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Abstract
The nitrous oxide (N_2O) emitted from soil was monitored to investigate the effect of sugarcane straw removal on the mechanisms that make mulch a "hot spot" of N_2O emissions under subtropical conditions. We conducted a field experiment with the first-ratoon sugarcane with four amounts of straw (0, 4, 8, and 12 Mg ha^{-1}) at the soil surface combined with 0 or 100 kg urea-N ha^{-1}. The urea-N was applied 52 days after straw application. Over the course of 1 year, we measured the N_2O and carbon dioxide (CO_2) emissions, mineral nitrogen (N), soil moisture and temperature, and remaining straw carbon (C) and N in the mulch. We observed two "hot moments" for N_2O emissions: the first one immediately after sugarcane straw application to soil and the second one after fertilizer-N application. High amounts of straw left on the soil led to an increase in the water-filled pore space (WFPS), and both WFPS and straw-C were strongly correlated with N_2O fluxes. Cumulative N_2O increased from 510 (0 Mg + N) to 1055 (12 Mg + N) g N_2O-N ha^{-1} for the fertilized straw treatments. The N_2O emission factors (EFs) of the sugarcane straw N and the fertilizer-N increased linearly with straw quantity, i.e., were not constant but were lower than the IPCC default values. Over 70% of the cumulative N_2O emissions measured in straw + fertilizer-N treatments for 1 year were attributed to the presence of straw mulch, which emphasized the importance of the straw layer at the soil surface as a hot spot for N_2O emissions.

Keywords Crop residue removal · Decomposition · Emission factor · Mulch · Nitrous oxide

Introduction

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

Management of plant residues is also recognized as an important factor that affects N_2O emissions (Mutegi et al. 2010), which could lead to "hot moments" and "hot spots" of N_2O emissions in soils (Kravchenko et al. 2017). Combined with reduced tillage or no-till, crop residues left as mulches after crop harvest in conservation agriculture or in semi-perennial cropping systems such as with sugarcane (Sousa Junior et al. 2018) or other bioenergy crops (e.g., Peyrard et al. 2016) can increase long-term soil C

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sequestration and CO_2 mitigation potential (Lal 2004). However, these practices can also influence emissions of non-CO_2 gases, such as N_2O, which alter the global warming potential (GWP) and could reduce the "savings" that are promoted by C sequestration (Crutzen et al. 2008; Lugato et al. 2018). In this context, the shift in harvest with burn to mechanized harvest without burn in sugarcane areas such as Brazil returns 7 to 25 Mg DM ha^{-1} $year^{-1}$ sugarcane residue as mulch onto soils (Leal et al. 2013), which has a high potential for bioenergy use (Manochio et al. 2017; Sindhu et al. 2016). Therefore, the important question is about the trade-offs between recycling and removal, which have led to an unprecedented research effort to quantify the agronomic and environmental consequences of managing plant biomasses, particularly in the sugarcane sector (de Bordonal et al. 2018; Carvalho et al. 2017), but not only in this sector (Cherubin et al. 2018). In particular, uncertainties in the interactions between residue mulches and fertilization and their effects on N_2O emissions (do Carmo et al. 2013; Pitombo et al. 2017; Siqueira Neto et al. 2016) further increase the need to understand how the quantity of residues left on soil (or vice versa, the quantity removed from the field) affects soil N_2O emissions.

In this context, our scientific objectives were (i) to assess the effect of sugarcane mulch removal on N_2O emissions from soil under subtropical conditions and (ii) to understand the mechanisms that make the mulch a "hot spot" of N_2O emissions during the sugarcane growing cycle. By following N_2O emissions over 1 year in a sugarcane crop under four scenarios of straw removal, with and without urea-N application, we examined the effects of mulch of various thicknesses on residue decomposition and soil environmental conditions and quantified the respective effects of straw mulch and fertilizer-N and their interaction on N_2O emissions. We hypothesized that high amounts of straw on the soil surface would increase the input of labile C and N from crop residues and favor the maintenance of soil moisture, which would lead to increased N_2O emissions from soil in both fertilized and non-fertilized sugarcane.

Materials and methods

Experimental site

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

Treatments and experimental design

The experiment was carried out in the first sugarcane ratoon from November 2015 to November 2016 and began after harvesting the cane plant on November 20, 2015. The sugarcane variety was RB95-6911, and the harvest was manual, removed all aboveground biomass (stalks, tops, and leaves), and left the soil uncovered. An area was demarcated with 32 plots of 22.4 m^2, which consisted of 4 rows 4 m long and spaced 1.4 m apart.

The experimental design had randomized blocks in a factorial scheme of 4 × 2 with four replicates. The first factor was four straw levels: 0, 4, 8, and 12 Mg DM ha^{-1} (0S, 4S, 8S, and 12S, respectively). The second factor was two doses of urea-N: 0 and 100 kg N ha^{-1}. This arrangement resulted in eight different treatments: 0S, 0S + N, 4S, 4S + N, 8S, 8S + N, 12S, and 12S + N. Straw was homogeneously distributed by hand on the soil surface in each plot. Urea-N was applied in a single dose on the soil surface (0S) or on the straw surface (4S, 8S, and 12S) in the tillering phase of sugarcane at day 52 after cane plant harvest in November 2015. At this moment, the amount of straw remaining on the soil surface was 2.5, 4.9, and 7.1 Mg DM ha^{-1} in treatments 4, 8, and 12 Mg ha^{-1}, respectively.

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

Straw-C and straw-N measurements

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

Samples for straw dry matter and C and N measurements were collected at 0, 15, 36, 51, 72, 103, 168, 238, 298, and 360 days after straw application. One microplot was destroyed per treatment at each measurement date, with four replicates. A straw sample was oven-dried at 65 °C for 48 h and was separated from adhering soil by dry cleaning; then, the subsample was finely ground in a ball mill for the determination of C and N contents using an elemental analyzer (Flash EA 1112; Thermo Electron Corporation, Milan, Italy).

N_2O and CO_2 measurements and analyses

Soil N_2O and CO_2 emitted were measured during 365 days after start of the experiment. Soil N_2O and CO_2 were measured using a static chamber method (Mosier et al. 1998). In each experimental plots, prior to straw application, a galvanized steel rectangular base (70 cm length, 40 cm width, and 10 cm height) was installed perpendicular to a cane row and inserted into the soil (5 cm) for gas measurements and the bases were left in place for the whole experimental period. For each treatment, the straw levels and urea dose were calculated to be equivalent to the area of each base. To measure soil-surface N_2O and CO_2 flux, an insulated, fan-mixed, non-flow-through, and non-steady-state chamber (70 cm length, 40 cm width, and 20 cm height) was placed on the base. In each measurement, the chamber was placed between 09:00 and 11:00 h to represent the daily soil N_2O and CO_2 flux. The measurements were performed before rainfall and the morning after rainfall in two to three times per week during the first month following straw and urea applications and less frequently thereafter. During chamber deployment, air samples were taken at 18-min intervals (t0, t18, and t36) using a 20-mL polypropylene syringe fitted with a three-way stopcock and immediately transferred to 12-mL pre-evacuated glass vials. All samples were analyzed at the Federal University of Santa Maria, Rio Grande do Sul, Brazil, using gas chromatographer Shimadzu GC-2014 (Shimadzu Co., Columbia, MD, USA). Air samples were analyzed for N_2O and CO_2 concentration within 7 days. The chromatographer was equipped with a packed column and an electron capture detector to analyze N_2O and CO_2 gas.

Soil measurements

The 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. A type-T copper-constantan thermocouple was installed on the soil surface and at 2.5 and 7.5 cm depths to measure soil temperature. Both sensors were coupled to a data logger (CR1000; Campbell Scientific, Logan, Utah, USA), and measurements were taken at a 10-min sampling interval. 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 as determined from the bulk density. Soil samples were collected from the surface layer (0–10 cm) 22 times during the experiment. Soil collection occurred frequently during the first month following straw and urea applications and then less frequently thereafter, but soils were always collected on days that had a GHG measurement. Soil samples consisting of six randomly distributed sampling points in each of the 22.4 m^2 plots were collected using a stainless steel auger (3 cm diameter). Mineral N (exchangeable NH_4^+ and NO_3^-) 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 and kept frozen until analysis. Exchangeable NH_4^+ and NO_3^- were quantified by distillation with sequential addition of MgO and Devarda's alloy, respectively, and titration with H_2SO_4 (Keeney and Nelson 1982). Gravimetric soil moisture content was determined by oven drying (105 °C for 24 h).

Calculations and statistical analyses

Soil N_2O and CO_2 fluxes were calculated considering the variation in the gas concentrations inside a chamber when the chamber remained closed, the volume of the chamber, the area of soil occupied at the base, and the molecular weights of N_2O and CO_2 gases (Jantalia et al. 2008). The molar volume of the gas was corrected for the temperature inside the chamber measured at the time of each sampling. The daily N_2O and CO_2 fluxes were calculated by linear interpolation, and cumulative N_2O-N losses were obtained by linear interpolation of the emission rates between the sampling dates as described by Aita et al. (2014). The N_2O EFs due to input of N from the crop residue and from urea were calculated by using the methodology described in the Guidelines for National Inventories of Greenhouse Gases (IPCC 2006). Two calculations were made for the crop residue EF: (i) EF of straw-N (total N recycled) is calculated as the difference in the cumulative N_2O between the straw treatments (4S, 8S, 12S) and the

bare soil (0S) divided by the amount of straw-N added for each straw treatment, and (ii) EF of the straw-N released, which takes into account the rate of straw decomposition after 1 year, is the difference in the cumulative N_2O from the straw treatments (4S, 8S, 12S) and the bare soil (0S) divided by straw-N released after 1 year for each straw treatment.

Interaction effects between the straw level (0S, 4S, 8S, and 12S) and N fertilization (0 N and 100 N) on N_2O and CO_2 fluxes; the cumulative N_2O, C, and N straw content; and the soil mineral N (exchangeable NH_4^+ and NO_3^-) were tested using two-way analysis of variance (ANOVA), and the means of each treatment were compared by the Tukey test at the 5% probability level. For the cumulative N_2O-N at the different levels of straw, a linear regression was fitted. The data were processed using the SISVAR software (Ferreira 2011).

The N_2O emissions from each straw quantity, soil variables, CO_2 emission, and straw-C remaining were subjected to multivariate analysis (principal component analysis, PCA) using Statistica® software (version 7.0). PCA was performed to address the variables that drive N_2O emissions. PCA was performed on the correlation matrix that was obtained from the results of soil temperature and WFPS (0–10 cm), soil-exchangeable NH_4^+ and NO_3^- contents, CO_2 and N_2O fluxes, and C remaining in the sugarcane straw. Only correlation coefficients (r) above 0.50 between the variables and ordination axes were considered significant. Correlations between the N_2O and variable drivers of N_2O emissions were considered significant at $P < 0.05$.

Results

Soil environmental conditions and WFPS

The cumulative rainfall during the 1-year experiment was 1487 mm, and the mean daily air temperature was 18 °C (Fig. 1a). From the time of straw application to the date of fertilization (day 52) and then to day 120, the WFPS varied greatly in the 0–5 cm and 5–10 cm soil layers and reached at most 71.6% in the 5–10 cm soil layer (Fig. 1b, c). The WFPS was different among the different straw treatments (Fig. 1b, c): during the drying periods, soils with no or low straw on the surface (0S and 4S) dried significantly faster than did the other treatments ($p < 0.05$), which led to an increase in the average WFPS with high amounts of straw. This tendency was observed until the end of the experiment. Soil temperature varied between 20.5 °C and 35 °C in the 0–5- and 5–10-cm layers during the year. Treatments with no or low straw had the highest soil temperatures at the soil surface and in the 0–5 cm soil layer (0S = 4S > 8S = 12S), with a mean difference of 2.0 °C and 1.6 °C, respectively, during the 0–68-day period. After day 68, we did not observe differences in soil temperature among treatments, which we attributed to the development of the sugarcane canopy, which decreased the relative effect of the mulch layer.

Dynamics of straw-C and -N

At the start of the experiment, the straw-C remaining on the soil surface represented 1.56, 3.13, and 4.69 Mg C ha^{-1} (Fig. 2a) and a mulch thickness of 1.91, 3.62, and 4.69 cm for the 4, 8, and 12 Mg DM ha^{-1} straw treatments, respectively. During the 0–52-day period, before fertilizer-N application, straw-C decreased rapidly in the 4S, 8S, and 12S treatments, and C loss represented, on average, 37.6 ± 2.0% of the initial C, without significant differences among straw levels, which indicated that the loss of straw-C was proportional to the initial amount. At day 52, immediately before N application, the remaining straw-C on the soil was 0.94 (4S), 1.99 (8S), and 2.98 Mg C ha^{-1} (12S). Until the end of the experiment, we found no significant difference in C loss between treatments with and without N applied. After 1 year of the experiment, C loss from mulch represented 72.1 ± 2.2, 73.9 ± 2.7, and 78.0 ± 4.2% of the initial straw-C for the 4S, 8S, and 12S treatments, respectively.

The straw-N content at the beginning of the experiment was 29.5, 59.0, and 88.4 kg N ha^{-1} for 4, 8, and 12 Mg DM ha^{-1} of straw, respectively (Fig. 2b). During the 0–36-day period, straw-N decreased rapidly, in parallel with the decrease in straw-C. After 1 year of the experiment, straw-N loss differed significantly among straw levels, with slightly slowed loss at the low straw level. Total straw-N loss represented 50.2 ± 6.1, 52.7 ± 4.4, and 58.2 ± 8.5% of the initial straw-N for the 4S, 8S, and 12S treatments, respectively.

Soil mineral N

The concentrations of soil mineral N were very low in the treatments without N, with averages of 1.9 kg NH_4^+-N ha^{-1} and 1.8 kg NO_3^--N ha^{-1}, and no difference in mineral N was found among straw levels (Fig. 3a, b). This low level persisted until the end of the experimental year. In plots receiving N fertilization, the amount of mineral N increased after urea application, as expected, with significant differences among straw treatments (Fig. 3a, b). The highest exchangeable NH_4^+-N and NO_3^--N contents were observed in soil between days 52 and 129, with significantly more exchangeable NH_4^+-N in the soil when the mulch was less thick. Although we observed an increase in the exchangeable NH_4^+-N and NO_3^-N contents in soil soon after N application, the highest peak was observed on day 65. For the 0S + N treament, the exchangeable NH_4^+-N content in soil remained significantly higher than that in the other treatments until day 129. The peak NO_3^--N content also occurred at day 65 and decreased rapidly afterward for all fertilized treatments. After day 129, no differences in soil-exchangeable NH_4^+-N and NO_3^--N contents were found among the N treatments.

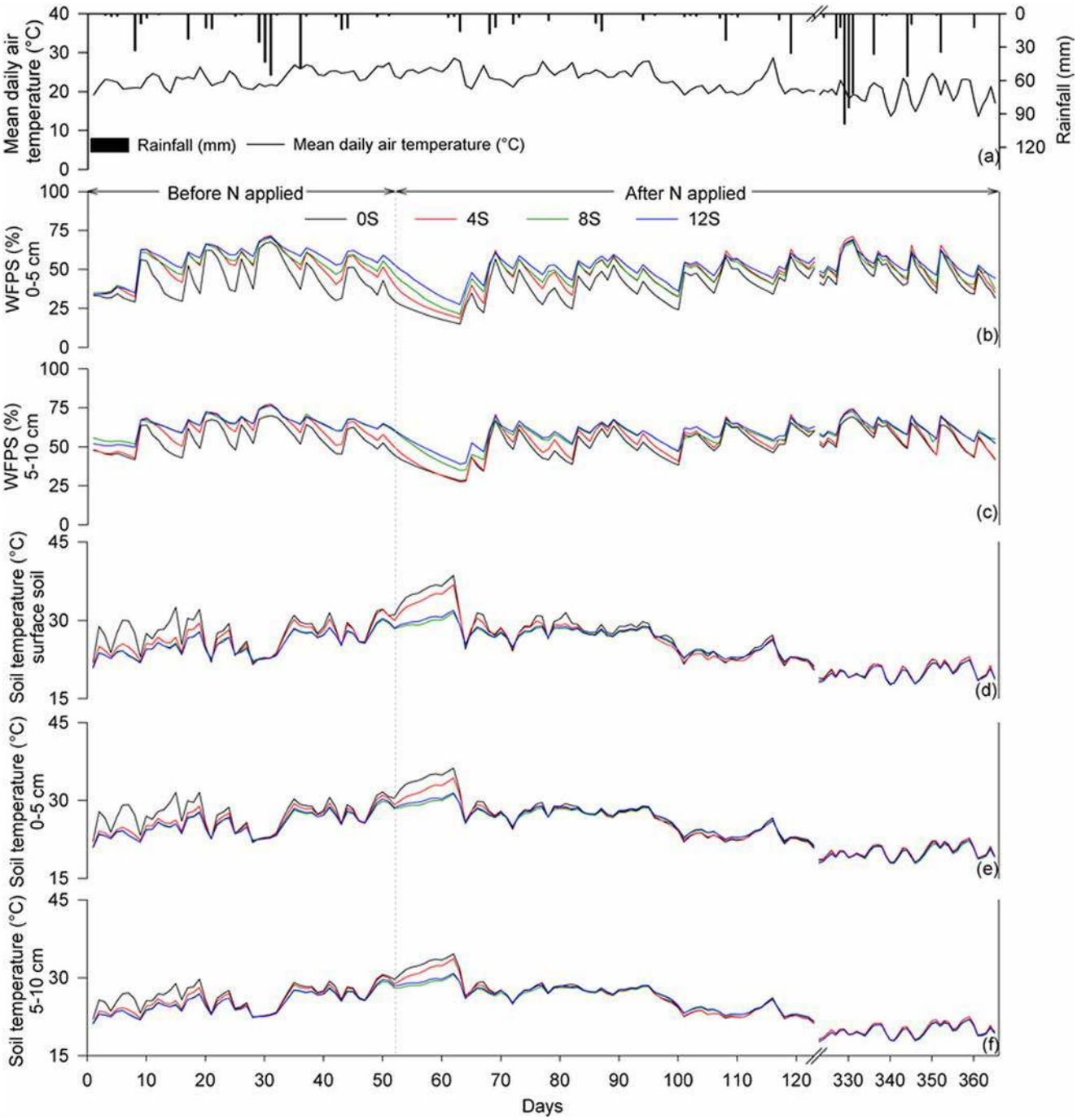

Fig. 1 Mean daily air temperature and rainfall (**a**), WFPS in the 0–5 cm soil layer (**b**), WFPS in the 5–10 cm soil layer (**c**), temperature on the soil surface (**d**), soil temperature in the 0–5 cm soil layer (**e**) and soil temperature in the 5–10 cm soil layer (**f**) in the first sugarcane ratoon with different initial amounts of straw added as mulch on soil [4 (4S), 8 (8S), and 12 Mg DM ha^{-1} (12S)]. The dotted line represents the time of urea fertilization

Soil N_2O and CO_2 emissions

Without fertilizer-N application

From sugarcane harvest to fertilizer-N application (0–52-day period), the different amounts of straw strongly influenced the N_2O and CO_2 emissions from the soil (Fig. 4). During this period, N_2O fluxes fluctuated from 0.84 to 14.6 g N_2O-N ha^{-1} day^{-1} depending on the days and treatments (Fig. 4a). In general, we observed that less N_2O was emitted with less straw (0S < 4S < 8S < 12S), and this pattern persisted until day 65. The highest N_2O fluxes occurred between days 9 and 34 in the 8S and 12S treatments, which corresponded to rainfall events and an increase in the WFPS (Fig. 1), with differences

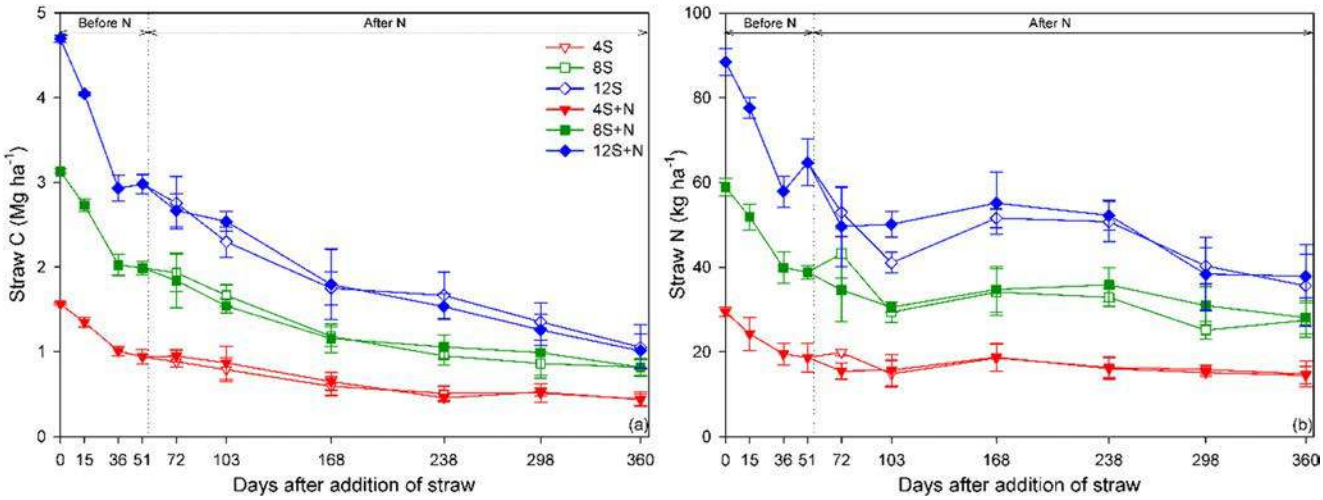

Fig. 2 Dynamics of straw-C (**a**) and straw-N (**b**) on soil from the harvest of sugarcane and for 1 year, with different initial amounts of straw added as mulch on soil [4 (4S), 8 (8S), and 12 Mg DM ha^{-1} (12S)]. Fertilizer-N (urea) was applied on day 52. The vertical bars represents the standard deviation. The dotted line represents the time of urea fertilization

between straw levels (Fig. 4). From days 65 to 365, N_2O emissions remained low for the 0S, 4S, 8S, and 12S treatments, with a mean of 0.8 g N_2O-N ha^{-1} day^{-1}, which was not significantly different for different amounts of straw. The same pattern was observed for CO_2 emissions. During the 0–52-day period, the CO_2 fluxes were immediately high and were ranked generally as 12S = 8S > 4S = 0S (Fig. 4b), but with large variations in each treatment between measurement days.

After fertilizer-N application

After the application of urea on straw plots on day 52, the N_2O emissions were much higher than those of the no-fertilizer plots (Fig. 4a). Under fertilizer-N treatments (0S + N, 4S + N, 8S + N, 12S + N), N_2O emissions varied from 1.1 to 23.8 g N_2O-N ha^{-1} day^{-1} between days 52 and 80, and different amounts of straw modified the N_2O emissions, with 0S +

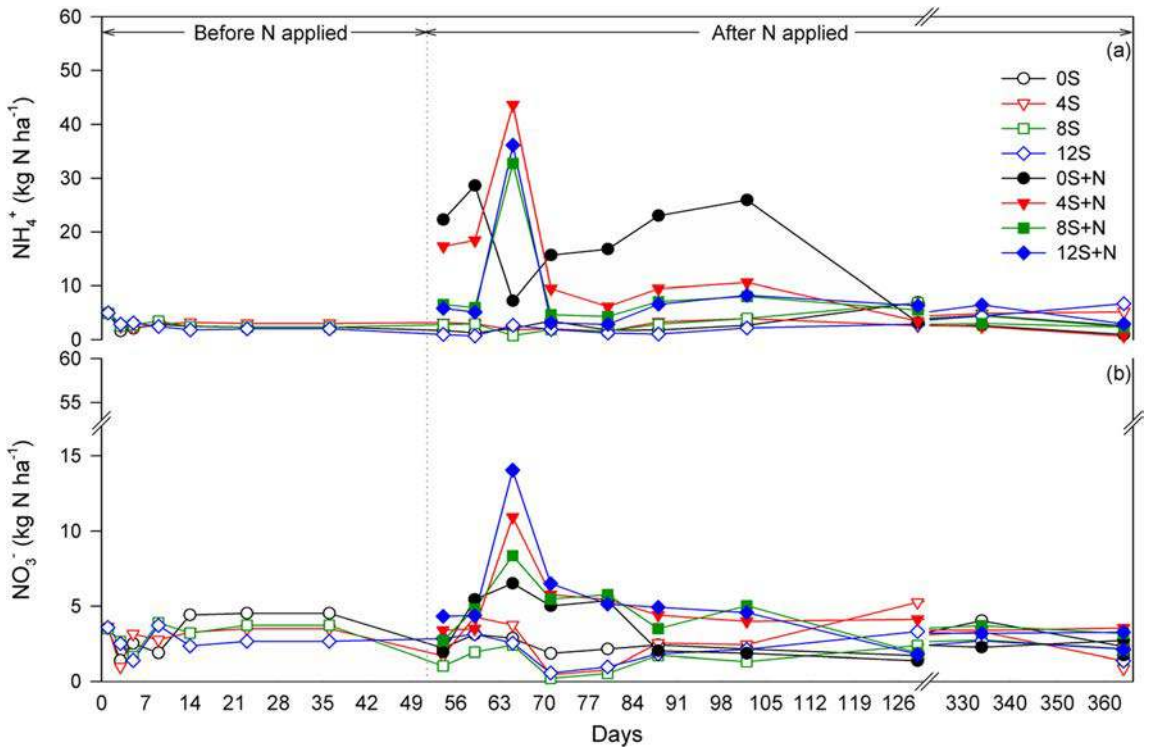

Fig. 3 Soil exchangeable NH_4^+ (**a**) and NO_3^- (**b**) in the 0–10 cm soil layer after 100 kg urea-N ha^{-1} (N) application over the different straw (S) amounts (0, 4, 8, and 12 Mg ha^{-1}) in the first-ratoon cane. The dotted line represents the time of urea fertilization

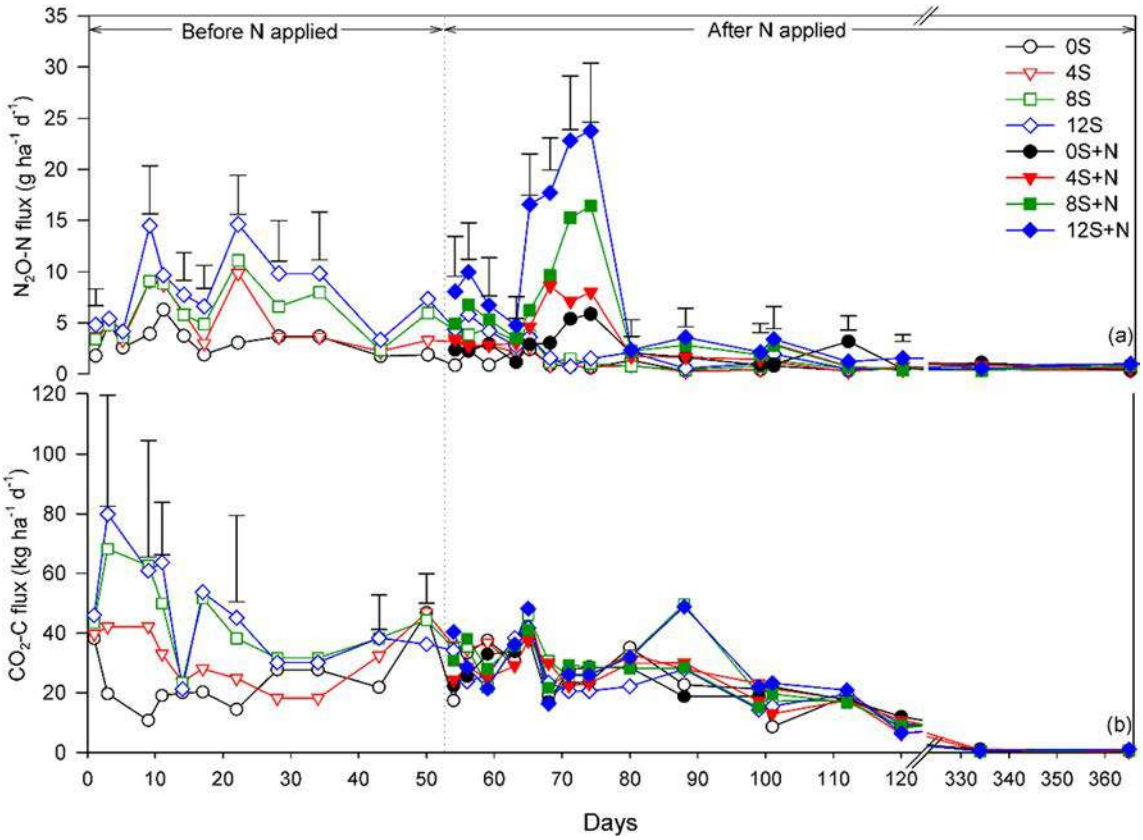

Fig. 4 N_2O-N flux (**a**) and CO_2-C flux (**b**) in the first-ratoon sugarcane, with or without application of 100 kg urea-N ha^{-1} (+N) over the different straw (S) amounts (0, 4, 8, and 12 Mg ha^{-1}) at day 52. The vertical bars represent the minimum significant difference between treatments by the Tukey test ($P < 0.05$). The dotted line represents the time of urea fertilization

N < 4S + N < 8S + N < 12S + N (Fig. 4a). We observed that the highest N_2O flux after fertilizer-N application was also triggered by rainfall events. Rainfall did not occur during the 12 days after N application (Fig. 1), and our results showed low N_2O emissions. For part of this period, the overall increases in N_2O fluxes were closely related to increases in the WFPS, with 12S + N ≥ 8S + N > 4S + N ≥ 0S + N (Fig. 1b, c). After day 120, N_2O fluxes returned to basal levels and did not differ significantly from those of the 0S, 4S, 8S, and 12S treatments. CO_2 fluxes decreased steadily throughout the year, which revealed the gradual depletion of the source of C from straw, with no significant difference among treatments. The fertilizer-N addition at day 52 did not lead to peaks in emissions, as was observed for N_2O, or to significant differences in the CO_2 that evolved with and without urea-N addition (Fig. 4b).

Drivers of N_2O emissions

For the 0–65-day period in treatments without urea-N application, when the highest N_2O fluxes occurred with straw, the first two components of PCA (PC1 and PC2) explained 58% of the variance in the data, with PC1 accounting for 40% and PC2 for 18% of the total variation (Fig. 5a). The PC1 showed that N_2O (0.79) was associated with WFPS (0.76) and straw-C (0.69) and separated from soil temperature (− 0.81). The PC2 represented the variability of exchangeable NH_4^+ (0.69) and NO_3^- (0.62). Correlation analysis indicated that N_2O emission was positively related to WFPS (0.70) and straw-C (0.53) and negatively related to soil temperature (− 0.45). The 52–120-day period was important for the N_2O emissions that were linked to N fertilization. Over this period, the first two components of PCA (PC1 and PC2) explained 69% of the variance in the data, with PC1 accounting for 41% and PC2 for 28% of the total variation (Fig. 5b). The PC1 showed that N_2O emissions (− 0.50) were associated with CO_2 emissions (− 0.84), soil temperature (− 0.69), and soil-exchangeable NH_4^+ (− 0.63) and NO_3^- (− 0.79) contents and separated from WFPS (0.60). The PC2 also explained the variability of N_2O (0.64), which was associated with WFPS (0.66) and straw-C (0.81). Correlation analysis indicated that N_2O emission was positively related to CO_2 emission (0.37), straw-C (0.50), and NO_3^- content (0.54).

Cumulative N_2O emissions and EFs

Cumulative N_2O emissions differed significantly among straw treatments with 12S > 8S > 4S > 0S (Fig. 6). For these

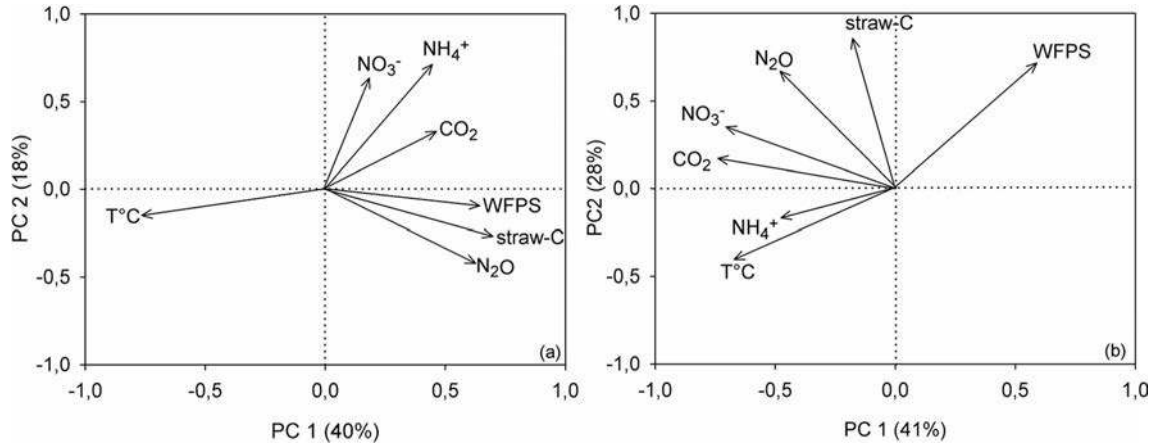

Fig. 5 Principal component analysis (PCA) of the 0–65-day period in treatments without urea-N application (**a**) and 52–120-day period in treatments with urea-N application (**b**) for N_2O fluxes from soil and soil-straw variables: nitrate—NO_3^-, exchangeable ammonium—NH_4^+, water-filled pore space—WFPS, soil CO_2 fluxes, soil temperature—T°C and straw-C content in the first-ratoon sugarcane, with or without the application of 100 kg urea-N ha^{-1} over different straw (S) amounts (0, 4, 8, and 12 Mg ha^{-1})

treatments, cumulative N_2O varied from 436.9 (0S) to 766.8 g N_2O-N ha^{-1} (12S) and was linearly correlated with the initial amount of straw at the soil surface (Table 1). A similar response was observed for treatments + N in which cumulative N_2O emissions increased from 510 (0S + N) to 1055 g N_2O-N ha^{-1} (12S + N), again with 12S + N > 8S + N > 4S + N > 0S + N (Fig. 6), and were strongly linearly correlated with the initial straw levels on the soil surface (Table 1). On average, straw contribution to total N_2O emitted by fertilized treatments represented 70% of N_2O emissions during the year.

The effect of the increase in straw quantity on cumulative N_2O emissions (calculated during the 52–365-day period) was not significantly different for straw treatments with (100 N) and without (0 N) urea application, although a trend was observed with the greater relative increase in N_2O emissions with the 100 N than with the 0 N treatments for the largest straw amounts (12S + N and 8S + N). The Y-intercept of the regression was obviously higher with the 100 N treatments than with the 0 N treatments, which reflected the fertilizer-N contribution to N_2O emissions. Using the mean of the 0 N and 100 N treatments, the relationship between straw amount and N_2O emissions ($y = 450.19 + 37.48x$, $R^2 = 0.97$) indicated that for each extra Mg of straw DM, 37.5 g N_2O-N ha^{-1} extra N_2O was emitted.

The EFs from crop residue-N and urea-N increased linearly with straw quantity (Table 1). When the crop residue EF was

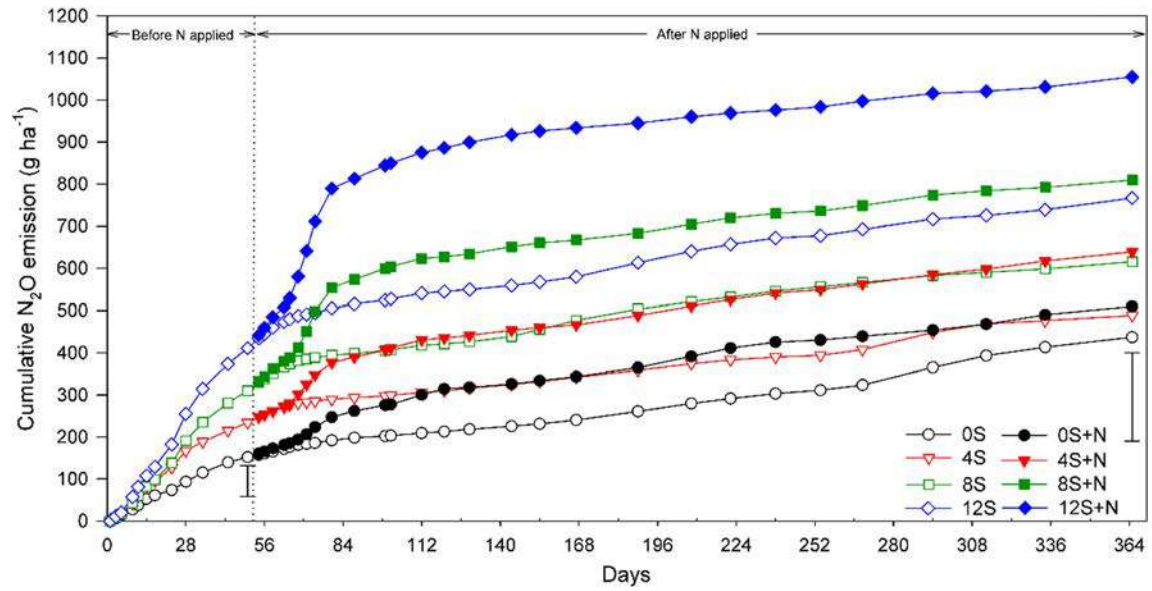

Fig. 6 Cumulative N_2O emissions during the first-ratoon sugarcane (365 days) after application of different straw (S) amounts (0, 4, 8, and 12 Mg ha^{-1}) with and without 100 kg urea-N ha^{-1} (+N). The vertical bar represents the minimum significant difference between treatments by the Tukey test ($P < 0.05$). The dotted line represents the time of urea fertilization

Table 1 Cumulative N_2O-N emission in the first-ratoon sugarcane with and without urea-N for the different straw (S) amounts (0, 4, 8, and 12 Mg ha^{-1}) and emission factor

Straw level (Mg ha^{-1})	Cumulative N_2O-N (g ha^{-1})		Emission factor (%)[b]		
	0 N[a]	100 N	Residue-N added	Residue-N released	Urea-N
0	436.9	510.0	–	–	0.07
4	488.4	639.2	0.16	0.33	0.15
8	696.7	809.5	0.28	0.54	0.19
12	766.8	1054.7	0.34	0.60	0.29
Regression	$y = 417.5 + 29.9*x$	$y = 482.7 + 45.1*x$	$y = 0.0817 + 0.0225*x$	$y = 0.2125 + 0.0347*x$	$y = 0.0730 + 0.0170*x$
R^2	0.94	0.98	0.97	0.92	0.98

*Significant at $p < 0.05$ according to the t test

[a] 0N, without urea-N; 100N, with 100 kg urea-N ha^{-1}

[b] Residue-N added, emission factor calculated as a function of total straw N added; Residue-N released, emission factor calculated as a function of total straw-N released during decomposition

calculated as a function of the actual residue-N released over 1 year, using the observed kinetics of the remaining straw-N, the EF values increased compared with those of the standard IPCC calculation, as expected. On average, the EF values differed for urea and straw-N sources, with lower EF values from urea-N than those from total straw-N or released straw-N.

Discussion

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

Effects of straw on N_2O emissions

Sugarcane straw had a major effect on N_2O emissions from soil. Our study showed, in a quasi-linear relationship, a direct correlation between N_2O emissions from soil and the amount of straw on the soil surface, with the notable conclusion that increasing the quantity of mulch increased N_2O emissions. These results were observed particularly in the period immediately following sugarcane harvest and the recycling of sugarcane straw, without N fertilizer and with a low mineral N concentration in the topsoil. In this period, the PCA showed that N_2O emissions were closely correlated with the WFPS and straw-C availability. First, our study showed a strong relationship between different amounts of straw on the soil surface, soil moisture, and WFPS, primarily during periods with a lack of rain, when the straw layer limited evaporation and thus slowed down soil drying (Hu et al. 2018). Similarly, Vargas et al. (2014) using sugarcane straw under laboratory conditions and Schaufler et al. (2010) using European soils under different land uses demonstrated a positive correlation between N_2O emissions and soil moisture. Many studies (e.g., Bateman and Baggs 2005; Davidson et al. 2000; Liu et al. 2017) demonstrated the highest N_2O emissions from soils at a WFPS between 50% and 70%, which alters soil aeration and gas diffusion and thus influences O_2 availability for microbial activity in soil. Furthermore, one indirect effect of mulch on the water dynamics in soil is its effect on soil temperature, which modifies evaporation rates among straw levels (Fu et al. 2018). In general, our results showed a wide temperature range (between 09:00 and 11:00, the time of N_2O measurements) in soil with no or low amounts of straw (0S and 4S), which varied from 21 °C to 35 °C, whereas for the 8S and 12S treatments, the maximum temperature did not exceed 30 °C, which confirmed the role of the mulch as a buffer against climate fluctuations in the soil. Additionally, no or low straw (0S and 4S) had less soil coverage (visual confirmation), which implied that more soil was exposed. This high temperature range that was associated with the 0S and 4S treatments could have led to an increase in evaporation rates, as reflected by the reduced soil water content in these treatments, as well as to conditions of microbial activity that are less favorable to the decomposition and mineralization of SOM and GHG emissions (Butterbach-Bahl et al. 2013; Liu et al. 2017; Schaufler et al. 2010). Thus, our results show that straw acted as a buffer for temperature changes and preserved soil moisture, particularly after high rainfall events followed by drying periods, which contributed to overall higher heterotrophic microbial activity and N_2O emissions from soil.

Another major effect of straw mulch was most likely related to the recycling of C and N in the soil, although the

contributions of the various drivers could not be quantified separately. The release of labile C and N from straw provides a substrate for growing aerobic microorganisms, which results in rapid consumption of O_2, thus leading to the development of "hot moments" and "hot spots" of N_2O emissions in soils, particularly in straw mulches or at the soil-straw interface (Kravchenko et al. 2017; Pugesgaard et al. 2017). Available C increases the heterotrophic microbial activity, which leads to an increase in denitrification potential and rapid consumption of O_2, favoring the denitrification process (Butterbach-Bahl et al. 2013; Chen et al. 2013). Several authors recently highlighted the importance of N_2O losses directly linked to crop residue management in the absence of fertilization (Chen et al. 2013; Guzman et al. 2015; Pugesgaard et al. 2017; Shan and Yan 2013; Zhao et al. 2018). The conditions of this scenario were met in the treatments without N application, which resulted in an increase in N_2O emissions linearly related to the amount of straw returned to the soil. A rapid release of straw-N and straw-C was observed during the first 7 weeks of the experiment, with almost 35% of the initial straw-N and straw-C lost before fertilizer-N application, which could be explained by the initial composition of the straw containing a high soluble content and low lignin content, promoting fast initial decomposition. In their meta-analysis, Shan and Yan (2013) showed a negative correlation between N_2O emissions from soil and crop residues in mulch at the soil surface and the C/N ratio of those residues, which confirms that the N content of crop residues influences N_2O emissions. In sugarcane systems with a straw C/N ratio similar to that of this study, Siqueira Neto et al. (2016) and Vasconcelos et al. (2018) did not observe significant differences in N_2O emissions with different amounts of sugarcane straw. However, as discussed previously, the favorable conditions of moisture and temperature associated with the fast decomposition that was observed in our study could explain the response observed. Overall, our study showed that 70% of the N_2O emitted over 1 year with fertilized sugarcane could be attributed to the presence of crop residues, which confirms recent studies that emphasize the importance of postharvest periods for high N_2O emissions and the role of crop residue management (e.g., Peyrard et al. 2017; Rezaei Rashti et al. 2017; Tongwane et al. 2016). This finding is particularly relevant in situations with perennial or semi-perennial crops and no-tilled arable systems in which crop residues are left at the soil surface, thereby promoting favorable conditions for emissions at the soil-straw interface (Peyrard et al. 2017; Shan and Yan 2013; Vasconcelos et al. 2018).

N_2O emissions from fertilizer and interaction with straw

The input of synthetic-N fertilizers is recognized as the main source in N_2O emissions from agricultural soils (Smeets et al. 2009), which can increase with crop residues on the soil surface (Jin et al. 2014); however, the linkage between synthetic-N fertilizer and crop residues is not fully understood (Chen et al. 2013). Our results showed clearly that increasing the amount of straw on the soil surface combined with a single quantity of applied fertilizer-N (100 kg N ha^{-1}) increased N_2O emissions. However, all peaks of N_2O that were observed are lower than those of other studies with sugarcane (do Carmo et al. 2013; Siqueira Neto et al. 2016) and other crops (Basche et al. 2014; Muhammad et al. 2011). At the end of the year, only 30% of the total N_2O emitted could be attributed to application of fertilizer, considering the difference in the N_2O emissions from straw treatments with and without fertilizer-N application. However, this calculation considers that the combined effect of the presence of straw and fertilizer is additive, i.e., the sum of the contribution of straw and fertilizer to N_2O emission. It cannot be excluded that the fertilizer-N input can boost the N-limited heterotrophic microbial activity associated with mulch decomposition, and combined with favorable environmental conditions (temperature, WFPS, N availability), increases in N_2O emissions were associated with straw. Similarly, an increased quantity of straw that maintains a high heterotrophic microbial activity (as evidenced by the higher CO_2 fluxes after straw input for 8S and 12S treatments) potentially allows for higher N losses from the fertilizer. Therefore, although the relationship between N_2O and straw quantity was not significantly different with and without fertilizer applied (Table 1), there are several reasons why increasing straw quantity in the presence of fertilizer-N should increase N_2O emissions, which is a trend that was observed in our study. Therefore, the presence of straw on the soil surface must be considered for its direct effect as a source of N in the system as well as for its two indirect but major effects: (i) effect on the physical properties of the soil-mulch system (water, temperature, evaporation) and (ii) effect on the biological functioning of the soil, either C-limited or N-limited, which influences C and N mineralization, denitrification potential, and N_2O emission. A future step to address this issue would be to study the dynamics of the biological component in an interaction with environmental conditions in the mulch and at the soil-mulch interface.

N_2O emissions are the result of microbial processes such as nitrification and denitrification (Domeignoz-Horta et al. 2018), which increase, principally, by N application (Miller et al. 2008; Wang et al. 2017). Similar to the results of our study, Fracetto et al. (2017) observed an increase in soil microbial activity after fertilizer-N application on sugarcane straw, which resulted in an increase in N_2O emissions from soil. N_2O production in soil during nitrification is traditionally considered to be minor in comparison with denitrification; however, when the WFPS is below 60%, nitrification becomes a major process for N_2O emissions from soil (Bateman and Baggs 2005; Liu et al. 2017). Our results

showed an increase in N_2O fluxes after N application followed by an increase in the soil NO_3^- content at a low WFPS (< 60%), which suggested that nitrification in soil during this period was the main process involved in N_2O production. This hypothesis is supported by PCA and correlation analyses, which showed a positive correlation between soil NO_3^- content and N_2O emissions after N fertilization ($r = +0.54$). At the first rainfall after N application, N_2O fluxes increased again, although the WFPS remained below 60%, which reinforced that nitrification was the main N_2O-producing process. However, the C available from the straw also contributes to a decrease in soil O_2 availability resulting from increases in microbial activity, which can be linked to the correlation observed between N_2O and CO_2 emissions in PCA analyses. Oxygen depletion and CO_2 emissions due to microbial activity during straw decomposition (Badagliacca et al. 2017; Peyrard et al. 2017) combined with a WFPS of approximately 60% after rain events might have favored N_2O production by denitrification with the appearance of anoxic spots, mainly at the soil-straw interface. In summary, our findings indicated that mulching provided favorable soil conditions for both nitrification and denitrification processes, which could occur simultaneously. The denitrifying community was favored by the reactive-N supply (NO_3^-) that resulted from nitrification and by the O_2 consumption of microorganisms after N fertilization.

EFs for fertilizer-N and straw-N

As a consequence of the cumulative N_2O emissions that were calculated over the full year of the sugarcane growing cycle, the quantity of sugarcane straw on the soil surface had a strong effect on the EFs calculated in our study, regardless of the N source. However, the EFs from the urea-N and crop-residue-N inputs that were calculated in our study were lower than the IPCC default value of 1% (IPCC 2014). Our results showed that the EF from crop residue was highly influenced by management (12S > 8S > 4S > 0S) in both residue-N added and residue-N released calculations of the EF, which suggested the limits of a standard IPCC default value based only on total N inputs. Additionally, we showed a higher contribution from crop residue to N_2O emissions than that of N fertilizer in the experimental conditions of this study. Several studies found a wide range of "regional" EFs in sugarcane fields for fertilizer-N, which were influenced by sugarcane straw at the time of N fertilization. The EFs from fertilizer-N ranged from 0.07% to 0.29% in our study and varied from 0.23% to 1.11% in sugarcane fields in Brazil's southeast region (do Carmo et al. 2013; Siqueira Neto et al. 2016). On the other hand, relatively high emissions could be found in different sugarcane fields worldwide, such as in Australia, which reached 6.70% (Allen et al. 2010) to 21% (Denmead et al. 2010) due to different N fertilizer rates and waterlogging conditions. Such a large variation most likely results from the difficulty in distinguishing between the contributions of crop residue and mineral N to N_2O emissions from the soil, which reflected the combined effects of biological factors, soil type, agricultural systems, and environmental conditions on soil N_2O emissions. This was evidenced in our study in which the crop residue management had impact on the emission of N_2O from straw and N fertilizer. EF increased linearly by increasing the amount of straw, and this was more due to the increase of N_2O from straw than to the proportional increase in N recycled, indicating that the constant EF value proposed by the IPCC is not adapted to take into account the effects of crop residue management. Our results can help to reduce the uncertainties of the values from the IPCC by quantifying the effects of mulch and the amount of straw on crop residue EFs.

Conclusion

This study showed a strong effect of leaving crop residues as mulch at the soil surface after sugarcane harvest, with increases in N_2O emissions and two "hot moments" for emissions, after sugarcane harvest and after urea fertilizer application. Mulches of increasing mass favored environmental conditions for emissions through nitrification and denitrification although microbial processes were not measured directly in this study. The placement of crop residues as mulch at the soil surface modified physical processes, which indicated that not only crop-residue-N inputs but also agricultural management should be considered when estimating GHG emissions. Therefore, extensive removal of straw for bioenergy production, although reducing GHG emissions in the short term, could also lead to a strong effect in the long term, thus accelerating the depletion of C and N stocks and therefore organic matter in the soil, thus reducing both the fertility of soils and the mitigation of climate change that are promoted by soil C sequestration. Additionally, the recycling of straw returns a considerable amount of N, which becomes available to plants after direct decomposition or via mineralization of soil organic matter and, in turn, reduces the requirement for N input via synthetic fertilizer. In our experimental and climatic conditions, it is important to underline that crop residues were the main source and/or cause of emitted N_2O during the year, and that the EF increased by increasing the amount of straw, which indicates the necessity for a better understanding and accurate quantification of this N source in GHG national inventories. Further studies should investigate soil and mulch microbial dynamics and colonization as well as the microbial contribution of nitrifiers and denitrifiers to N_2O emission to better understand the complex interactions between mulch masses, physical properties, and microbial activity linked to soil N_2O emissions.

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