Are CH₄, CO₂, and N₂O Emissions from Soil Affected by the Sources and Doses of N in Warm-Season Pasture?

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Abstract: The intensification of pasture production has increased the use of N fertilizers—a practice that can alter soil greenhouse gas (GHG) fluxes. The objective of the present study was to evaluate the fluxes of CH₄, CO₂, and N₂O in the soil of Urochloa brizantha ‘Marandu’ pastures fertilized with different sources and doses of N. Two field experiments were conducted to evaluate GHG fluxes following N fertilization with urea, ammonium nitrate, and ammonium sulfate at doses of 0, 90, 180, and 270 kg N ha⁻¹. GHG fluxes were quantified using the static chamber technique and gas chromatography. In both experiments, the sources and doses of N did not significantly affect cumulative GHG emissions, while N fertilization significantly affected cumulative N₂O and CO₂ emissions compared to the control treatment. The N₂O emission factor following fertilization with urea, ammonium nitrate, and ammonium sulfate was lower than the United Nations’ Intergovernmental Panel on Climate Change standard (0.35%, 0.24%, and 0.21%, respectively, with fractionation fertilization and 1.00%, 0.83%, and 1.03%, respectively, with single fertilization). These findings are important for integrating national inventories and improving GHG estimation in tropical regions.

Keywords: GHG; mitigation; livestock; N fertilization; nitrous oxide; soil methane; soil respiration; Brachiaria grass; Marandu fertilization

1. Introduction

N fertilization is one of the main practices in pasture intensification to increase forage yield and improve forage quality [1]. According to the Food and Agriculture Organization (FAO), Brazil is the fourth largest importer of raw material for N fertilizer production worldwide, and increased fertilizer use is directly linked to the increasing demand for pasture fertilization [2,3]. However, anthropogenic N deposition from fertilizers directly affects ecosystem processes and greenhouse gas (GHG), primarily nitrous oxide (N₂O), fluxes.

Methane (CH₄), carbon dioxide (CO₂), and N₂O are the three major GHGs that play important roles in regulating the global climate. Although CO₂ is cycled in greater quantities through root and rhizomicrobial respiration and soil organic matter (OM) decomposition, the warming potential of CH₄ and N₂O is respectively 25 and 298 times greater than that of CO₂ [4]. CH₄ is produced by methanogenic archaea during anaerobic OM digestion, while N₂O is mainly produced via two microbial processes, namely nitrification and denitrification [5,6].

N addition to the pasture system markedly increases N₂O emissions [7–10], increases the efficiency of soil C sequestration [11] and reduces the atmospheric concentrations of CO₂ [12]. Although the effects of soil N deposition on CH₄ fluxes remain debatable, fertilization may increase the rate of CH₄ oxidation in the soil [10,13,14], increase its emissions, reduce its consumption [15,16], or produce no effect [17].
According to the International Fertilizer Industry Association, urea is the main N fertilizer used in agriculture [1]. However, this source has a high potential for N loss [18]. Therefore, alternative fertilizers to urea have been used to minimize N loss and increase fertilization efficiency. For instance, N fertilizers in the ammoniacal and/or nitric forms are available. In this light, the environmental impacts of fertilization must be regularly monitored. The emission factor (EF) of N$_2$O is specific to different types of fertilizers. According to the United Nations’ Intergovernmental Panel on Climate Change (IPCC) [19], the EFs of urea, ammonium nitrate, and ammonium sulfate are 1.1%, 2.9%, and 0.7%, respectively.

According to Bruulsema et al. [20], adequate fertilizer management, such as appropriate source selection and application rate, contributes to sustainable agriculture and offers economic, social, and environmental benefits. The fractionation of N doses is important for supplying N during the period of the greatest crop demand and ensuring a higher crop yield [21,22]. In addition, fractionation increases the efficiency of N fertilization and reduces N loss via leaching and denitrification, implying benefits in mitigating GHG emissions [23,24].

However, despite extensive research on the effects of N fertilization on soil GHG emissions in the temperate regions, little is known regarding these effects in the tropical regions. Factors controlling these fluxes under local conditions must be elucidated, and studies focusing on the sources and amount of N applied should be designed to develop specific EFs, improve national inventories, and adopt management measures that can mitigate GHG emissions. To this end, the objective of the present study was to evaluate the effects of different fertilizers (urea, ammonium nitrate, and ammonium sulfate) and various edaphoclimatic factors on CH$_4$, CO$_2$, and N$_2$O emissions from Marandu pastures as well as to determine the applicability of the standard N$_2$O EF under tropical conditions. We hypothesized that the use of ammonium sulfate as the N source would reduce GHG emissions and that N$_2$O emissions would be higher with ammonium nitrate, while CH$_4$ and CO$_2$ emissions would be greater with urea as the N source.

2. Materials and Methods

2.1. Experimental Sites

Field experiments were conducted on Urochloa brizantha ‘Marandu’ pastures established in 2001 and located in the Forage and Grasslands Sector of the São Paulo State University, “Julio de Mesquita Filho” (UNESP) (Jaboticabal, São Paulo, Brazil) (21°15′22″ S, 48°18′58″ W; 595 m altitude). According to the Köppen system, the climate in the region is of the Aw type (tropical, characterized by dry winters). The mean annual precipitation is 1424 mm, and the mean ambient temperature is 22.3 °C. The soil is Rhodic Ferralsol [25] derived from basalt. The soil, at 0–20 cm depth, has a bulk density of 1.20 g cm$^{-3}$, contains approximately 430 g kg$^{-1}$ of clay (sandy clay soil), The physicochemical characteristics of soil at the beginning of the experiment are presented in Table 1.

| Experiment | P resin | S–SO$_4^{2-}$ | OM | pH | CaCl$_2$ | K$^+$ | Ca$^{2+}$ | Mg$^{2+}$ | H$^+$Al | Al$^{3+}$ | CEC | V% |
|------------|--------|---------------|----|----|---------|-------|----------|----------|--------|--------|------|-----|
| 1          | 12     | 16            | 25 | 5.6| 26      | 36    | 11       | 22       | 0      | 98     | 72   | 69  |
| 2          | 21     | 11            | 27 | 5.1| 58      | 37    | 17       | 38       | 0      | 98     | 61   |     |

P = phosphorus, S = sulfur, OM: organic matter, K: potassium; Ca = calcium, Mg = Magnesium, Al = aluminum, CEC = soil exchange capacity; V = % of soil CEC occupied by bases. Experiment 1 was 50 m far from experiment 2. One dm$^3$ equal 1.20 kg dry soil.

2.2. Experimental Design and Treatments

Two experiments were performed on Marandu pastures to evaluate CH$_4$, CO$_2$, and N$_2$O emissions from N–fertilized soil. During the evaluation period, the experimental area was not grazed upon to avoid any disturbance or effect of animal excretion. Forty
experimental plots were allotted to each experiment. The distance between plots (chambers) was approximately 1.5 m.

The first experiment was conducted from 13 December 2017, to 12 November 2018, and the second experiment from 27 November 2018 to 14 November 2019. The experiments were arranged in a randomized block design, with four replicated, in a $3 \times 3 + 1$ factorial scheme. The treatments comprised three N fertilizers (urea, ammonium nitrate, and ammonium sulfate) and three N doses (90, 180, and 270 kg ha$^{-1}$ year$^{-1}$); the treatment without N fertilization was applied as the control.

In the first experiment, the N doses were applied as single fertilization (13 December 2014). In the second experiment, the N doses were divided into three fractions (27 November 2018, 12 January 2019, and 16 February 2019), representing 30, 60, and 90 kg N per application, distributed manually after standardization cuts.

2.3. Quantification of CH$_4$, CO$_2$, and N$_2$O Emissions

We used the closed static chamber technique [26] to collect air samples. Polyurethane chambers (height, 29 cm) were covered with thermal insulation mantles. The chamber headspace was 0.27 m$^3$. The chambers were deployed on round metal bases at the beginning of each sampling event at 9:00–10:00 h, as recommended by Alves et al. [27]. The chambers were equipped with a rubber belt to seal the chamber base and an output valve for sample retrieval. The linearity of gas accumulation in the chamber was successfully tested in a preliminary experiment with intensive sampling every 10 min for 1 h. Air samples were obtained using 50 mL polypropylene syringes at the deployment ($t_0$), 20 minutes ($t_{20}$) and 40 minutes ($t_{40}$) after. The air temperature outside and inside the chambers was recorded using a digital thermometer. The air samples were transferred to 20 mL pre-evacuated vials (Shimadzu flasks; Tokyo, Japan).

In the first experiment, after fertilization, samples were collected daily in the first week, every 2 days in the second week, twice a week for the remainder of the first month, weekly between 30 and 60 days, and every 15 days thereafter. In the second experiment, after the first and second fertilization, samples were collected daily in the first week, every 2 days in the second week, twice a week for the remainder of the first month, and weekly until subsequent fertilization; after the third fertilization, the schedule of the first experiment was followed. There were 47 and 68 sampling events in the first and second experiment, respectively.

Samples were analyzed by gas chromatography (Shimadzu Greenhouse 2014) under the following conditions: (1) CH$_4$ measurement: flame gas, H$_2$ (30 mL min$^{-1}$) and flame ionization detector temperature, 280 °C; (2) CO$_2$ measurement: thermal conductivity detector temperature, 250 °C; and (3) N$_2$O measurement: injector temperature, 250 °C, column temperature, 80 °C, carrier gas, N$_2$ (30 mL min$^{-1}$), and electron capture detector temperature, 325 °C.

CH$_4$ ($\mu$g CH$_4$ m$^{-2}$ h$^{-1}$), CO$_2$ (mg C m$^{-2}$ h$^{-1}$), and N$_2$O ($\mu$g N$_2$O m$^{-2}$ h$^{-1}$) fluxes were calculated considering the linear increase of gas concentration during the incubation period, ambient temperature and pressure, chamber volume, and area of the metal bases [28]. Cumulative emission (g m$^{-2}$) was calculated by integrating hourly fluxes over time.

2.4. Soil and Meteorological Parameters

Soil samples from the 0 to 20 cm layer were collected at each air sampling event to quantify inorganic N, gravimetric water content (by drying soil at 105 °C), and percent water-filled pore space (%WFPS). Soil bulk density in the 0–10 cm layer was measured using a cylinder (diameter, 50 mm; height, 50 mm). WFPS was calculated based on the gravimetric water content and bulk density assuming a particle density of 2.65 g cm$^{-3}$.

For mineral N analysis, on field–moist samples were extracted with 2 M KCl and corrected for water content. NH$_4$–N was quantified using the Berthelot reaction with spectrometry at 650 nm [29]. NO$_3$–N was quantified using ultraviolet absorption spectrometry at 460 nm [30,31]. Daily maximum, mean, and minimum temperature and daily
precipitation data were obtained from a meteorological station located 1.5 km from the experimental site.

2.5. Statistical Analysis

CH₄, CO₂, and N₂O fluxes were reported as the mean and standard error of the mean. Integrated data for each experiment were submitted (cumulative emission) to analysis of variance after testing for normality and equal variance using R 3.1.2 (2020), and when significance was found, orthogonal polynomial contrast analysis was performed at 5% probability. Multiple linear regression analysis was used to test for the relationships between transformed GHG fluxes and %WFPS, soil moisture, NH₄–N, NO₃–N, and soil and ambient temperature using data from each sampling event of the two experiments.

3. Results

3.1. Climatic Variables

Meteorological data were collected throughout the experimental period; the distribution of rainfall after fertilization presented a different pattern between the two experiments (Figure 1a,b). In the first experiment, the total annual precipitation was 827.5 mm, of which 452.4, 33.8, 100.6, and 250.7 mm occurred during the summer, fall, winter, and spring of 2018, respectively. The mean temperature during these periods was 24.4, 22.1, 21.0, and 24.1 °C, respectively (Figure 1a).

In the second experiment, the total annual precipitation was 994.8 mm, of which 39.6, 572.3, 157.2, 48.1, and 177.6 mm occurred during the late spring of 2018, and summer, fall, winter, and spring of 2019, respectively. The mean temperature during these periods was 25.3, 24.7, 22.3, 21.6, and 25.2 °C, respectively (Figure 1b). The mean annual precipitation during the experimental period (827.5 and 994.8) was lower than the historical mean from 1956 to 2015 in the experimental area (1398 mm) [32].

The mean temperature during the sampling period was 23.1 °C. The lowest ambient temperature was recorded in July 2019 (3.3 °C) and the highest in August 2018 (39.2 °C). During periods when the chambers were closed, indoor temperature ranged from 14.5 to 34.9 °C. Overall, the temperature was high during the sampling period; however, it declined when the sky changed from sunny to cloudy.

The %WFPS of the surface soil (0–20 cm) varied seasonally in response to precipitation (Figures 1 and 2), being higher in summer. In both experiments, the %WFPS of soil increased after the summer rains, but there was no total pore saturation during the experimental period (Figure 2). Isolated rain events in August and September 2018 also increased the %WFPS of soil, and long periods of low %WFPS (~30%) were recorded from April to August of the same year, probably because of low precipitation (Figure 2a).

![Figure 1. Cont.](image-url)
Figure 1. Daily ambient temperature (minimum, mean, and maximum; T; °C) and daily precipitation (P; mm). Data were obtained from the Agrometeorological Station, Department of Exact Sciences, FCAV/UNESP, located 1.5 km from the experiment site. Experiment 1 (a) and 2 (b).

Figure 2. Descriptive averages of water–filled pore space (%) in experiment 1 (a) and 2 (b).

3.2. CH₄ Flux

In the first experiment, CH₄ production was higher in spring and uptake rates were higher in winter (Figure 3a–c). In the second experiment, CH₄ emissions were higher in summer but CH₄ consumption was higher in the spring of 2018 and summer of 2019 (Figure 3d–f). In both experiments, the peak CH₄ emissions were higher using ammonium sulfate as the N source (387, 404, and 523 µg CH₄ m⁻² h⁻¹ in September 2018 and 149, 671, and 745 µg CH₄ m⁻² h⁻¹ in January 2019 at doses of 90, 180, and 270 kg N ha⁻¹, respectively).
respectively) (Figure 3c,d). The highest CH$_4$ uptake rate was recorded during the dry season in winter 2018, when inflows were respectively −905, −529, and −663 μg CH$_4$ m$^{-2}$ h$^{-1}$ using urea, ammonium nitrate, and ammonium sulfate as the N sources (Figure 3a–c).

**Figure 3.** Descriptive of average CH$_4$ fluxes (μg m$^{-2}$ h$^{-1}$) from pastures managed with N fertilizers in two experiments. (a) Urea, (b) ammonium nitrate, and (c) ammonium sulfate in experiment 1. (d) Urea, (e) ammonium nitrate, and (f) ammonium sulfate in experiment 2.
The CH\textsubscript{4} fluxes were correlated with NH\textsubscript{4}–N content, ambient temperature, and CO\textsubscript{2} emissions in both experiments. In addition, CH\textsubscript{4} flux was positively correlated with soil temperature in the first experiment but negatively correlated with %WFPS in the second experiment (Table 2).

Table 2. Multiple linear regression to determine the association between edaphoclimatic variables and greenhouse gas emissions.

| Factor          | Effect | Experiment 1 | Experiment 2 |
|-----------------|--------|--------------|--------------|
|                 | (+, − or NS) | N\textsubscript{2}O | CH\textsubscript{4} | CO\textsubscript{2} | N\textsubscript{2}O | CH\textsubscript{4} | CO\textsubscript{2} |
| T° Air          | (+<0.01) | (+<0.01)      | (+<0.001)     | (−<0.001)     | (−<0.001)     | (+<0.01)      | (+<0.001)     |
| T° Soil         | (−<0.001) | (+<0.001)     | (−<0.001)     | (+<0.001)     | NS            | NS            | (−<0.001)     |
| % WFPS          | NS      | NS            | NS            | (−<0.001)     | (−<0.01)      | +<0.001)      | +<0.001)      |
| Moisture        | NS      | NS            | NS            | NS            | NS            | NS            | NS            |
| NH\textsubscript{4}–N | (+<0.01) | (+<0.001)     | (+<0.05)      | (−<0.05)      | (−<0.01)      | NS            | NS            |
| NO\textsubscript{3}–N | NS      | NS            | +<0.01)       | NS            | NS            | +<0.001)      | +<0.001)      |
| CO\textsubscript{2} | NS      | NS            | NS            | NS            | NS            | NS            | NS            |

Positive, negative, or not significant; \( p \) values for variables in the best-fit model selected according to the Akaike information criterion are shown in parentheses. T°: Temperature; WFPS: Water-filled pore space.

3.3. CO\textsubscript{2} Flux

In both experiments, the highest CO\textsubscript{2} fluxes occurred in summer and the lowest in winter (Figure 4). The highest emission peaks of 1149, 1444, and 1185 mg CO\textsubscript{2} m\textsuperscript{−2} h\textsuperscript{−1} were recorded in December 2017 (Figure 4a–c) and of 1563, 1860, and 1574 mg CO\textsubscript{2} m\textsuperscript{−2} h\textsuperscript{−1} were recorded in November 2018 (Figure 4d–f) using urea, ammonium nitrate, and ammonium sulfate as the N source, respectively.

In the first experiment, CO\textsubscript{2} flux was positively correlated with soil NH\textsubscript{4}–N and NO\textsubscript{3}–N levels and ambient temperature but negatively correlated with soil temperature. In the second experiment, CO\textsubscript{2} flux was positively correlated with %WFPS and ambient temperature (Table 2).

3.4. N\textsubscript{2}O Flux

Peak N\textsubscript{2}O emissions occurred four days after fertilization using urea and ammonium nitrate as the N sources in the first experiment, with mean values of 112 and 240 \( \mu \text{g} \) N\textsubscript{2}O m\textsuperscript{−2} h\textsuperscript{−1}, respectively (Figure 5a,b); using ammonium sulfate as the N source, no peak was observed after fertilization, but higher emissions were recorded in spring (18 September 2018), with a mean flux of 200 \( \mu \text{g} \) N\textsubscript{2}O m\textsuperscript{−2} h\textsuperscript{−1} (Figure 5c). Peaks N\textsubscript{2}O emissions were also recorded after precipitation events following a long dry period (Figure 1a) in August and September 2018 (Figure 5a–c).
3.3. CO2 Flux
In both experiments, the highest CO2 fluxes occurred in summer and the lowest in winter (Figure 4). The highest emission peaks of 1149, 1444, and 1185 mg CO2 m$^{-2}$ h$^{-1}$ were recorded in December 2017 (Figure 4a–c) and of 1563, 1860, and 1574 mg CO2 m$^{-2}$ h$^{-1}$ were recorded in November 2018 (Figure 4d–f) using urea, ammonium nitrate, and ammonium sulfate as the N source, respectively.

In the first experiment, CO2 flux was positively correlated with soil NH4–N and NO3–N levels and ambient temperature but negatively correlated with soil temperature. In the second experiment, CO2 flux was positively correlated with %WFPS and ambient temperature (Table 2).

![Figure 4. Descriptive average of CO2 fluxes (mg m$^{-2}$ h$^{-1}$) of pastures fertilized with N fertilizers in two experiments: experiment 1: (a) urea, (b) ammonium nitrate, (c) ammonium sulfate; experiment 2: (d) urea, (e) ammonium nitrate, (f) ammonium sulfate.](image-url)
Figure 5. Descriptive averages of N\textsubscript{2}O fluxes (\(\mu g \text{ m}^{-2} \text{ h}^{-1}\)) from pastures managed with N fertilizers in two experiments. (a) Urea, (b) ammonium nitrate, and (c) ammonium sulfate in experiment 1. (d) Urea, (e) ammonium nitrate, and (f) ammonium sulfate in experiment 2.
Negative N\(_2\)O fluxes were observed in approximately 32% of all sampling events, particularly in winter, when %WFPS was the lowest (Figure 2a,b). The highest N\(_2\)O consumption rate was recorded on 13 November 2018, with mean values of −77, −98, and −58 µg N\(_2\)O m\(^{-2}\) h\(^{-1}\) using urea, ammonium nitrate, and ammonium sulfate as the N sources, respectively (Figure 5a–c).

In the second experiment, N\(_2\)O emissions were higher in summer, with peak mean fluxes of 257, 340, and 273 µg N\(_2\)O m\(^{-2}\) h\(^{-1}\) recorded in November 2018 and of 265, 134, and 157 µg N\(_2\)O m\(^{-2}\) h\(^{-1}\) recorded in December 2018 using urea, ammonium nitrate, and ammonium sulfate as the N sources, respectively. Negative fluxes greater than −50 µg N\(_2\)O m\(^{-2}\) h\(^{-1}\) were observed throughout the experiment, mainly in November 2018 and May and July 2019 (Figure 5d–f).

N\(_2\)O flux was significantly correlated with ambient and soil temperature and NH\(_4\)–N content. In both experiments, N\(_2\)O fluxes were positively correlated with CO\(_2\) fluxes. In the second experiment, N\(_2\)O fluxes were negatively correlated with %WFPS and positively correlated with soil moisture (Table 2).

The effects of ambient and soil temperature on N\(_2\)O fluxes were dependent on fertilization management. At high N doses, N\(_2\)O fluxes increased with temperature; however, when fertilization was fractioned, N\(_2\)O fluxes were negatively correlated with temperature. The correlation between soil temperature and N\(_2\)O flux was positive under single fertilization and negative under fertilization fractionation.

### 3.5. Inorganic N

Inorganic N content was low almost throughout the experimental period. This content increased at 7 days after fertilization. The NH\(_4\)–N and NO\(_3\)–N levels during the year did not vary significantly with and without N fertilization (Figures 6 and 7). Soil NH\(_4\)–N levels were higher and were affected to a greater extent by fertilization than NO\(_3\)–N levels. The NH\(_4\)–N levels ranged from 3 to 35 mg N kg\(^{-1}\) of dry soil, and the NO\(_3\)–N levels ranged from 3 to 18 mg N kg\(^{-1}\) of dry soil. NH\(_4\)–N content was correlated with N\(_2\)O, CH\(_4\), and CO\(_2\) fluxes in the first experiment and with N\(_2\)O and CH\(_4\) fluxes in the second experiment; NO\(_3\)–N content was only correlated with CO\(_2\) fluxes in the first experiment (Table 2).

### 3.6. Cumulative GHG Emissions

N sources and doses did not significantly affect CH\(_4\), CO\(_2\), and N\(_2\)O cumulative emissions in either experiment (\(p > 0.05\)). In contrast, N applied as single fertilization, regardless of the source, promoted CO\(_2\) and N\(_2\)O emissions in the first experiment, and the cumulative emissions under N fertilization were significantly different from those under the control treatment (\(p < 0.05\)) (Table 3).

In both experiments, CH\(_4\) consumption was observed under the control treatment and positive fluxes were observed under the fertilizer treatments. The mean CO\(_2\) and N\(_2\)O emissions under N fertilization were 1909.0 mg CO\(_2\) m\(^{-2}\) and 79.6 mg N\(_2\)O m\(^{-2}\), respectively. In the second experiment, the mean CO\(_2\) and N\(_2\)O fluxes did not differ significantly between the control and N fertilizer treatments; however, similar to that in the first experiment, in the second experiment, N fertilization increased annual CO\(_2\) and N\(_2\)O emissions by 28% and 151%, respectively, compared with the control treatment.

The N\(_2\)O EF did not differ among the evaluated fertilizer sources and was lower in the second experiment when the fertilization was fractionated (Table 4).
The effects of ambient and soil temperature on N\textsubscript{2}O fluxes were dependent on fertilization management. At high N doses, N\textsubscript{2}O fluxes increased with temperature; however, N\textsubscript{2}O content increased at 7 days after fertilization. The NH\textsubscript{4}–N and NO\textsubscript{3}–N levels during the year did not vary significantly with and without N fertilization (Figures 6 and 7). Soil NH\textsubscript{4}–N content was correlated with N\textsubscript{2}O, CH\textsubscript{4}, and CO\textsubscript{2} fluxes in both experiments. In the second experiment, N\textsubscript{2}O fluxes were negatively correlated with %WFPS and positively correlated with soil moisture (Table 2). In the first experiment, in the second experiment, N\textsubscript{2}O fluxes were positively correlated with CO\textsubscript{2} fluxes. The correlation between soil temperature and N\textsubscript{2}O flux was positive under single fertilization and negative under fertilization fractionation. Inorganic N content was low almost throughout the experimental period. This content was only correlated with CO\textsubscript{2} fluxes in the first experiment (Table 2).

In both experiments, CH\textsubscript{4} consumption was observed under the control treatment (Figures 6 and 7). Descriptive averages of NO\textsubscript{3}–N content of soil (mg NO\textsubscript{3}–N kg\textsuperscript{-1} dry soil) under N fertilization were 1909.0 mg CO\textsubscript{2} m\textsuperscript{2} and 1486.6 mg CO\textsubscript{2} m\textsuperscript{2} under the control treatment (Figures 6 and 7). Cumulative GHG Emissions (Table 3).

| GHG Source | Emission (mg) | Experiment 1 | Experiment 2 |
|------------|--------------|--------------|--------------|
| CO\textsubscript{2} | Urea | 2208.9 ± 102.8a | 1796.2 ± 132.3a |
| CH\textsubscript{4} | Urea | 25.5 ± 82.4a | 20.4 ± 83.6a |
| CO\textsubscript{2} | Control | 1523.4 ± 66.6b | 1486.6 ± 170.3a |
| CH\textsubscript{4} | Control | 13/1/1827/1/19 | 13/2/1827/2/19 |
| CO\textsubscript{2} | Ammonium nitrate | 2206.5 ± 77.6a | 1887.7 ± 99.6a |
| CH\textsubscript{4} | Ammonium nitrate | 122.0 ± 33.7ab | 75.3 ± 14.9a |
| CO\textsubscript{2} | Ammonium sulfate | 2115.6 ± 113.4a | 2043.5 ± 170.3a |
| CH\textsubscript{4} | Ammonium sulfate | 162.6 ± 109.2a | 2.6 ± 134.8a |

Figure 6. Descriptive averages of NH\textsubscript{4}–N content of soil (mg NH\textsubscript{4}–N kg\textsuperscript{-1} dry soil). Experiment 1 (a) and 2 (b).

Figure 7. Descriptive averages of NO\textsubscript{3}–N content of soil (mg NO\textsubscript{3}–N kg\textsuperscript{-1} dry soil). Experiment 1 (a) and 2 (b).
Table 3. Cumulative CH\textsubscript{4} (mg CH\textsubscript{4} m\textsuperscript{-2}), CO\textsubscript{2} (mg CO\textsubscript{2} m\textsuperscript{-2}), and N\textsubscript{2}O (mg N\textsubscript{2}O m\textsuperscript{2}) emissions from Marandu pastures fertilized with different N sources and doses in two experiments.

| GHG       | Source          | Experiment 1          | Experiment 2          |
|-----------|----------------|-----------------------|-----------------------|
| CH\textsubscript{4} | Urea           | 25.5 ± 82.4a          | 20.4 ± 83.6a          |
|           | Ammonium nitrate | 177.4 ± 90.4a         | –3.9 ± 88.4a          |
|           | Ammonium sulfate | 162.6 ± 109.2a        | 2.6 ± 134.8a          |
|           | Control         | –99.8 ± 40.8a         | –77.4 ± 33.5a         |
| CO\textsubscript{2} | Urea           | 2208.9 ± 102.8a       | 1796.2 ± 132.3a       |
|           | Ammonium nitrate | 2206.5 ± 77.6a        | 1887.7 ± 99.6a        |
|           | Ammonium sulfate | 2115.6 ± 113.4a       | 2043.5 ± 170.3a       |
|           | Control         | 1523.4 ± 66.6b        | 1486.6 ± 170.3a       |
| N\textsubscript{2}O | Urea           | 153.4 ± 27.7a         | 94.7 ± 20.0a          |
|           | Ammonium nitrate | 122.0 ± 33.7ab        | 75.3 ± 14.9a          |
|           | Ammonium sulfate | 158.9 ± 28.9a         | 68.7 ± 16.1a          |
|           | Control         | –26.6 ± 4.2b          | 31.7 ± 22.9a          |

Means followed by the same letter in the column are not significantly different (Tukey’s test, alpha = 5%).

Table 4. Annual N\textsubscript{2}O emission factor (g N per 100 g N applied).

| Treatment                 | Experiment 1          | Experiment 2          |
|---------------------------|-----------------------|-----------------------|
| Urea                      | 1.00 ± 0.2a           | 0.35 ± 0.1a           |
| Ammonium nitrate          | 0.83 ± 0.2a           | 0.24 ± 0.1a           |
| Ammonium sulfate          | 1.03 ± 0.3a           | 0.21 ± 0.1a           |

Means followed by the same letter in the column are not significantly different (Tukey’s test, alpha=5%).

4. Discussion

4.1. CH\textsubscript{4} Flux

In the present study, the highest CH\textsubscript{4} emissions were observed during the warmest and rainiest periods (Figure 3). During the period of high rainfall, anaerobic sites can form even in well-drained soils, and elevated temperature increases CH\textsubscript{4} production, with temperatures around 35 °C being the most suitable for CH\textsubscript{4} formation in soil [33–35].

Throughout the experimental period, CH\textsubscript{4} fluxes were correlated with ambient temperature. In 2018, soil temperature also strongly affected CH\textsubscript{4} fluxes (Table 2), with higher CH\textsubscript{4} consumption during the coldest period (Figure 3a–c). CH\textsubscript{4} consumption in grasslands is significantly correlated with ambient temperature and soil temperature and moisture [8,36], which are the key factors determining CH\textsubscript{4} uptake; as such, moisture content around 21–24% and temperatures near 10 °C are conducive to CH\textsubscript{4} consumption [37,38].

In the present study, we noted a positive correlation between ambient temperature and CH\textsubscript{4} fluxes in the first experiment but a negative correlation in the second experiment, indicating that the relationship between these two variables depends on the type of fertilization management (single or fractioned). Similarly, Cardoso et al. [39] noted a positive correlation between CH\textsubscript{4} emissions and temperature in Marandu pastures using conventional urea, and Jiang et al. [40] observed a positive correlation between CH\textsubscript{4} consumption and ambient and soil temperature.

According to Agostinetto et al. [41], environmental variables, such as temperature and rainfall, and soil properties, such as OM content, moisture, redox potential, and pH, alter the constitution and release rate of exudates and OM, ultimately affecting CH\textsubscript{4} production.

Methanogens can adapt to both temperature conditions and available C in the soil; at high temperatures, methanogens of the Methanosarcinaceae family are dominant, which can use H\textsubscript{2}/CO\textsubscript{2} and acetate as precursors to produce CH\textsubscript{4}; meanwhile, at low temperatures, methanogens of the Methanosaetaceae family are dominant, which can only use acetate as the CH\textsubscript{4} precursor [42–44]. This explains the higher CH\textsubscript{4} emission observed in summer (Figure 3) and its positive relationship with CO\textsubscript{2} emission (Table 2), which was
also higher during this period, indicating greater C availability in the soil. Consistently, Chu et al. [45] have reported positive correlations between CH4 and CO2 fluxes.

The effects of mineral fertilization on soil CH4 emissions reported in the literature are complex and sometimes contradictory [10,17,46]. In the present study, the NH4–N content of soil was closely related to CH4 emissions (Table 2), and the largest variations in fluxes occurred after fertilization in the second experiment, when the NH4–N content was greater than that during the first experiment (Figure 6a,b). Cardoso et al. [39] have reported similar results that the variations in CH4 fluxes were greater following N application and CH4 emissions were closely and directly related to soil NH4–N content.

The positive relationship between CH4 fluxes and NH4–N content is attributed to the inhibitory effect of NH4–N on methanotrophy, during which CH4 in the soil is oxidized; thus, when a large amount of NH4–N is available, methanotrophic bacteria oxidize NH4–N at the expense of CH4 [47,48], leading to higher net CH4 emissions from the soil.

In the present study, the relationship between NH4–N and CH4 fluxes was dependent on the amount of N applied. At lower N doses under fertilization fractionation, there was a negative correlation between NH4–N and CH4 fluxes, while at higher N doses under single fertilization, CH4 fluxes increased with NH4–N content. Consistent with our results, Zhang et al. [13] have reported a negative correlation between CH4 consumption and NH4–N content, resulting in positive CH4 emission from the soil.

4.2. CO2 Flux

In the present study, CO2 fluxes were higher during summer, similar to N2O and CH4 fluxes, and lower in winter (Figure 4). These results are consistent with those reported by Raposo et al. [10] and Brito et al. [49]; in an experiment on Marandu grass pastures, the authors observed that CO2 emissions varied depending on soil temperature and precipitation, with higher emissions in summer and lower emissions in winter. According to Moreira and Siqueira [50], biotic and abiotic factors of the soil, such as substrate supply, temperature, moisture, oxygen, N, texture, and pH, affect CO2 production by roots and organisms and, consequently, the gaseous exchange between the soil and the atmosphere.

Precipitation events drive the seasonal variations in CO2 fluxes; thus, increased CO2 emissions in summer are related to increased soil moisture, which enhances root respiration due to plant growth and microbial activity involved in labile OM decomposition in the soil [51,52]. In addition, N fertilizers are often applied during summer, a practice that increases soil microbial activity, and subsequent entry of water into the soil via precipitation favors the displacement of gases in the soil and promotes CO2 release [50,53].

Another factor that can increase CO2 emissions is the longest growing season in the tropical regions and the highest photosynthetic efficiency of C4 plants, leading to increase in the yield and root area of forage and microbial respiration. In addition, grasses in pasture ecosystems have dense root systems that favor biological activity and increase CO2 fluxes [39,49].

CO2 emissions were positively correlated with mineral N content in the first experiment, but this content did not explain the variations in fluxes in the second experiment (Table 2); however, higher emission rates were observed after fertilization when N–NH4 and NO3–N levels were higher (Figure 4). Several studies have reported that high mineral N levels promote the decomposition of plant residues and soil OM [54,55], consequently stimulating CO2 flux [10].

According to Fang et al. [56], CO2 emissions were positively correlated with N–NH4 content and aboveground biomass, highlighting the relevance of autotrophic respiration. Moreover, the authors proposed that N addition to the soil affects CO2 fluxes by altering plant growth and renewing soil C reserves. N fertilization likely alters the major pathways related to CO2 fluxes since it also increases forage accumulation [57]; therefore, the response of CO2 fluxes to N is consistent with that of plants. Alternatively, N fertilization stimulates heterotrophic respiration through high availability of C and N in the substrate and increase in biomass and microbial activity [58,59].
The positive correlation of CO$_2$ fluxes with ambient temperature and %WFPS may be attributed to the effects of temperature and moisture on soil respiration and C flux, which may vary across seasons of the year; therefore, even small changes in these variables can greatly affect the magnitude of CO$_2$ flux [39,49]. Furthermore, temperature can act more effectively by accelerating soil microbial activities and decomposition, which strongly affect CO$_2$ emissions from soil to the atmosphere.

In the present study, seasonal variations in CO$_2$ fluxes were directly related to variations in ambient temperature. According to Jiang et al. [40], an increase in temperature in the future may have a major impact on soil respiration. This may be attributed to the exponentially increase in soil heterotrophic respiration and root autotrophic respiration with temperature [60].

4.3. N$_2$O Flux

The higher N$_2$O fluxes observed in summer were determined by the higher amount of rainfall and the consequent increase in soil moisture; there was a strong positive correlation between soil moisture and N$_2$O flux in the second experiment (Table 2). The highest fluxes occurred when the %WFPS was between 50% and 60% (Figures 2 and 5), indicating that nitrification was the main process responsible for N$_2$O emissions.

Dobbie and Smith [61] reported that the nitrification rate increases with an increase in %WFPS up to 60%; subsequently, the rate of nitrification decreases and that of denitrification increases as a function of increase in moisture content, reaching the maximum value at soil saturation. This explains the lack of correlation between N$_2$O flux and %WFPS in the first experiment and their negative correlation in the second experiment (Table 2), as N$_2$O emission via nitrification was favored under the conditions of lower %WFPS.

The correlation between soil moisture and N$_2$O emissions (Table 2) was comparable to that observed in other experiments on grasslands reporting greater variations in N$_2$O emissions coinciding with the periods of higher precipitation [10,36,39,62,63].

The N$_2$O fluxes recorded in the present study were similar to those reported previously for tropical soils. Low N$_2$O emissions [9,64–67] are attributed to denitrification as the main process of N$_2$O production, which is favored under anaerobic soil conditions.

Even after heavy rainfall, the %WFPS did not exceed 60% (Figure 2), which would allow the predominance of anoxic zones and, therefore, high denitrification rates [68]. However, N$_2$O fluxes and NH$_4^+$–N levels were correlated in both experiments (Table 2), reinforcing the assumption that nitrification was the main process responsible for N$_2$O emissions. This assumption can be validated based on the classification of Ferralsols as free–draining [25]; therefore, rapid percolation of water in the soil, together with high evapotranspiration during the summer, can drastically reduce the duration for which soil %WFPS is maintained at 50% or above, which may limit N$_2$O emissions [68].

Likewise, Jantalia et al. [64] reported that N$_2$O fluxes are usually lower in Ferralsols because of their excellent drainage, as nitrification is more common under the conditions of low % WFPS. Higher rates of N$_2$O consumption were mainly observed during the dry seasons and during periods of low %WFPS (Figures 2 and 5). Bento et al. [69] also observed that throughout their study, N$_2$O fluxes were almost zero when the soil was dry, suggesting that the nitrification rate was relatively low.

Increases in soil NH$_4^+$–N levels due to fertilizer application stimulated N$_2$O emissions in the rainy season, and fluxes tended to be lower when NH$_4^+$–N levels were low (Figures 5 and 6). According to Bouwman [70], mineral fertilization provides additional NH$_4^+$ and NO$_3^-$ substrates and tends to increase N$_2$O emissions from soils by stimulating microbial activity. This explains the positive correlation between NH$_4^+$–N content and N$_2$O fluxes at high N doses under single fertilization as opposed to that at low N doses under fertilizer fractionation (Table 2).

High availability of mineral N in the soil combined with high moisture can induce N$_2$O fluxes [68], provided that no other important limiting factor operates in the system; thus, increased N$_2$O emissions during the rainy season in the present study can be explained
by elevated NH$_4$–N levels after fertilization. Similarly, Campanha et al. [66] observed that higher mineral N content immediately after fertilization promoted N$_2$O emissions.

Almost throughout the experimental period, NO$_3$–N levels remained low (average of 5 mg N kg$^{-1}$ of soil), which explains the lack of correlation between NO$_3$–N levels and N$_2$O fluxes. According to Ryden [71], at NO$_3$–N levels below 5–10 mg N kg$^{-1}$ of dry soil, denitrification was limited in pastures. Mazzeto et al. [36] also observed that when soil NO$_3$–N levels were low, N$_2$O emission was reduced and N$_2$O consumption was enhanced.

Changes in soil moisture and temperature could explain up to 95% of the temporal variation in soil N$_2$O emissions [72]. In both experiments, soil and ambient temperatures were the key drivers of variations in N$_2$O fluxes (Table 2), with emission peaks occurring in warmer months (Figures 1 and 5).

Increases in N$_2$O emissions accompanied increases in CO$_2$ emissions throughout the experimental period (Figures 4 and 5), with a positive correlation between the two variables (Table 2). Bento et al. [69] reported a positive correlation between N$_2$O and CO$_2$ fluxes in pastoral and agricultural areas; according to the authors, fertilizer application was the primary factor explaining this correlation through stimulating the activity of nitrifying and denitrifying bacteria and microbial respiration in the rhizosphere [45].

Considering that N$_2$O production is mediated by soil microbial communities, specifically nitrifiers and denitrifiers, and that CO$_2$ emission is an indicator of soil C availability and heterotrophic respiration, the correlation between CO$_2$ and N$_2$O fluxes may be explained as follows: denitrifying organisms are predominantly heterotrophic and therefore require a source of C; consequently, increased C availability, as reflected by CO$_2$ emission, directly increased denitrifier activity and N$_2$O production [73], even though denitrification was not the main pathway of N$_2$O production in the present experiment.

These findings underscore the importance of precipitation, %WFPS, CO$_2$ emission, temperature, and NH$_4$–N content as factors influencing soil microbial activity and thus regulating the magnitude of N$_2$O emissions.

**4.4. Cumulative GHG Emissions**

N fertilization treatments did not significantly affect CH$_4$ emissions; however, the cumulative mean emission of all fertilizer treatments was higher than that of the control treatment (Table 3).

N fertilization can affect CH$_4$ oxidation by elevating NH$_4^+$ production; both NH$_4^+$ and CH$_4$ require monoxygenase for their oxidation, and in this competition, NH$_4^+$ frequently acts as the inhibitor of CH$_4$ oxidation, leading to greater emissions [74–76]. However, contradictory results have been reported regarding the effects of N on CH$_4$ oxidation and emission [14,16,17]. According to Mohanty et al. [77], the effect of N depends on the type of soil microbial community; therefore, to better understand the effects of N addition on CH$_4$, the assessment of microbial communities should be included in future studies [10].

In the present study, fertilization as a single application significantly increased CO$_2$ fluxes compared with the control treatment (Table 3). This result is consistent with previous reports of increased CO$_2$ emissions from N–fertilized soils [10,69,78,79]. According to Liu et al. [80], the highest CO$_2$ emissions from fertilized soils may be explained by the greater root respiration due to active growth. According to Li et al. [81], the anthropogenic deposition of N affects the global GHG budget by increasing in CO$_2$ and N$_2$O emissions.

In the present study, N$_2$O emission was not affected by the sources and doses of N; however, fertilization with urea and ammonium sulfate as a single application significantly increased emissions compared with the control treatment (Table 3). Several studies have reported increased N$_2$O emissions following N fertilization [10,39,82]. However, the factors involved in N$_2$O production and consumption in soils are complex and may generate different results, although N addition does not significantly affect N$_2$O emissions [83,84].

According to Li et al. [81], the effects of N deposition on GHG emissions in pastures are highly uncertain, and the emission responses may be attributed to other factors, such as local edaphoclimatic conditions. In the present study, we observed that the type of
fertilization management had a greater impact on the cumulative emissions of CH$_4$, CO$_2$, and N$_2$O than the sources and doses of N, and fertilization fractionation reduced annual GHG emissions.

According to Vanderzaag et al. [85], different sources of N fertilizers differ in their ability to induce N$_2$O emissions from the soil. For instance, amidic and ammoniacal sources are expected to increase emissions by affecting N$_2$O formation through nitrification and denitrification [86], while in nitric and nitrate fertilizers, which only produce N$_2$O through denitrification, are expected to reduce emissions (Table 3).

4.5. EFs of N$_2$O

According to the IPCC [19], approximately 1.1%, 2.9%, and 0.7% of N applied in the form of urea, ammonium nitrate, and ammonium sulfate fertilizers, respectively, is lost as N$_2$O. In the present study, only the EFs of N$_2$O under urea and ammonium sulfate fertilization as a single application approached the IPCC values. Under fertilization fractionation, the average EFs were below 0.36%, representing only 32%, 8%, and 30% of the IPCC values for urea, ammonium nitrate, and ammonium sulfate fertilizers, respectively (Table 4). Similarly, Nascimento et al. [9] observed EFs below 0.36% in Marandu grass pastures fertilized with urea and ammonium sulfate in Brazil.

We found that under the edaphoclimatic conditions of the Brazilian Cerrado, the N$_2$O EFs of Ferralsols managed with split N fertilization were much lower than the IPCC values; therefore, fertilization fractionation, regardless of the N source, is a recommended strategy to mitigate N$_2$O emissions from soil.

In another study on Marandu pastures near our experimental area, Cardoso et al. reported EFs of N$_2$O ranging from 0.37% to 0.41% under biofertilizer treatment [87] and from 1.22% and 0.53% over 2 experimental years under urea fertilization [8]. In a recent study on Marandu pastures in Brazil, Dos Santos et al. [88] reported an EF of 0.5% using urea as a fertilizer. Taken together, the previous reports and our results indicate that N$_2$O EFs in Brazil differ from the IPCC values and generally below 1% [7,64,66].

5. Conclusions

The present study is the first to report CH$_4$, CO$_2$, and N$_2$O emissions as a function of different N fertilizer sources in tropical pastures. Our results revealed that although cumulative GHG emissions did not vary as a function of fertilizer source, N addition promoted CO$_2$ and N$_2$O emissions and seasons regulated changes in GHG fluxes throughout the year.

Under fertilization fractionation, N$_2$O EFs differed from the IPCC standards, being 77% lower on average. Therefore, the IPCC standard EFs for this type of fertilization management of tropical pastures are not appropriate, and fertilization fractionation may serve as an option to mitigate GHG emissions from pastures.

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