from wheat straw than from vetch and the nonsignificant differences among the three mulch masses.

As expected, the N₂O emissions were dependent on the occurrence of precipitation, as observed during the first 30 days in which three precipitation events > 15 mm caused high and short-lived N₂O fluxes during this dry period. The increase in N₂O emitted after precipitation probably results from the direct and indirect effects of water on microbial activity and on the availability of O₂ in the soil. The high O₂ consumption from the stimulus of microbial activity is supported in our study by the significant increase in CO₂ fluxes after the rainfall events, which coincided with the increase in N₂O fluxes. In accordance with this, the correlation between CO₂ and N₂O fluxes indicated that high N₂O fluxes were connected with high decomposer activity, as revealed by the amount of CO₂ emitted (Millar & Baggs, 2005; Chen et al., 2013). Precipitation also leached out soluble C and N, and notably, with vetch, induced transient accumulation of NH₄⁺-N observed on days 15 and 30, promoting subsequent nitrification. It was not possible in this study to quantify the respective contribution of nitrification and denitrification to N₂O production from the soil, which would require other methodologies (Butterbach-Bahl et al. 2013), but crop residue left as mulch on

the soil surface in no-till systems (i.e., compared to buried residues) creates a highly stratified soil-mulch system, both from a chemical and biological point of view and in terms of the diffusion of solutes and gas. In such systems, nitrification and denitrification likely coexist, with a particular hot spot of denitrification at the soil-mulch interface (Kravchenko et al., 2017).

In addition to quality, mulch quantity can also alter the drivers responsible for the emission of N₂O. One of these factors is the WFPS, which was positively correlated with N₂O fluxes, as shown by correlation analyses. In our study, the WFPS ranged from 33 to 74% for the two residues at high initial masses (6 and 9 Mg DM ha⁻¹), which again suggests that both nitrification and denitrification were responsible for the emission of N₂O. Such a result was evidenced in several studies (e.g., Bateman and Baggs, 2005; Chen et al., 2013) in which it was accepted that nitrification dominates the N₂O production of aerated soils in the range of 30 to 60% WFPS, and denitrification is considered the main process responsible for the production of N₂O when the WFPS is greater than 50-90%. Since we observed that the WFPS and temperature were similar at the two highest mulch masses for both wheat and vetch, while different N₂O emissions were observed, the amount of C and N applied may explain the differences observed.

An abundant body of literature attempts to clarify the effect of C (nature and quantity) and N availability on N₂O emissions (Pugesgaard et al., 2017). It is difficult to distinguish the two because they generally vary together, especially in crop residues, and these two drivers act simultaneously on the composition of the community and on enzymatic activities, modifying the total potential denitrification as well as the $[N_2O/(N_2O+N_2)]$. The available C seems to increase the total denitrification and decrease the $[N_2O/(N_2O+N_2)]$, while the availability of NO₃⁻ favors the production of N₂O, thus increasing the $[N_2O/(N_2O+N_2)]$ (Saggar et al., 2013). The high values (0.7-0.9) for $[N_2O/(N_2O+N_2)]$ observed in this study are in the upper range of values obtained by Domeignoz-Horta et al. (2015) for a range of agrosystems and agricultural practices. Using the C/NO₃⁻ ratio proposed by Saggar et al. (2013), we showed that a high $[N_2O/(N_2O+N_2)]$ was obtained with wheat residues (3, 6 and 9 Mg ha⁻¹) and vetch at 3 Mg ha⁻¹ for low to medium values of Csw/NO₃⁻ (≤ 8), while for higher Csw:NO₃⁻ (=12-14), the [N₂O/(N₂O+N₂)] starts to decrease (notably with vetch at 9 Mg ha⁻¹). Therefore, C_{sw}/NO_3^- fairly well described the variation in the proportion of N₂O emitted across residue type, mulch mass and time at two dates, and we attribute the lack of N₂O increase with vetch 9 compared to with vetch 6 to the observed decrease in the $[N_2O/(N_2O+N_2)]$ in the vetch 9 treatment during the first 30 days. This change in $[N_2O/(N_2O+N_2)]$ occurs when the C/NO₃⁻ is high (Weier et al., 1993; Senbayram et al., 2012) and indicates a more complete reduction of NO₃⁻ to N₂ via denitrification. In this study, we chose to calculate the available C from the depletion of the Csw from the mulch, while nitrate availability was calculated as the average content in the top 0-10 cm of soil. These results indicate that higher amounts of vetch residues, even with the corresponding higher WFPS and availability of C and N in soil, may not increase N₂O emissions, since the reduction of N₂O to N₂ is favored. This result contradicts our hypothesis that there is a linear relationship between the quantity of residues and the emission of N₂O.

Despite higher N₂O emissions with vetch residues, the emission factor (EF) calculated as a function of residue N recycled and averaged for the three mulch quantities of each type showed a higher EF for wheat (EF= 4.64) than for vetch (EF=1.75). High EF values with N-poor crop residues, although little reported, were also observed by Weiler et al. (2018) with millet residues (C/N = 75, EF = 1.49) on the soil surface and by Liu et al. (2011) with wheat residues (C/N = 79, EF = 2.32) incorporated into the soil. In our study, the high EF value for the wheat residue can be explained by the relatively high availability of mineral N (NH₄⁺ and NO₃⁻) in the soil, which remained between 15 and 27 kg N ha⁻¹ in the first 105 days despite some net immobilization. Under these conditions, the presence of a mulch and the input of C from wheat residue combined with the establishment of low O_2 availability may have enhanced N₂O production from the soil N source. Aulakh et al. (1984) demonstrated that the addition of wheat residue to the soil surface under high N availability conditions doubled N₂O emissions compared to the application of straw to the same soil with low N availability. It is a strong limitation on EF calculation for crop residues, which expresses N₂O in relation to the residue N source, without taking into account the management conditions (here, mulch) that strongly affect soil processes.

Regarding the effect of residue quantity, the EF did not vary significantly as a function of mulch mass for a given residue type, and this result differed from earlier results with sugarcane mulches where an increase (Pinheiro et al., 2019) or a decrease (Vasconcelos et al., 2018) in EF was obtained with increasing amounts of mulch. The EF was equal to the 1% proposed by the IPCC (2014) only for vetch 9 and was far above 1% in the other treatments. An EF value (=0.75%) lower than the IPCC standard for vetch mulch under subtropical conditions was observed by Gomes et al. (2009). In a previous work, Weiler et al. (2018) studied different summer cover crops in two years of experiments and obtained

EFs below 1% for all cover crops except showy rattlebox (EF=1.11%) during the second year. Other studies, such Davis et al. (2019), observed a higher EF with vetch (4.7%) than with rye (2.2%), and both residues presented EF values higher than the IPCC value. It should be noted that several attempts have been made to generate EF for crop residues, but estimates varied widely. Our results confirm the major uncertainty in calculating soil N₂O emissions linked to the presence of residues, which is understandable considering the synergistic and antagonistic effects of combined soil drivers (Butterbach-Bahl et al. 2013), particularly with crop residues left as mulch.

3.5.4. Consequences for management in cropping systems

The inclusion of legume cover crops such as vetch in no-till systems is considered a best management practice to increase soil organic C sequestration and consequently mitigate climate change (Minasny et al., 2017; Veloso et al., 2018). However, the use of legumes affects N₂O emissions, as observed in our study, leading to a possible trade-off between N₂O emissions and C sequestration (Lugato et al., 2018). From a greenhouse gas emission (GHG) perspective, the maximum acceptable increase in N₂O-N emission in legume cover-cropbased cropping systems is 0.88 kg per 0.10 Mg C new (GWP $N_2O = 265$, IPCC, 2014). In our study, the average N₂O measured from vetch residues was 3.46 kg ha⁻¹ (- N₂O control), which would neutralize a C sequestration rate of 0.39 Mg ha⁻¹ year⁻¹. This value is 2.18 times higher than the estimated rate for Brazilian soils in the 0-30 cm layer under the target "4 per 1000" initiative (Veloso et al., 2018). Our estimate may be too high if we consider that N₂O-N emissions measured in our study may be high for the region and climate (EF = 0.75%, Gomes et al., 2009; mean EF = 0.61%, Weiler et al., 2018). Conducting our experiment in the absence of plants must have contributed to maintaining larger amounts of available N and allowed a longer period of time for the processes involved in N₂O production to take place. Under conditions where N₂O emissions are low with vetch mulch (Gomes et al., 2009; Bayer et al., 2015), emissions are strongly neutralized by soil C storage (Bayer et al., 2016). The use of strategies that improve the N use efficiency of legume cover crops can contribute to reducing N₂O emissions and thereby can contribute to reducing net GHG emissions from no-till systems.

3.6 Conclusions

The chemical composition and the amount of crop residues added to soils had a strong effect on N₂O emissions, with an interaction between the two that depended on the chemical quality of the residues. The combined effects of residue N and C as substrates for soil microbial activity and the presence of mulches at the soil surface, particularly when applied in large quantities, affected the proximal drivers of N₂O emissions by maintaining soil moisture and moderating the soil temperature. At a similar amount of applied DM, vetch residues emitted 2.6 times more N₂O than wheat residues, but expressed relative to the N content (Emission Factor), the opposite result was obtained, with wheat EF >> vetch EF. This result highlights the absolute need to take into account the effects of crop residue management on emissions, in this case the role of mulches on the physical and biological factors that influence N₂O emissions. Another important factor to take into account is the nature of the residue C added (and not only the residue C/N or the N content), as it affects the dynamics of residue degradation as well as the processes involved in the reduction step of N₂O to N₂.

The destruction of legume cover crops and the presence of their residues in the form of a mulch on the soil surface therefore present an increased risk of N₂O emissions compared to the risk from bare soil. Nevertheless, other important services are provided by these cover crops, particularly in terms of the production and cycling of biomass, C and nutrients, by preventing nitrate leaching, protecting the soil surface, etc. It can therefore be seen that farming practices must seek to minimize the accumulation of mineral N during crop residue subsequent degradation, in particular by rapidly sowing a crop that is likely to trap N or by the use of crop rotations that alternate legumes and nonlegumes, making it possible to immobilize more N in an attempt to mitigate emissions.

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Tables

Table 1 Initial chemical composition of the vetch and wheat residues used in the field experiment

| Residues | С | N | SOL | CEL | HEM | LIG | Csw | Nsw | C:N | LCI |
|----------|---------|----------|----------|--------------------|----------|--------|----------|----------|-----------|-----------|
| | | | | g kg ⁻¹ | | | | | | |
| Vetch | 428±3.2 | 35.6±1.4 | 530±20 | 307±16.1 | 101±13.6 | 62±5.9 | 72.5±5.7 | 15.8±1.1 | 12.0±0.45 | 0.13±0.02 |
| Wheat | 441±0.7 | 5.3±1.2 | 162±18.2 | 418±14.1 | 346±9.2 | 74±2.6 | 23.9±2.6 | 1.4±0.3 | 83.2±9.0 | 0.09±0.01 |

C total C, N total N, SOL soluble fraction, CEL cellulose, HEM hemicellulose, LIG lignin, Csw water soluble C, Nsw water soluble N, LCI lignocellulose index (LIG/CEL + HEM + LIG). Means (n = 3) \pm standard deviation

| Straw quantities | Cumulative en | nissions | EF | EF | | | |
|---------------------------|----------------------------|-------------------|------------|------------------|--|--|--|
| | (kg N ₂ O- N ha | L ⁻¹) | (% of N ap | (% of N applied) | | | |
| | Vetch | Wheat | Vetch | Wheat | | | |
| 0 | 0.60C | 0.60A | - | - | | | |
| 3 | 2.86Ba | 1.47Ab | 2.07Aa | 5.63Aa | | | |
| 6 | 5.20Aa | 2.17Ab | 2.11Aa | 5.10Aa | | | |
| 9 | 4.11ABa | 2.10Ab | 1.07Aa | 3.20Aa | | | |
| Average | 3.19a | 1.59b | 1.75 b | 4.66 a | | | |
| ANOVA (P value) | | | | | | | |
| Crop residue | < 0.001 | | 0.037 | 0.037 | | | |
| Quantities | < 0.001 | | 0.560 | 0.560 | | | |
| Crop residue x quantities | 0.040 | | 0.916 | 0.916 | | | |

Table 2 Cumulative N_2O emissions during decomposition of three quantities (3, 6 and 9 Mg ha⁻¹) of vetch and wheat crop residues on the soil surface and for soil without residues and N_2O emission factor (EF).

Means followed by the same capital letters in columns and by the same lowercase letters in rows do not differ significantly according to Tukey's test (P value < 0.05).

| | | N ₂ O-N (μg | , kg soil h ⁻¹) | [N ₂ O/(N | I ₂ O+N ₂)] | Csw/NO3 ⁻ | | |
|-----------|---------------------------------|------------------------|---------------------------------|----------------------|------------------------------------|----------------------|---------|---------|
| Treatment | 15 days | | 30 days | | 15 days | 30 days | 15 days | 30 days |
| | N ₂ O+N ₂ | N ₂ O | N ₂ O+N ₂ | N ₂ O | | | | |
| Soil | 51.3Aa | 44.0Aa | 14.5Aa | 13.0BC | 0.87A | 0.97A | - | - |
| Vetch 3 | 49.9Aa | 34.5Aa | 17.3Aa | 14.8BC | 0.72A | 0.94A | 7.6C | 5.6C |
| Vetch 6 | 61.9Aa | 45.2Aa | 16.0Aa | 14.2BC | 0.79A | 0.84A | 10.3B | 9.4B |
| Vetch 9 | 36.4Aa | 18.6Ab | 12.8Aa | 7.1C | 0.46B | 0.53B | 12.9A | 12.4A |
| Wheat 3 | 62.7Aa | 42.7Aa | 24.9Aa | 19.1ABC | 0.70A | 0.87A | 0.8D | 1.9E |
| Wheat 6 | 56.8Aa | 37.5Aa | 37.4Aa | 28.8AB | 0.70A | 1.00A | 1.4D | 3.3DE |
| Wheat 9 | 50.6Aa | 35.1Aa | 38.3Aa | 32.1A | 0.72A | 0.90A | 1.9D | 4.0D |

Table 3 Potential denitrification activity (PDA = N_2O+N_2), potential N_2O production (N_2O), denitrification end-product ratio [$N_2O/(N_2O+N_2)$] and available Csw to NO_3^- -N ratio (Csw/ NO_3^-) measured at 15 and 30 days in the 0-5 cm soil layer.

Means followed by the same capital letters in columns and by the same lowercase letters in rows do not differ significantly according to Tukey's test (P value < 0.05). ns N_2O+N_2 : potential denitrification activity (PDA) measured with acetylene

N₂O: potential N₂O production measured without acetylene



Fig. 1. Rainfall and mean daily air temperature (a), water filled pore space (WFPS) (b, c) and soil temperature (d, e) in the 0-5 cm soil layer for three quantities of crop residue (3, 6 and 9 Mg ha⁻¹) of vetch and wheat and for soil without residues over the 360 days of the experiment.



Fig. 2. Dynamics of total straw-C, (a, b) straw-N, (c, d) water-soluble C (Csw) (e, f), N (Nsw) (g, h) in the remaining mulch for three quantities of vetch (a, c, e, g) and wheat (b, d, f, h).the vertical errors bars indicate the minimum significant difference between treatments (Tukey's test at P<0.05).



Fig. 3. Soil NH₄⁺-N (a) and NO₃⁻-N (b) contents and net mineral N (c) in the 0-10cm soil layer during decomposition of vetch and wheat straw. The vertical error bars indicate the minimum significant difference between treatments (Tukey's test at P<0.05).



Fig. 4. N₂O fluxes (a) and CO₂ fluxes (b) during decomposition of three quantities (3, 6 and 9 Mg ha⁻¹) of vetch and wheat crop residues on the soil surface and for soil without residues over the 360 days of the experiment. The vertical error bars indicate the minimum significant difference between treatments (Tukey's test at P<0.05).



Fig. 5. Cumulative N_2O emissions during decomposition of three quantities (3, 6 and 9 Mg ha⁻¹) of vetch and wheat crop residues on the soil surface and for soil without residues over the 360 days of the experiment



Fig. 6. Denitrification end-product ratio $[N_2O/(N_2O + N_2)]$ as a function of available Csw to NO_3^- -N ratio (Csw/NO₃⁻) at days 15 and 30 after addition of 3, 6 and 9 Mg of DM ha⁻¹ of vetch and wheat on soil surface.

Supplementary data

| | WFPS (%) | | | | | | | | | |
|-----------|--------------|------|------|----------|----------------|------|-------|-----------------|------|--|
| Treatment | 0 to 60 days | | | 61 to 10 | 61 to 105 days | | | 106 to 360 days | | |
| | Mean | Min. | Max. | Mean | Min. | Max. | Mean | Min. | Max. | |
| Soil | 48.0a | 31.7 | 61.4 | 46.2a | 38,2 | 57,4 | 47.3a | 33,0 | 67,7 | |
| Vetch 3 | 51.2ab | 34,5 | 63,3 | 47.9a | 39.4 | 63.4 | 47.6a | 33,2 | 67,8 | |
| Vetch 6 | 58.7ab | 35,7 | 71,6 | 50.7a | 39,4 | 63,4 | 49.6a | 32,1 | 73,2 | |
| Vetch 9 | 59.1ab | 32,6 | 73,9 | 51.2a | 45,1 | 62,8 | 48.8a | 34,7 | 70,4 | |
| Wheat 3 | 51.7ab | 30,0 | 69,9 | 52.2a | 43,5 | 68,1 | 51.8a | 36,6 | 69,9 | |
| Wheat 6 | 57.3ab | 37,8 | 69,7 | 55.6a | 50,7 | 65,5 | 54.6a | 40,6 | 73,4 | |
| Wheat 9 | 61.0a | 36,1 | 71,0 | 57.5a | 54,5 | 68,4 | 53.9a | 44,3 | 70,5 | |

Table S1 Water filled pore space (WFPS) during three periods following applications of crop residues during the entire experiment (November 2016 to November 2017).

Means followed by the same letters in columns do not differ significantly according to Tukey's test

(P < 0.05).

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4 DISCUSSÃO GERAL

Os resultados deste estudo (artigos I e II) evidenciam que a composição química dos resíduos culturais tem forte influência na decomposição e liberação dos nutrientes (N, P e S) dos resíduos, bem como na emissão de óxido nitroso (N₂O). Por outro lado, o efeito da quantidade de resíduos na superfície do solo sobre esses processos foi reduzido.

A dinâmica de decomposição dos resíduos de ervilhaca e trigo apresentaram uma cinética clássica, com uma fase inicial rápida seguida de outra mais lenta. No entanto, independentemente da quantidade na superfície do solo, os resíduos de ervilhaca apresentaram taxa de decomposição 5 vezes maior do que os resíduos de trigo, resultando em um $t_{1/2}$ de apenas 25 para a ervilhaca, contra 123 dias para o trigo. Nos primeiros 45 dias os resíduos de ervilhaca perderam 75% do C inicial contra apenas 25% no trigo. O elevado teor de N (baixa C: N) e fração solúvel, combinado a menores valores de CEL e HEM na leguminosa, comparado aos resíduos de trigo, devem ter favorecido a decomposição dos resíduos da leguminosa pela população decompositora (THIPPAYARUGS et al., 2008). A liberação de N, P e S também foi mais intensa e maior com os resíduos de ervilhaca do que com os de trigo, seguindo uma dinâmica relativamente semelhante a observada para a decomposição. Segundo Prescott, (2005) e Gama-Rodrigues et al., (2007) o tempo de liberação dos nutrientes é determinado e está associada diretamente à taxa de decomposição dos resíduos culturais, a qual também depende do teor desses nutrientes nos resíduos. A ervilhaca apresentou os maiores teores de N e P (menores relações C: N e C: P) e não diferiu do trigo em relação ao teor de S, mas apresentou relação C: S menor, o que deve ter contribuído também para a sua maior liberação no resíduo da leguminosa. Ao final de um ano, enquanto mais de 94% do N, P e S foram liberados dos resíduos na ervilhaca esse índice foi de 64% para o N, 77% para o P e 38% para o S no resíduo de trigo.

Aliado a rápida decomposição e liberação dos nutrientes dos resíduos da ervilhaca, nos primeiros 60 dias após a adição dos resíduos no solo, foram observados os maiores fluxos de emissão de N₂O. Isso deve ter ocorrido em resposta ao incremento na disponibilidade de C e N no solo e também pelo o aparecimento de microsítios de anaerobiose pela intensa atividade microbiana que consome o O_2 durante a decomposição dos resíduos. Aumentos significativos de NH₄⁺ e NO₃⁻ foram observados no solo com os resíduos de ervilhaca nos primeiros 30 dias após a adição dos resíduos ao solo. Já os resíduos de trigo, com baixo teor de N e fração solúvel, foram decompostos mais lentamente pelos microrganismos e provocaram imobilização líquida de N, gerando baixas emissões de N₂O (MUHAMMAD et al., 2011; PIMENTEL et al., 2015), as quais não diferiram do solo sem resíduos. Isto sugere que resíduos culturais que decompõem rapidamente possuem maior potencial em promover a emissão de N₂O (WEILER et al., 2018; PEYRARD et al., 2016), mas esse efeito é observado principalmente na fase inicial do processo de decomposição (80% das emissões nos primeiros 60 dias). A rápida decomposição dos resíduos de ervilhaca resulta no rápido esgotamento das frações solúveis, permanecendo nos resíduos em decomposição compostos de mais difícil degradação (isto é, lignina, celulose e hemicelulose) que protegem os constituintes celulares do ataque microbiano (COBO et al., 2002). Com isso, após esse período inicial as emissões de N₂O são reduzidas pelo decréscimo na disponibilidade de substratos (C lábil e N mineral), mesmo em condições ambientais (baixa disponibilidade de O₂) favoráveis a produção de N₂O no solo. Após um ano, a emissão acumulada de N₂O na ervilhaca foi o dobro do que no trigo (3,19 *vs.* 1,58 kg N ha⁻¹), mas o fator de emissão apresentou comportamento inverso, sendo maior com a gramínea do que com a leguminosa (4,64 *vs.* 1,75 % do N aplicado).

O aumento da quantidade de resíduos na superfície do solo (3, 6 e 9 Mg ha⁻¹) não reduzem a taxa de decomposição, mesmo que esses tratamentos diferiram quanto a espessura e a proporção do mulch em contato com o solo. Tal constatação invalida a hipótese de que o contato solo-resíduo é o fator determinante da decomposição do mulch (THORBURN et al. al., 2001; FINDELING et al., 2007). Os resultados do presente estudo são similares aos obtidos por Willians et al., (2018) em que a quantidade de palha de centeio variando de 2 a 15 Mg ha⁻¹ não resultou na redução na taxa de decomposição do mulch. No estudo de Dietrich et al., 2019 foi claramente demonstrado que a dinâmica da água no mulch é o principal fator controlador da decomposição de diferentes quantidades de resíduos na superfície do solo.

Quando analisamos a dinâmica de decomposição e da água das camadas de resíduos que formam os mulches com 6 e 9 Mg ha⁻¹ observamos que a umidade dos resíduos nas camadas inferiores foram maiores do que nas camadas superiores, o que favoreceu a atividade biológica e o aumento da decomposição da camada inferior. Esses resultados estão de acordo com os obtidos por Dietrich et al., (2019), que verificaram que para mulches com 8 e 12 Mg ha⁻¹ de palha de cana-de-açúcar as camadas inferiores do mulch em contato direto com o solo foram quase sempre mais úmidas do que as camadas superiores, mais distantes do solo. Estes resultados onde a camada inferior possui maior umidade, estão relacionados

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com o maior aporte de resíduo e a menor radiação solar incidente sobre a camada inferior do mulch resultando em uma menor evaporação de água desta quantidade de resíduo que está em contato com o solo. Desta forma, o mulch tem ação protetora no solo e pode alterar a interação entre o solo e a atmosfera, reduzindo a evaporação da água no solo e a amplitude térmica (IQBAL et al., 2013).

O aumento da quantidade de resíduos na superfície do solo tanto para a ervilhaca como para o trigo provocou aumento na umidade do solo e no espaço poroso ocupado por água (EPSA), condição que favorece a produção e emissão de N_2O no solo (WEIER et al., 1993; DAVIDSON et al., 2000). Contudo, a adição das diferentes quantidades de resíduos de trigo no solo não aumentou significativamente a emissão de N₂O, possivelmente pela baixa disponibilidade de N mineral no solo devido os resíduos de trigo terem provocado imobilização líquida de N. Por outro lado, a adição dos resíduos de ervilhaca aumentou a emissão de N₂O até a quantidade de 6 Mg ha⁻¹, embora um aumento linear na emissão de N₂O era esperado com o aumento da quantidade de resíduos da ervilhaca. No entanto, os resultados obtidos na determinação do potencial de desnitrificação indicaram que no tratamento com 9 Mg ha⁻¹ houve nos primeiros 45 dias uma redução na relação N₂O/N₂O+N₂, indicando o favorecimento da redução completa do NO₃⁻ até N₂ via desnitrificação. Weier et al., (1993) demonstrou que a redução na relação N₂O/N₂O+N₂ ocorre quando a relação C disponível/NO3⁻ é alta. Essa condição parece ter sido estabelecida no tratamento com 9 Mg ha-1 em relação ao tratamento com 6 Mg ha-1, já que a disponibilidade de NO₃⁻ no solo desses dois tratamentos foi semelhante, mas a quantidade de C adicionada ao solo foi 1,5 vezes maior no tratamento com 9 Mg ha⁻¹. Esses resultados indicam que maiores quantidades de resíduos de ervilhaca mesmo promovendo o aumento do EPSA e disponibilidade de C e N no solo podem não resultar em aumento na emissão de N_2O_2 , já que a redução de NO_3^- a N_2 é estimulada nessas condições.

Apesar das maiores emissões de N₂O com os resíduos de ervilhaca, o fator de emissão (FE) foi maior para o trigo (FE = 4,64) do que para a ervilhaca (FE = 1,75). Fator de emissão maior com resíduos de gramíneas do que com leguminosas foram relatados por Weiler et al., (2018). O FE não variou significativamente em função da massa de resíduos conforme verificado por Pitombo et al., 2017, mas difere do estudo de Pinheiro et al. (2019), também com palha de cana-de-açúcar. Observamos para os dois resíduos, que os valores encontrados superaram o índice de 1% estipulado pelo IPCC (2014).

5 CONCLUSÕES GERAIS

A decomposição dos resíduos culturais e liberação de nutrientes (N, P e S), independentemente da quantidade de resíduos, foram maiores com os resíduos da ervilhaca (ricos em N e fração solúvel) do que com os de trigo (pobres em N e ricos em CEL e HEM). Independentemente do tipo de resíduo utilizado no estudo a taxa de decomposição não reduziu com o aumento da quantidade. Comportamento semelhante ocorreu com a liberação de N, P e S, a qual não foi alterada pela quantidade de resíduos na superfície do solo.

A emissão de N₂O, independentemente da quantidade de resíduos, foi duas vezes maior com os resíduos da ervilhaca do que com os de trigo. A maior parte da emissão de N₂O emitida em um ano foi medida nos primeiros 60 dias, período que coincide com a intensa decomposição e liberação dos nutrientes dos resíduos culturais. Nesse período os fluxos de N₂O foram dependentes da ocorrência de precipitações. O efeito da quantidade de resíduos sobre a emissão de N₂O foi significativo apenas para o resíduo de ervilhaca até a dose de 6 Mg ha⁻¹. A emissão de N₂O não diferiu entre as três quantidades de resíduos e na média das quantidades foi maior com a gramínea do que com a leguminosa (4,64 *vs.* 1,75 % do N aplicado).

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