UNIVERSIDADE ESTADUAL PAULISTA – UNESP
CÂMPUS DE JABOTICABAL

EFEITO DA FONTE E DOSE DE NITROGÊNIO NA EMISSÃO DE GASES DE EFEITO ESTUFA, ACÚMULO DE FORRAGEM E COMPOSIÇÃO QUÍMICA DE *Urochloa brizantha* CV MARANDU

Darlena Caroline da Cruz Corrêa
Engenheira Agrônoma
Mestre em Ciência animal

2021

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Orientadora: Profª. Dra. Ana Cláudia Ruggieri
Coorientador: Dr. Abmael da Silva Cardoso

Tese apresentada à Faculdade de Ciências Agrárias e Veterinárias – Unesp, Câmpus de Jaboticabal, como parte das exigências para a obtenção do Título de Doutora em Zootecnia.

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CERTIFICADO DE APROVAÇÃO

TÍTULO DA TESE: EFEITO DA FONTE E DOSE DE NITROGÊNIO NA EMISSÃO DE GASES DE EFEITO ESTUFA, ACÚMULO DE FORRAGEM E COMPOSIÇÃO QUÍMICA DE *Urochloa brizantha* CV MARANDU

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Jaboticabal, 25 de março de 2021

DADOS CURRICULARES DO AUTOR

DARLENA CAROLINE DA CRUZ CORRÊA – nascida em 26 de maio de 1992 no município de Castanhal, Pará, iniciou o curso de graduação em Agronomia no Instituto Federal de Educação, Ciência e Tecnologia do Pará (IFPa), Castanhal - PA, em março de 2010. Durante a graduação foi bolsista do Programa de Educação Tutorial (PET), sob tutoria da Profª Dra Louise Ferreira Rosal, e foi monitora da disciplina de Zootecnia sob orientação da Profª Dra Célia Maria Costa Guimarães. Em fevereiro de 2015 diplomou-se Engenheira Agrônoma e em março do mesmo ano ingressou no Mestrado em Ciência Animal, com bolsa de estudos da Capes, na Universidade Federal do Pará – UFPa – Campus de Castanhal – PA, onde desenvolveu estudos na área de Forragicultura sob orientação do Prof. Dr. Felipe Nogueira Domingues. Recebeu o título de Mestre em Ciência Animal em fevereiro de 2017. Em março do mesmo ano, iniciou o Doutorado em Zootecnia pela Faculdade de Ciências Agrárias e Veterinárias – UNESP – Campus de Jaboticabal – SP, com bolsa de estudos da Capes, na área de Forragicultura e pastagens sob orientação da Profa. Dra. Ana Cláudia Ruggieri, e coorientação do Dr. Abmael da Silva Cardoso.

Epígrafe

“Não fui eu que lhe ordenei? Seja forte e corajoso! Não se apavore, nem se desanime, pois o Senhor, o seu Deus, estará com você por onde você andar".
(Josué 1:9)

Dedicatória

Aos meus pais, Joana D'arc e Francisco, pelo amor, carinho, apoio e orações.

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A Deus.

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SUMÁRIO

EFEITO DA FONTE E DOSE DE NITROGÊNIO NA EMISSÃO DE GASES DE EFEITO ESTUFA, ACÚMULO DE FORRAGEM E COMPOSIÇÃO QUÍMICA DE *Urochloa brizantha* CV MARANDU

RESUMO – A intensificação da produção em pastagens ocasionou o aumento do uso de fertilizantes nitrogenados, prática que merece atenção devido ao alto potencial de perda de nitrogênio (N) por volatilização, e que também pode alterar os fluxos de gases de efeito estufa (GEE) do solo como o dióxido de carbono (CO_2), óxido nitroso (N_2O) e metano (CH_4). A magnitude dessas emissões em pastagens tropicais ainda é pouco conhecida e o entendimento dos fatores que as modificam pode ajudar a mitigar a emissão de GEE e melhorar a eficiência da fertilização com N. O objetivo desta pesquisa foi investigar os efeitos de três fertilizantes (ureia, sulfato de amônio e nitrato de amônio) aplicados de forma única e parcelada, e quatro doses (0, 90, 180 e 270 kg ha^{-1} ano^{-1}) de N, nos fluxos de CO_2, N_2O e CH_4, na volatilização de amônia (NH_3) e nas características produtivas e químicas da forragem em pastagem de capim *U. brizantha* cv Marandu. A captação do N perdido como NH_3 foi realizada de acordo com a técnica de câmaras semi-abertas. Para avaliação da forragem, foram feitas parcelas de 3x4 m manejadas em regime de cortes a uma altura de dossel de 30 cm e resíduo de 15 cm e realizadas as análises químicas de proteína bruta (PB), fibra em detergente ácido (FDN) e fibra em detergente neutro (FDA). As emissões de GEE foram medidas usando câmaras estáticas fechadas e as análises dos gases realizadas por cromatografia gasosa. As perdas por volatilização de NH_3 provenientes dos fertilizantes com N nas formas nítrica e amoniacal foram menores que a da ureia, e o parcelamento da fertilização reduziu em média 47% as perdas de N. A fertilização nitrogenada aumentou linearmente o acúmulo de forragem apresentando médias de 232, 264, 285 e 304 kg ha^{-1} dia^{-1} nas doses de 0, 90, 180 e 270 kg ha^{-1} ano^{-1}, respectivamente. Os teores de PB e FDN aumentaram linearmente com o aumento das doses de N. Os fatores de emissão (FE) de NH_3 foram de 20,69; 3,70 e 2,82% nos fertilizantes ureia, nitrato e sulfato de amônio, respectivamente, diferindo dos padrões estabelecidos pelo IPCC. Os fluxos de N_2O, CH_4 e CO_2 do solo não variaram em função dos fertilizantes e doses de N. Os fluxos de GEE diferiram em função das condições climáticas e as principais variáveis determinantes que controlam as emissões foram espaços porosos saturados com água (%EPSA), temperatura e teor de (N amoniacal) N-NH_4^+. Os FE de N_2O foram 0,35; 0,24 e 0,21% nos fertilizantes ureia, nitrato e sulfato de amônio, quando a fertilização foi parcelada, diferindo do FE padrão do IPCC. As condições ambientais impactaram diretamente nas respostas da planta e dos gases. A utilização de fertilizantes alternativos a ureia pode diminuir as perdas de N por volatilização e aumentar o acúmulo de forragem, ao passo que, o fracionamento da fertilização, além de diminuir perdas de NH_3 reduzem as emissões de N_2O, mostrando-se uma alternativa para a mitigação de GEE.

Palavras-chave: Fertilizantes nitrogenados, capim-marandu, volatilização, N_2O, fator de emissão, gases de efeito estufa.

EFFECT OF NITROGEN SOURCE AND DOSE ON GREENHOUSE GAS EMISSION, FORAGE ACCUMULATION AND CHEMICAL COMPOSITION OF *Urochloa brizantha* CV MARANDU

ABSTRACT – The intensification of pasture production increased nitrogen (N) fertilizers use. A practice that deserves attention due to the high potential for N loss through volatilization, which can also alter the fluxes of greenhouse gases (GHG) from the soil, such as dioxide carbon (CO_2), nitrous oxide (N_2O), and methane (CH_4). The magnitude of these emissions in tropical pastures is still poorly understood. Understanding the factors that modify them may help mitigate GHG emissions and improve the N fertilization efficiency. The objective of this research was to investigate the effects of different sources (urea, ammonium sulfate and ammonium nitrate) applied in a unique and parceled way, and doses (0, 90, 180 and 270 kg ha^{-1} $year^{-1}$) of N, in the CO_2, N_2O, and CH_4 fluxes, in the ammonia (NH_3) volatilization and in the forage production and chemical characteristics in pasture of *U. brizantha* cv Marandu grass. The capture of N lost as NH_3 volatilized was performed according to the semi-open chamber technique. For forage evaluation, plots of 3x4 m were managed in a cutting regime at a canopy height of 30 cm and stubble height of 15 cm and the chemical analysis of crude protein (CP), neutral detergent fiber (NDF) and acid detergent fiber (ADF) were performed. Greenhouse gases emissions were measured using closed static chambers and gas analysis performed by gas chromatography. Ammonia volatilization from nitrate and ammonium were lower than urea, and parceled fertilization reduced on average 47% N losses. Nitrogen fertilizer linearly increased forage accumulation (232, 264, 285, and 304 kg ha^{-1} day^{-1} at doses of 0, 90, 180, and 270 kg ha^{-1} $year^{-1}$, respectively. The contents of CP and NDF were significantly affected by increasing doses of N, with linear effect of the two variables. The emission factors (EF) of NH_3 were 20.69, 3.70, and 2.82% for urea, nitrate, and ammonium sulfate, respectively, differing from the default value estimated by the IPCC. Soil N_2O, CH_4, and CO_2 fluxes did not vary as a function of N sources and doses. The GHG fluxes differed depending on climatic conditions and the main determinant variables controlling emissions were water filled pore spaces (%WFPS), temperature, and (amoniacal N) NH_4-N content. The EF of N_2O were 0.35, 0.24, and 0.21% in urea, nitrate and ammonium sulfate fertilizers when fertilization was applied in split doses, differing from the IPCC standard EF. Environmental conditions directly impacted plant and gas responses. The use of alternative sources to urea can decrease N losses by NH_3 volatilization and increase forage accumulation, while split fertilization, besides decreasing NH_3 losses, reduces N_2O emissions, proving to be an alternative for GHG mitigation.

Keywords: Nitrogen fertilizers, marandu grass, volatilization, N_2O, emission factor, greenhouse gases.

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1. INTRODUÇÃO

Devido ao aumento da população global e consequente demanda por mais alimentos, os sistemas de produção de ruminantes estão em constante intensificação, visando aumentar a eficiência na exploração das áreas de pastagens e o aumento do lucro. Desta forma, as diferentes práticas de manejo adotadas interferem direta e indiretamente nos fluxos de gases de efeito estufa (GEE). O setor agropecuário é responsável por 31,3% das emissões de GEE no Brasil, sendo responsável por 61% e 82% das emissões totais brasileiras de óxido nitroso (N_2O) e metano (CH_4), respectivamente (MCTI, 2017).

Na intensificação dos sistemas de produção pecuária, a combinação do uso de tecnologias, como a melhoria das técnicas de manejo do pasto e do incremento na suplementação alimentar dos rebanhos, tem potencial para melhorar a produtividade animal e das pastagens, sendo possível contribuir para mitigação das emissões de GEE. Neste cenário, a produção forrageira tem importância fundamental, e a fertilização nitrogenada é uma das práticas utilizadas para maximizar as produções de forragem e melhorar sua qualidade (DUPAS et al., 2016).

A importação de fertilizantes pelo Brasil tem aumentado consideravelmente. De acordo com a Food and Agriculture Organization (FAO), atualmente o país é o quarto no ranking dos maiores consumidores de fertilizantes sintéticos do mundo, sobretudo de fertilizantes nitrogenados sendo que o aumento desta utilização está vinculado diretamente a crescente fertilização de pastagens (PIRES et al., 2015; TIRITAN et al., 2016). Ao passo que a fertilização com nitrogênio (N) melhora as características produtivas e químicas da forragem, o aumento deposição de N também tem impacto nas perdas de N para o sistema e nos fluxos de GEE do solo (HOFMAN e CLEEMPUT, 2004; JONES et al., 2005).

A fertilização nitrogenada, especialmente com ureia, provoca perdas principalmente por volatilização de amônia (NH_3) e emissões de N_2O, resultando em menor eficiência de uso de N e maiores preocupações ambientais (HARRISON e WEBB, 2001; RAIJ, 2017). Nessa perspectiva, o emprego de fertilizantes que ocasionem menores perdas é uma estratégia capaz de aumentar a eficiência de utilização do N pelas plantas e diminuir as emissões de GEE (LIU et al., 2017).

São amplos os estudos avaliando o efeito da deposição de N em diferentes ecossistemas, contudo, o impacto da deposição de N na produção e/ou consumo de GEE e nas perdas por volatilização de amônia em pastagens não é bem compreendido, e pesquisas que reportam os fluxos de gases do solo e características da forragem em função de diferentes fertilizantes ainda não foram realizadas em pastagens tropicais.

As hipóteses desta pesquisa são: i) as emissões de GEE são diferentes entre os fertilizantes nitrogenados e aumentam conforme a elevação da dose ii) as menores perdas de N por volatilização são verificadas nos fertilizantes com N na forma amoniacal e nítrica; iii) o aumento na dose de N aumenta a produção e melhora a composição química da forragem; iv) existe variação nos fluxos de gases de acordo com as condições climáticas da região.

Em função das hipóteses apresentadas os dois objetivos principais desta Tese são: i) Quantificar as emissões de gases de efeito estufa (CO_2, CH_4 e N_2O) e a volatilização de N-NH_3 do solo em pastos de *Urochloa brizantha* cv marandu sob fertilização nitrogenada em diferentes condições climáticas ii) Avaliar o efeito das diferentes fertilizações no acúmulo e na composição química da forragem.

2. REVISÃO DE LITERATURA

2.1 Pecuária e pastagens de gramíneas tropicais

O setor agropecuário tem destaque no cenário econômico nacional, e em 2017 contribuiu com 23,5% do Produto Interno Bruto (PIB), com um Valor Bruto da Produção Agropecuária (VBP) de R$ 548 bilhões, o maior dos últimos 30 anos (MAPA, 2017). De acordo com o censo agropecuário de 2017, a área de todos os estabelecimentos agropecuários no Brasil é de 350.253.329 ha, dos quais 158.622.704 ha são ocupados por pastagens, cerca de 19% do território nacional, com um efetivo bovino de 172 milhões de cabeças (IBGE, 2018).

Quase a totalidade deste rebanho é criado em pastagens, que é uma característica importante da pecuária brasileira, definida pelas boas condições climáticas para a produção vegetal e a vasta extensão de terras do país (FERRAZ e FELÍCIO, 2010). Contudo, estima-se que entre 54% das áreas de pastagens brasileiras apresentam algum grau de degradação (LAPING, 2018), que em termos globais é ocasionada pelo manejo inadequado, em particular o uso sistemático de altas taxas de lotação, que excedem a capacidade do pasto de se recuperar e ausência de fertilizações periódicas (DIAS-FILHO, 2014).

Gramíneas forrageiras representarem a forma mais econômica de alimentação de ruminantes e são amplamente utilizadas. No entanto, o seu potencial produtivo ainda não é adequadamente explorado, devido à baixa eficiência de uso da forragem, que se relaciona diretamente com a ausência ou insuficiência do atendimento das exigências nutricionais das plantas (DUPAS et al., 2016). Nesse contexto, iniciou-se a busca por sistemas pastoris mais produtivos, aplicando-se o conceito de manejo sustentável das pastagens, visando a otimização da produção e conservação do meio ambiente (VASQUES et al., 2019).

Para que o sistema de produção agropecuário seja sustentável, é necessário como primeiro pré-requisito que a produção total de nutrientes minerais exportados em produtos úteis, ou perdidos para o meio ambiente, não exceda sua entrada. Este é um ponto crucial a ser considerado visto que as pastagens utilizadas, principalmente para produção de bovinos de corte, caracterizam-se pela baixa exportação de nutrientes em produtos de origem animal (BODDEY et al., 2004). Dessa forma, a fertilização tem potencial para melhorar a produção animal em pastagens, bem como os demais sistemas agrícolas (FORRESTAL et al., 2016).

As gramíneas dos gêneros *Urochloa (*Syn*. Brachiaria), Megathyrsus (*Syn*. Panicum), Pennisetum* e *Cynodon* são as mais utilizadas na formação de pastagens no Brasil, cada espécie pertencente a estes gêneros apresenta particularidades em suas características morfológicas, de manejo e de tipo de solo ideal para cultivo (CORRÊA e SANTOS, 2003). De acordo com Zimmer et al. (2012), o gênero *Urochloa* ocupa 70% das áreas de pastagens no país, dentre estas, 90% são formadas pelas espécies *U. brizantha* (principalmente as cultivares Marandu, Xaraés e BRS Piatã) e *U. decumbens* (com predominância da cultivar Basilisk).

2.2 *Urochloa brizantha* cv Marandu

A *Urochloa brizantha* (Hochst. ex A. Rich.) Webster (Syn. *Brachiaria brizantha* (Hochst. ex A. Rich.) é a espécie destaque entre as gramíneas forrageiras e a cultivar Marandu popularmente conhecida como capim-marandu é a mais utilizada nas pastagens (COSTA et al., 2006). Esta cultivar foi lançada pelo Centro Nacional de Pesquisa do Gado de Corte (CNPGC-EMBRAPA, MS), e posteriormente estudada pelo Centro Nacional de Pesquisa Agropecuária dos Cerrados (CNPAC-EMBRAPA, DF), entre os anos de 1983 e 1984. Originária da África tropical e África do Sul, o nome “marandu” significa na língua Tupi Guarani “novidade”, e foi introduzida no mercado pela Empresa Brasileira de Pesquisa em Agropecuária (EMBRAPA) como uma opção para a região dos Cerrados devido à tolerância a solos ácidos (COSTA et al., 2006).

Estudos iniciais sobre esta cultivar na região resultaram em valores de proteína bruta (PB) entre 10 – 11% e produção entre 8 – 20 t MS ha^{-1} ano^{-1}, com fertilizações variando entre 0 a 400 kg N ha^{-1} (NUNES et al., 1985). Atualmente, em pastagens fertilizadas, tem sido relatados teores de PB de até 16% em pastos fertilizados com 270 kg N ha^{-1} ano^{-1} (DELEVATTI et al., 2019) e produções entre 16 e 17 t MS ha^{-1} ano^{-1} com fertilizações com 100 kg N ha^{-1} $corte^{-1}$ (DUPAS et al., 2016).

O capim-marandu responde a fertilização nitrogenada, com efeitos positivos na maior parte das características da planta, como aumentos lineares no acúmulo de massa de forragem e dos teores de PB (GIMENES et al., 2011; SILVEIRA et al., 2013). Em trabalho avaliando o capim-marandu fertilizado com doses de 0, 50, 150 e 200 kg N ha^{-1}, Dupas et al. (2010), reportou que a os teores de fibra da forragem diminuíram com as doses de N. Os autores relataram ainda variações nos teores de PB entre 7 e 14%, fibra em detergente neutro (FDN) de 65 e 61% e fibra em detergente ácido (FDA) de 36 e 34% nas doses 0 e 200 kg N, respectivamente, com o capim sendo manejado em intervalo de cortes fixos e altura de resíduo de 15 cm.

A cultivar Marandu agrega adaptabilidade à diferentes condições de solo e clima, tem grande flexibilidade de uso e manejo e alta produção de forragem. Além disso, apresentam poucos problemas com pragas (como a cigarrinha das pastagens) e doenças, sendo de fácil estabelecimento e alta persistência no período seco em comparação a outras cultivares. Essas características despertaram o interesse dos pecuaristas nos diferentes sistemas de criação fazendo com que o capim-marandu se expandisse rapidamente por todo país (COSTA et al., 2006; ZIMMER et al., 2012).

2.3 Respostas das gramíneas forrageiras ao nitrogênio

O N tem um papel fundamental no processo produtivo da pastagem, e geralmente o seu suprimento natural no solo não atende a demanda de gramíneas com alto potencial produtivo, assim, fertilizações nitrogenadas tem impacto direto no aumento da produtividade e na melhoria das características químicas da forragem (DUPAS et al., 2016; MARQUES et al., 2017; McROBERTS et al., 2017).

Diversos compostos orgânicos essenciais às plantas são constituídos por N, como as proteínas, aminoácidos, hormônios, clorofila e ácidos nucleicos. As principais formas de N inorgânico absorvidas pelas plantas são o nitrato (NO_3^-) e amônio (NH_4^+), e a maior absorção de uma forma em relação à outra está relacionada a variação de pH do meio (HOLFMAN e CLEEMPUT, 2004).

No solo, o N está sujeito a inúmeros processos que resultam em transformações de formas orgânicas em inorgânicas, e a dinâmica desses processos poderão resultar em ganhos ou perdas no sistema como um todo (Figura 1). O balanço da quantidade de N mineral no solo pode ser descrito conforme a equação abaixo (DI e CAMERON, 2002):

$$N = Np + Nb + Nf + Nu + Nm - Npl - Ng - Ni - Nl – Ne$$

Onde: onde Np é a deposição atmosférica, Nb é a fixação biológica do N_2, Nf é o N aplicado pelo fertilizante, Nu é o retorno do N ao solo via urina e fezes, Nm é a mineralização do N orgânico, Npl é a absorção pela planta, Ng é a perda de formas gasosas de N, Ni é a imobilização do N pelos micro-organismos, Nl é a perda do NO_3^- por lixiviação e, Ne é a perda por erosão e escorrimento superficial.

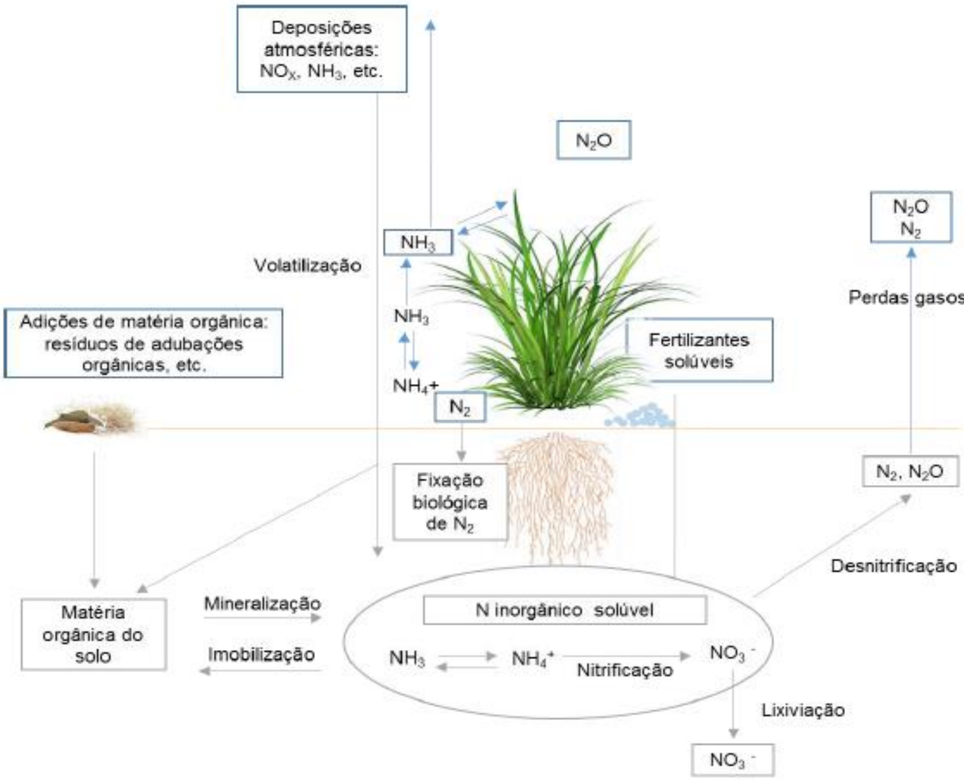

Figura 1: Ciclo do nitrogênio no sistema solo-planta-atmosfera. Adaptado de Cantarella por Pinheiro (2018).

Os processos de deposição de N, juntamente com a matéria orgânica (MO) natural do solo, fertilizações orgânicas e ciclagem de nutrientes dos resíduos vegetais podem suprir quantidades significativas de N para as culturas, contudo, com o aumento da produtividade dos cultivos a necessidade de aporte de N pelas plantas aumenta, exigindo a adição de fertilizantes nitrogenados (RAIJ, 2017).

Estudos revelaram que o aumento das doses de N promove incremento significativo na produção de forragem, e afeta positivamente as características morfogênicas e estruturais das plantas, com aumento do perfilhamento, taxa de aparecimento foliar e alongamento de folha (SANTOS et al., 2018; CARVALHO et al., 2019; RODRIGUES et al., 2019). De acordo com Lima et al. (2016), a produção de massa seca do capim-marandu pode variar de 1631 a 3096 kg MS ha^{-1} $corte^{-1}$ em pastagens não fertilizadas e fertilizadas com 300 kg N ha^{-1} ano^{-1}, respectivamente, enquanto a proporção de folhas pode aumentar linearmente com a fertilização (LOPES et al., 2017).

Além do acúmulo de forragem, o valor nutritivo (VN) das plantas forrageiras é, sem dúvida, um dos fatores mais importantes relacionados com a produção animal. Uma característica utilizada para estimar o VN das gramíneas é a composição química, que é afetada por fatores como idade da planta, nutrientes disponíveis no solo e condições climáticas (LEAL et al., 2017).

Entre os componentes que mais interferem no VN estão os teores de PB, carboidratos fibrosos e não fibrosos, e a digestibilidade das diferentes frações, de forma que, o conhecimento destas podem auxiliar na identificação da disponibilidade de nutrientes para os animais, visto que as suas quantidades resultam em diferentes produtos do processo digestivos dos ruminantes (LEAL et al., 2017).

Forrageiras tropicais sem melhoramento genético apresentam baixos valores de PB, que também é ocasionada pelo uso de técnicas de manejo inadequadas. A fertilização com N é uma ferramenta eficiente para aumentar os conteúdos de PB na maioria das espécies de gramíneas forrageiras, como relatado por Dupas et al. (2016). Os autores obtiveram média de 10% de PB em pastos sem fertilização e de 15% de PB em pastos fertilizados com nitrato de amônio enquanto Delevatti et al. (2019) obtiveram média de 11% de PB sem fertilização e de 17% de PB no tratamento fertilizado com 270 kg N ha^{-1} ano^{-1} na forma de ureia.

Com a inovação tecnológica no processo de fabricação de fertilizantes, tornou-se possível modificar a forma com que o nitrogênio estará disponível na solução do solo, e adicionalmente interferir no melhor aproveitamento pelas plantas e nos processos relacionados às perdas de N (CANTARELLA, 2007). Por conseguinte, as quantidades de $N\text{-}NO_3^-$, $N\text{-}NH_4^+$ e a proporção deles pode interferir na recuperação do N aplicado (RNA), a eficiência do uso de N (EUN), no rendimento de matéria seca (RMS) e composição química dos pastos (SILVA et al., 2011; SALES et al., 2014). Segundo Dupas et al. (2016), a RNA no sulfato de amônio e no sulfato-nitrato de amônio, por exemplo, é maior do que nos fertilizantes a base de ureia, isto porque a perda de N pela volatilização dos sais de amônio é menor que da ureia.

2.4 Fertilizantes nitrogenados

A busca por fertilizantes que apresentem melhor eficiência de uso, menores impactos ambientais e que promovam altas produções de forragem associadas a melhor composição química e características morfológicas e estruturais da planta tem sido cada vez maior.

O consumo total mundial de fertilizantes atingiu 181,9 milhões de toneladas métricas (Mt) de nutrientes em 2014/2015, dos quais 102,5 Mt N, 45,9 Mt P_2O_5 e 33,5 Mt K_2O. Estima-se que desse total, 4,7% dos fertilizantes nitrogenados destinaram-se a aplicação em pastagens, contudo, este valor provavelmente é subestimado devido à falta de informações em alguns países, de acordo com o International Fertilizer Association e o International Plant Nutrition Institute (IFA e IPNI, 2017).

O Brasil é o quarto maior importador de matéria-prima para a produção de fertilizantes nitrogenados do mundo. Segundo a FAO, o consumo de ureia na agricultura brasileira entre 2002 e 2017 cresceu 162%, e do total de 5 milhões de toneladas consumidas em 2017, 4,6 milhões de toneladas foram importadas. Segundo as projeções da organização, até 2021 este consumo será de 8 milhões de toneladas, e o país continuará dependente das importações para suprir o abastecimento interno de ureia, fosfato e potássio.

Todo o processo de fabricação dos fertilizantes nitrogenados utiliza inicialmente amônia anidra, fabricada a partir de ar e gás natural pelo processo de Haber-Bosch, sob alta temperatura, através da reação da reação química (VIEIRA, 2017):

$$[3H_2 + N_2 \rightarrow 2NH_3]$$

Esse processo foi desenvolvido na Alemanha alguns anos antes da 1ª Guerra Mundial e é considerado um dos grandes avanços tecnológicos do século XX. E a partir desse método, foi possível obter-se uma variedade de formulação de fertilizantes, com diferentes propriedades e finalidades de uso mais adequados a cada tipo de sistema de produção agrícola (VIEIRA, 2017).

Os principais fertilizantes nitrogenados minerais consumidos no mundo são: ureia, sulfato de amônio, nitrato de amônio, fosfato monoamônio (MAP), nitrocálcio, amônia anidra, aquamônia, uran, fosfato diamônio (DAP), nitrato de sódio, nitrato de cálcio e nitrofosfatos. No Brasil, entre os fertilizantes de N mais utilizadas, estão a ureia (44 a 46% N), o sulfato de amônio (20 a 21% N) e o nitrato de amônio (32 a 33% N) (COSTA et al., 2006).

A ureia é um produto derivado de amônia (NH_3), formado pela reação com o CO_2 em alta pressão, ela é predominantemente usada como fertilizante direto, mas também pode compor outros fertilizantes como o NPK (nitrogênio – fósforo

– potássio), além disso, também é utilizada em vários segmentos industriais. Esta fonte é a mais utilizada por ser mais vantajosa do ponto de vista econômico, com menor custo por kg de N, menor custo de transporte, estocagem e aplicação por unidade de N, sendo também de fácil manipulação (REETZ, 2016).

A ureia apresenta desvantagens, como a elevada higroscopicidade, possibilidade de perdas por lixiviação devido a sua alta solubilidade, elevadas perdas por volatilização de N-NH_3 por possuir N na forma amídica e alta atividade de urease, passando pelo processo de hidrólise enzimática e liberando NH_3, e potencial perda por desnitrificação resultando em menor eficiência de uso do N (HARRISON e WEBB, 2001; RAIJ, 2017).

A segunda fonte mais utilizada no país é o sulfato de amônio, este fertilizante é obtido principalmente como subproduto de várias indústrias, mas também pode ser obtido pela reação de NH_3 com ácido sulfúrico; esta fonte além de fornecer N (23%) também é uma fonte de enxofre (S, 23%) (REETZ, 2016).

O sulfato de amônio possui baixa higroscopicidade e boas propriedades físicas, caracteriza-se por acidificar o solo em comparação a ureia, e comparativamente, reduzir as perdas por volatilização de NH_3 (DELBEM et al., 2011; CORRÊA et al., 2018). Além disso, a fertilização com sulfato de amônio é recomendada para cultivo de *U. brizantha* cv Marandu e espécies semelhantes, pois aumenta a absorção de N e S pela planta, melhora o crescimento da gramímea, o VN e o rendimento de matéria seca (DE BONA et al., 2013). Esses dois nutrientes são limitantes na biossíntese de proteínas, a capitação e a assimilação deles depende da relação N:S no tecido da planta e das formas de N disponíveis no solo (DE BONA et al., 2011).

Apesar das vantagens no uso do sulfato de amônio na fertilização das pastagens, o maior custo por kg de N em comparação a outras fertilizantes, como ureia e nitrato de amônio, e por não possuir comumente o produto em forma granulada, limitam sua adoção pelos pecuaristas (CABRAL et al., 2016; CANTARELLA, 2007).

O nitrato de amônio é um produto à base de NH_3 obtido pela reação com ácido nítrico. É uma fonte eficiente de N, possui metade na forma amoniacal, que pode ser absorvida diretamente pelas raízes ou gradualmente convertido em NO_3^- pelos micro-organismos do solo, fornecendo uma liberação mais lenta de

N; e a outra metade na forma nítrica, a qual fica imediatamente disponível para as plantas, podendo ser rapidamente absorvido pela planta com menores perdas por volatilização. Além disso, a alta solubilidade desse fertilizante torna-o eficiente para aplicação foliar por meio da fertirrigação (REETZ, 2016).

O nitrato de amônio possui teor de N relativamente alto (32 a 33% N), e geralmente acidifica menos o solo comparado com ao sulfato de amônio, por fornecer menos NH_4^+, o qual durante o processo de nitrificação reduziria o pH (PROCHNOW e ABDALLA, 2007). Contudo, o nitrato de amônio pode ser fabricado como um produto de baixa densidade para ser usado em segmentos industriais, essencialmente como explosivos, havendo assim dificuldade no comércio, transporte e armazenamento (IFA). Além disso, existe uma série de regras básicas de segurança para o manuseio em grandes quantidades, como não superaquecer e assegurar-se de que os materiais em contato são compatíveis (PROCHNOW e ABDALLA, 2007).

A fertilização de pastagens com nitrato de amônio até pouco tempo atrás era uma prática pouco realizada no Brasil. As pesquisas que utilizaram esta fonte de fertilizante mostraram aumento no acúmulo de matéria seca, maior recuperação no N aplicado e absorção de nutrientes e elevação do valor nutritivo da forragem (DE BONA et al., 2013; DUPAS et al., 2016).

2.5 Os gases de efeito estufa e a pecuária

Os gases de efeito estufa de vida longa mais importantes são o metano (CH_4), o dióxido de carbono (CO_2) e o óxido nitroso (N_2O) estes gases juntamente com o CFC-12 e o CFC-11 respondem por aproximadamente 96% do forçamento radiativo devido a GEE de vida longa. De acordo com o último boletim do Programa WMO, em 2018 as concentrações desses gases atingiram novos picos, com CO_2 a 407,8 ± 0,1 ppm, CH_4 a 1869 ± 2 ppb e N_2O a 331,1 ± 0,1 ppb. Esses valores representam, respectivamente, 147%, 259% e 123% dos níveis pré-industriais (WMO, 2019).

O aumento das emissões dos principais GEE tem causado preocupação e estimulado o desenvolvimento de pesquisas que visam avaliar em vários ecossistemas a forma com que as atividades antropogênicas interferem na grandeza das emissões desses gases para a atmosfera (BENTO et al., 2018), com o objetivo de reduzir as incertezas do efeito de diferentes práticas de manejo, e avaliar as opções potenciais de mitigação dos GEE.

A agricultura e a pecuária contribuem significativamente para as emissões de GEE devido às práticas frequentemente realizadas alterarem os principais processos biogeoquímicos que regulam a dinâmica do carbono (C) e do N nos solos (BENTO et al., 2018). No Brasil, estudos recentes sobre a intensificação do manejo de pastagens levantaram questões importantes em relação aos fluxos de GEE no setor pecuário.

De acordo com Cardoso et al. (2017), o aumento da intensidade de pastejo pode reduzir linearmente as emissões acumuladas de N_2O e aumentar linearmente as emissões acumuladas de CO_2. Da mesma forma, a recuperação de pastagens e a manutenção do potencial produtivo podem mitigar as emissões de GEE por meio do sequestro CO_2 atmosférico e conservação desse C no solo, possibilitando a pecuária ser uma atividade economicamente mais rentável e ambientalmente mais eficiente (ANDRADE et al., 2016; ANDRADE et al., 2017).

Dióxido de Carbono

O CO_2 é o GEE antropogênico mais importante na atmosfera, contribuindo com aproximadamente 66% do forçamento radiativo por GEE de vida longa. Este gás é responsável por cerca de 82% do aumento da força radiativa na última década e cerca de 81% do aumento nos últimos cinco anos (WMO, 2019).

O C está em três grandes compartimentos, na atmosfera, nos oceanos e nos sistemas terrestres. O ciclo do C pode ser dividido em três fases: fase anabólica do CO_2 atmosférico, realizada, principalmente, pelos vegetais fotossintetizantes: fase de liberação dos produtos fotossintetizados e de acumulação e estabilização no solo; e a fase de mineralização de substratos orgânicos e de transferência do CO_2 (produto da decomposição dos resíduos do solo à atmosfera) (MOREIRA e SIQUEIRA, 2006). A maior parte da segunda e da terceira fase ocorre no solo, constituindo o ciclo interno do C, onde a biomassa microbiana tem importância central, por controlar a maior parte das reações desse ciclo e equilibrar a entrada e a saída de C por meio da respiração edáfica (PULROLNIK, 2009).

A fertilização nitrogenada e a recuperação das pastagens, por exemplo, aumentam a eficiência do sequestro de C no solo, em função do aumento na cobertura vegetal, maior incorporação de resíduos agrícolas, e aumento no teor de MO no solo (GURGEL e COSTA, 2015). Nesse sentido, as pastagens apresentam potencial para mitigar as emissões de GEE, por meio da redução nas concentrações atmosféricas de CO_2. No Bioma Cerrado, estudos comprovam que pastagens bem manejadas e fertilizadas com N apresentam alto potencial para sequestrar CO_2 (ANDRADE et al., 2017; CARDOSO et al., 2017).

Metano

O CH_4 contribui com cerca de 17% da força radiativa dos GEE de vida longa, sendo que, aproximadamente 40% do CH_4 é emitido para a atmosfera por fertilizantes naturais (por exemplo, áreas alagadas) e cerca de 60% é proveniente de fertilizantes antropogênicas (por exemplo, pecuária, cultivo de arroz, exploração de combustíveis fósseis, aterros e queima de biomassa) (WMO, 2019).

Em 2018, a média global da concentração de CH_4 calculada a partir de observações *in situ* atingiu uma nova alta, aumento de 10 ppb em relação ao ano anterior, sendo superior ao aumento de 7 ppb no período de 2016 a 2017 e ao aumento médio anual na última década (WMO, 2019). Em 2015, 82% e 61% das emissões totais de CH_4 e N_2O do Brasil, respectivamente, foram atribuídas à atividade pecuária (MCTI, 2017).

No solo, o CH_4 é produzido pela decomposição anaeróbia da MO, promovida por *Archeas* metanogênicas. Essa matéria orgânica, primeiramente, é decomposta por processos aeróbicos e depois é atacada anaerobicamente por bactérias não-metanogênicas, formando compostos mais simples como celulose, aminoácidos, açúcares e óleos. Essas substâncias simples são quebradas em pequena cadeia de compostos orgânicos que formam os substratos para as *Archeas* metanogênicas (CARDOSO et al., 2001; KREUZER e HINDRICHEN, 2006).

O solo pode atuar como fonte ou dreno de CH_4, dependendo da comunidade bacteriana presente, sendo esta dependente de diversos fatores ambientais, principalmente da drenagem e do tipo de solo (McDONALD et al., 2008). Além dos aspectos edafoclimáticos, diferentes manejos, como a fertilização nitrogenada pode afetar processos importantes envolvidos no orçamento e emissões de CH_4 em pastagens, isto é, metanogênese, oxidação de CH_4, mineralização e nitrificação (BODELIER et al., 2000).

A fertilização com N pode promover altas oscilações nos fluxos de CH_4

logo após sua aplicação (ZANATTA et al., 2010), correlacionando-se principalmente com o conteúdo de N-mineral do solo, devido ao efeito inibitório do $N\text{-}NH_4^+$ no processo de metanotrofia, responsável pela oxidação do CH_4 no solo (HÜSTCH, 1998; HÜTSCH, 2001). Por outro lado, devido os fluxos de CH_4 dependerem das condições de solo e clima locais, a deposição de N através de fertilizantes sintéticos pode não ter efeito sobre os fluxos desse gás, sendo que emissões de CH_4 estão mais relacionadas as características do solo (CARDOSO et al., 2018).

Óxido nitroso

O óxido nitroso (N_2O) contribui com cerca de 6% do forçamento radiativo pelos GEE de vida longa, sendo o terceiro gás mais importante do forçamento combinado. O N_2O é emitido na atmosfera a partir de fertilizantes naturais (cerca de 60%) e antropogênicas (aproximadamente 40%), incluindo oceanos, solos, queima de biomassa, uso de fertilizantes e vários processos industriais (WMO, 2019).

De acordo com Firestone e Davidson (1989), o N_2O é produzido nos solos por meio dos processos de nitrificação (oxidação de NH_4^+ a NO_3^-) e desnitrificação (redução de NO_3^- ao N_2), sendo o N_2O produto intermediário em ambos os processos. A desnitrificação é realizada por diversos gêneros de bactérias heterotróficas anaeróbicas facultativas e ocorre em condições anaeróbicas, enquanto, a nitrificação é realizada por bactérias autotróficas e dependem de sítios contendo oxigênio no solo, e estes processos são influenciados pela temperatura do solo, umidade, pH, disponibilidade de matéria orgânica solúvel e concentração de N-mineral (BOUWMAN, 1990; DOBBIE et al., 1999).

Na produção em pastagens, a principal causa do aumento nas emissões de N_2O é a utilização de fertilizantes nitrogenados; a aplicação de N estimula a produção de N_2O e NO (óxido nítrico), principalmente através dos processos bioquímicos de nitrificação (aeróbia) e desnitrificação (CONRAD, 1983; DAVIDSON, 1991). Neste processo, o N não absorvido pela planta ou imobilizado no solo pode ser volatilizado na forma de NOx e NH_3, e outra parte pode ser emitida na forma de N_2O (BUTTERBACH-BAHL et al., 2013).

O fator de emissão (FE) de N_2O induzido pelos fertilizantes estabelecidos pelo painel de especialistas do IPCC (2019) é de 1,1%, 2,9% e 0,7% do N aplicado via fertilizantes ureia, nitrato de amônio e sulfato de amônio, respectivamente. Embora, na ausência de medidas específicas, essa abordagem metodológica seja útil para estimar as emissões, o uso de dados padrão, principalmente utilizando FE de outros países, pode levar a grandes erros no inventário de GEE. Pesquisas realizadas no Brasil evidenciaram que o FE direta do IPCC, é superior às condições da agropecuária brasileira, sendo de extrema necessidade a utilização de dados específicos regionais para calcular os FE (JANTALIA et al., 2008; OLIVEIRA et al., 2008; CARDOSO et al., 2017).

Os principais fatores edafoclimáticos que afetam a produção do N_2O, CH_4 e CO_2 no solo são: umidade e textura do solo (TELLES et al., 2003), temperatura (VIEIRA, 2017), pH (SAGGAR et al., 2013), teores de N, quantidade de oxigênio (COSTA, 2006; MORLEY et al., 2008) e C solúvel e prontamente decomponível (HENRY et al., 2008). O aumento na concentração de N no solo proporcionada pela fertilização, podem estimular o processo de desnitrificação por aumentar o conteúdo de NO_3^- no solo, assim como elevar o estoque de MO no solo aumentando os teores de C, o que também interfere na atividade das *Archeas* metanogênicas e fluxos de CH_4 (GURGEL e COSTA 2015; VIEIRA, 2017).

2.6 Volatilização de amônia por fertilizantes nitrogenados

Grande quantidade de NH_3 pode ser perdida do solo após a aplicação de fertilizantes nitrogenados nos sistemas agrícolas, essas perdas podem atingir valores próximos a 50% do N aplicado (TASCA et al., 2011; STAFANATO et al., 2013). As perdas por volatilização de NH_3 podem variar de acordo com as práticas de manejo, quantidade de N aplicado, cultura e condições ambientais locais (VIEIRA, 2017).

No Suldeste do Brasil, Cardoso et al. (2019) obtiveram FE NH_3 de 16,9% na ureia (80 kg N ha^{-1}) aplicada em pastos de capim-marandu, enquanto Meirelles et al. (2017) registraram perdas que 12,5 e 17,9% em pastos de *U. decumbens* fertilizados com a mesma fonte nas doses de 100 e 200 kg N ha^{-1} ano^{-1}, respectivamente. Nascimento et al. (2013) registraram perdas de 10% em cultivo de cana de açúcar fertilizado com ureia. O autor explicou que as menores perdas ocorreram em função da alta precipitação (50 mm) nos primeiros dias após a fertilização.

A volatilização de NH_3 é considerada como a principal responsável na baixa eficiência do uso dos fertilizantes nitrogenados em sistemas agrícolas, especialmente na utilização da ureia (HARRISON e WEBB, 2001).

Volatilização é o processo de perda de N na forma gasosa, que são predominantemente na forma de amônia [$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$)], mas também nas formas de N_2, NO e N_2O, como relatado anteriormente. De acordo com Sommer et al. (2004) a volatilização da NH_3 é um processo físico influenciado pela concentração total de N amoniacal na solução do solo (N-NH_3 + N-NH_4) e pela resistência do NH_3 ao movimento da matriz do solo. A emissão da forma gasosa de NH_3 no solo ocorre conforme a equação:

$$NH_4^+ \leftrightarrow NH_3 \uparrow + H^+$$

A volatilização é uma reação química que ocorre predominantemente em condições alcalinas, sendo influenciada principalmente por fatores de clima e de solo, como pH, textura, umidade, temperatura, fertilizantes de N, capacidade de troca de cátions (CTC) e tipo de solo (HARRISON e WEBB, 2001; BOLAN et al., 2004).

As perdas de N por volatilização de NH_3 podem ser potencializadas em função da presença de resíduos vegetais na superfície do solo, que atuam como barreira física entre o fertilizante e o solo, diminuindo a adsorção N-NH_3 (produto da hidrólise) aos colóides orgânicos e inorgânicos, facilitando sua volatilização (CANTARELLA et al., 2008). Dessa forma, a fertilização de cobertura nas pastagens pode aumentar volatilização de N-NH_3, em função da menor incorporação do fertilizante ao solo (SU et al., 2014). Portanto, o parcelamento da fertilização é considerado com uma estratégia para reduzir essas perdas, o qual irá diminuir a quantidade de NH_4^+ disponível no solo (TIMILSENA et al., 2015).

O aumento nas emissões de N-NH_3 pode provocar efeitos adversos no ambiente e na saúde pública. Embora não seja considerado um GEE, suas transformações na biosfera podem contribuir para o aquecimento global, por atuar como fonte secundária de N_2O e por reagir com óxidos de enxofre formando sulfato de amônio, que por meio da chuva pode causar acidificação do solo (VIEIRA, 2017).

Enquanto o fator padrão do IPCC (2019) para a volatilização de N-NH_3 é de 14,2%, 3,0% e 9,5% da quantidade de N aplicado ao solo via fertilizantes ureia, nitrato de amônio e sulfato de amônio, respectivamente, há uma grande incerteza quanto a estes FE para regiões tropicais, já que a maioria dos FE foram desenvolvidos a partir de estudos em regiões de clima temperado, havendo poucos estudos que compararam a magnitude das emissões de NH_3 associadas a diferentes fertilizantes nitrogenados em pastagens (de Morais et al., 2013; Cardoso et al., 2020; Longhini et al., 2021). Consequentemente, preocupações foram levantadas sobre o mérito econômico do uso de ureia em comparação com outras fertilizantes de N (ECKARD et al., 2003).

Além do parcelamento da fertilização, práticas como a incorporação dos fertilizantes ao solo, aplicação nas épocas chuvosas, utilização de fertilizantes de eficiência aumentada, utilização de fertilizantes com características ácidas e/ou neutras, e a manipulação da dieta dos animais visando diminuir o N depositado via urina e fezes, são utilizadas como estratégias para reduzir as perdas de N por volatilização NH_3 (VIEIRA, 2017).

Em estudo avaliando a volatilização de NH_3 de fertilizantes amídicos, amoniacais e orgânicos, Ribeiro et al. (2016), observaram que o parcelamento da fertilização promoveu redução nas perdas de N-NH_3 em todas os fertilizantes. Enquanto, menores volatilizações foram relatadas em fertilizantes amoniacais e nítricos, em função das diferenças de pH em relação a ureia, que permitem que o íon amônio permaneça na forma iônica NH_4^+ não sendo convertido em NH_3 (DELBEM et al., 2011; SOUZA et al., 2017; MEIRELLES et al., 2017).

Para se reduzir perdas por volatilização do N e aumentar eficiência da fertilização nitrogenada, são necessários avanços nos estudos com fertilizantes quanto ao tipo, a quantidade aplicada, o tempo e forma de aplicação, parâmetros que têm implicações diretas nas perdas de N. Portanto, além do estudo em diferentes regiões e épocas do ano, a seleção adequada do tipo de N aplicado deve ser avaliada para estimar o FE mais correto e buscar alternativas de manejo para reduzir as perdas de N, e mitigar a emissão de GEE.

3. REFERÊNCIAS

Andrade RG, Bolfe ÉL, Victoria DC, Nogueira SF (2016) Recuperação de pastagens no cerrado. **AgroAnalysis** 36:30-32.

Bento CB, Filoso, S, Pitombo LM, Cantarella H, Rossetto R, Martinelli LA, do Carmo JB. Impacts of sugarcane agriculture expansion over low-intensity cattle ranch pasture in Brazil on greenhouse gases (2018) **Journal of environmental management** 206:980-988.

Boddey RM, Macedo R, Tarré RM, Ferreira E, de Oliveira OC, Rezende DP, Cantarutti RB, Pereira JM, Alves BJR, Urquiaga S (2004) Nitrogen cycling in *Brachiaria* pastures: the key to understanding the process of pasture decline. **Agriculture, Ecosystems & Environment** 103:389-403.

Bodelier PL, Hahn AP, Arth IR, Frenzel P (2000) Effects of ammonium-based fertilisation on microbialprocesses involved in methane emission from soilsplanted with rice **Biogeochemistry**, 51:225-257.

Bolan NS, Saggar S, Luo J, Bhandral R, Singh J (2004) Gaseous emissions of nitrogen from grazed pastures: processes, measurements and modeling, environmental implications, and mitigation. **Advances in agronomy** 84:120.

Bouwman AF (1990) **Exchange of greenhouse gases between terrestrial ecosystems and the atmosphere**. In: Bouwman, A. F. (Ed.), Soils and the Greenhouse Effect. John Wiley, New York, p. 61– 127.

Butterbach-Bahl K, Baggs EM, Dannenmann M, Kiese R, Zechmeister-Boltenstern, S (2013) Nitrous oxide emissions from soils: how well do we understand the processes and their controls? **Phil. Trans. R. Soc. B** 368(1621), 20130122.

Cabral CEA, da Silva Cabral L, Silva EMB, dos Santos Carvalho K, Kroth BE, Cabral CHA (2016) Resposta da *Brachiaria brizantha* cv. Marandu a fertilizantes nitrogenados associados ao fosfato natural reativo. **Comunicata Scientiae** 7:66-72.

Cantarella H (2007) Uso eficiente de fertilizantes nitrogenados: Uso eficiente de nitrogênio em novos fertilizantes no Brasil. **Informações Agronômicas IPNI** 120:12-13.

Cantarella H, Trivelin PCO, Contin TLM, Dias FLF, Rossetto R, Marcelino R, Coimbra RB, Quaggio JA (2008) Ammonia volatilisation from urease inhibitor-treated urea applied to sugarcane trash blankets. **Scientia Agricola** 65:397-401.

Cardoso AS, Barbero RP, Romanzini EP, Teobaldo RW, Ongaratto F, Fernandes MHMR, Ruggieri AC, Reis RA (2020) Intensification: A Key Strategy to Achieve Great Animal and Environmental Beef Cattle Production Sustainability in *Brachiaria* Grasslands. **Sustainability** 12:6656.

Cardoso A da S, Alves BJR, Urquiaga S, Boddey RM (2018) Effect of volume of urine and mass of faeces on N_2O and CH_4 emissions of dairy-cow excreta in a tropical pasture. **Animal Production Science** 58:1079-1086.

Cardoso A da S, de Figueiredo Brito L, Janusckiewicz E R, da Silva Morgado E, Barbero R P, Koscheck JFW, Reis RA, Ruggieri AC (2017) Impact of grazing intensity and seasons on greenhouse gas emissions in tropical grassland. **Ecosystems** 20:845-859.

Cardoso A da S, Oliveira S C, Janusckiewicz ER, Brito LF, da Silva Morgado E, Reis RA, Ruggieri AC (2019) Seasonal effects on ammonia, nitrous oxide, and methane emissions for beef cattle excreta and urea fertilizer applied to a tropical pasture. **Soil & Tillage Research** 194:104341.

Cardoso AN, Saminês TC, Vargas A (2001) Fluxo de Gases-traço de Efeito Estufa na Interface Solo / Atmosfera em Solos de Cerrado. **Boletim de pesquisa e desenvolvimento/Embrapa Cerrados** 17:23.

Carvalho ZG, Sales ECJD, Monção FP, Vianna MCM, Silva EA, Queiroz DS (2019) Morphogenic, structural, productive and bromatological characteristics of Braquiária in silvopastoral system under nitrogen doses. **Acta Scientiarum. Animal Sciences** 41.

Conrad R, Seiler W, Bunse G (1983) Factors influencing the loss of fertilizer nitrogen into the atmosphere as nitrogen oxide. **Journal of Geophysical Research** 88:6709-6718.

Corrêa DCC, Cardoso A da S, Souza NCS, Toniello AD, Reis RA, Ruggieri AC (2018) Effect of nitrogen source and level on ammonia volatilization in marandu-grass pasturelands. In: 2nd INTERNATIONAL CONFERENCE ON FORAGES **Anais…** Lavras: UFLa, 2018. ISBN: 978.85.8179.153-1.

Corrêa LA, Santos PM (2003) **Manejo e utilização de plantas forrageiras dos gêneros *Panicum, Brachiaria* e *Cynodon***. Embrapa Pecuária Sudeste. (INFOTECA-E Documentos, 34). ISSN 1518-4757.

Costa KA de P, Oliveira IP de, Faquin V (2006) **Fertilização Nitrogenada para Pastagens do Gênero *Brachiaria* em solos do Cerrado**. (Documentos Embrapa Arroz e Feijão) ISSN 1678-9644; 192.

Davidson EA (1991) **Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems**. In: Rogers, J.E., Whitman, W.B. (Eds.), Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes. American Society of Microbiology, Washington DC, p. 219-235.

de Bona FD, Fedoseyenko D, Von Wirén N, Monteiro FA (2011) Nitrogen utilization by sulfur-deficient barley plants depends on the nitrogen form. **Environmental and Experimental Botany** 74:237-244.

de Bona FD, Schmidt F, Monteiro FA (2013) Importance of the nitrogen source in the grass species *Brachiaria brizantha* responses to sulfur limitation. **Plant Soil** 373:201-216.

De Morais, RF, Boddey, RM, Urquiaga, S, Jantalia, CP, Alves, BJ (2013)

Ammonia volatilization and nitrous oxide emissions during soil preparation and N fertilization of elephant grass (*Pennisetum purpureum* Schum.). **Soil Biology and Biochemistry** 64:80-88.

Delbem FC, Scabora MH., Soares Filho V, Heinrichs R, Crociolli CA, Cassiolato AMR (2011) Fertilizantes e doses de fertilização nitrogenada na atividade microbiana e fertilidade do solo cultivado com *Brachiaria brizantha*. **Acta Scientiarum. Agronomy** 33:361-367.

Delevatti LM, Cardoso AS, Barbero RP, Leite RG, Romanzini EP, Ruggieri AC, Reis RA (2019) Effect of nitrogen application rate on yield, forage quality, and animal performance in a tropical pasture. **Scientific reports** 9:7596.

Di, H. J. e Cameron, K. C. Nitrate leaching in temperate agroecosystems: fertilizers, factors and mitigating strategies. **Nutrient Cycling in Agroecosystems**, v. 64, n. 3, p. 237-256, 2002.

Dias-Filho MB (2014) **Diagnóstico das pastagens no Brasil**. (Embrapa Amazônia Oriental-Documentos INFOTECA-E).

Dobbie KE, McTaggart IP, Smith KA (1999) Nitrous oxide emissions from intensive agricultural systems: variations between crops and seasons, key driving variables, and mean emission factors. **Journal of Geophysical Research: Atmospheres** 104:26891-26899.

Dupas E, Buzetti S, Rabêlo FHS, Sarto AL, Cheng NC, Galindo FS, Dinalli RP, de Niro Gazola R (2016) Nitrogen recovery, use efficiency, dry matter yield, and chemical composition of palisade grass fertilized with nitrogen fertilizers in the Cerrado biome. **Australian Journal of Crop Science** 10:1330.

Eckard RJ, Chen D, White RE, Chapman DF (2003) Gaseous nitrogen loss from temperate perennial grass and clover dairy pastures in south-eastern Australia. **Australian Journal of Agricultural Research**, 54:561-570.

FAO. **Food and Agriculture Organization.** Disponível em:< http://www.fao.org/faostat/en/#data/RFN> Acesso em: 20 de outubro de 2019.

Ferraz JBS, Felício PE (2010) Production systems—an example from Brazil. **Meat Science** 84:238–243.

Firestone MK, Davidson EA (1989) Microbiological basis of NO and N_2O production and consumption in soil. In: Andrea MO and Schimel DS (Eds.) **Exchange of trace gases between terrestrial ecosystems and the atmosphere**. John Wiley and Sons, New York, NY, p. 7-27.

Forrestal PJ, Harty M, Carolan R, Lanigan GJ, Watson CJ, Laughlin RJ, McNeill G, Chambers BJ, Richards KG (2016) Ammonia emissions from urea, stabilized urea and calcium ammonium nitrate: insights into loss abatement in temperate grassland. **Soil use and Management** 32:92-100.

Gimenes FDA, da Silva SC, Fialho CA, Gomes MB, Bernedt A, Gerdes L, Colozza MT (2011) Ganho de peso e produtividade animal em capim-marandu sob pastejo rotativo e fertilização nitrogenada. **Pesquisa Agropecuária Brasileira** 46: 751-759.

Gurgel ÂC e Costa CF (2015) **Invertendo o sinal de carbono da agropecuária brasileira: uma estimativa do potencial de mitigação de tecnologias do Plano ABC de 2012 a 2023**. (Observatório do Plano ABC) p.1-32.

Harrison R e Webb J (2001) A review of the effect of N fertilizer type on gaseous emissions. **Advances in Agronomy** 73:65–108.

Hofman G e Van Cleemput O (2004) **Soil and plant nitrogen**. 1ª Ed. International Fertilizer Industry Association. Paris, France.

Hütsch BW (1998) Methane oxidation in arable soil as inhibited by ammonium, nitrite and organic manure with respect to soil pH. **Biology and Fertility of Soils** 28:27–35.

Hütsch BW (2001) Methane oxidation in non-flooded soils as affected by crop production - invited paper. **European Journal of Soil Science** 14:237–260.

IBGE, Instituto Brasileiro de Geografia e Estatística. Censo agropecuário 2017: resultados preliminares. Disponível em:< https://biblioteca.ibge.gov.br/visualizacao/periodicos/3093/agro_2017_resultados_preliminares.pdf> Acesso em: outubro de 2019. ISSN: 01036157. 2018.

IFA e IPNI (2017) **Assessment of Fertilizer Use by Crop at the Global Level.** International Fertilizer Association (IFA) and International Plant Nutrition Institute (IPNI). Disponível em: < https://www.ifastat.org/plant-nutrition > Acesso em: outubro de 2019.

IPCC (2019) Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. **Guidelines for National Greenhouse Gas Inventories**. P. International Panel on Climate Change (IPCC). p. 546-554.

IPCC (2006) **Guidelines for National Greenhouse Gas Inventories**. P. International Panel on Climate Change (IPCC). p. 546-554.

Jones SK, Rees RM, Skiba UM, Ball BC (2005) Greenhouse gas emissions from a managed grassland. **Global and Planetary Change** 47: 201-211.

Kreuzer M e Hindrichen IK (2006) Methane mitigation in ruminants by dictary means: The role of their methane emission from manure. In: 2nd INTERNATIONAL CONFERENCE ON GREENHOUSE GASES AND ANIMAL AGRICULTURE. Zurich: Switzerland. **International Congress Series**. 1293:199–208

Leal DM, França ADS, Oliveira LG, Correa DS, Arnhold E, Ferreira RN, Bastos DC, Brunes LC (2017) Fracionamento de carboidratos e proteínas da *Brachiaria* híbrida 'Mulato II'sob fertilização nitrogenada e regime de cortes. **Archivos de zootecnia** 66:181-188.

LAPING - Laboratório de Processamento de Imagens e Geoprocessamento

(2018). Disponível em: <https://pastagem.org/atlas/map> Acesso em: 18 mai. 2021.

Lessa ACR, Madari BE, Paredes DS, Boddey RM, Urquiaga S, Jantalia CP, Alves BJR (2014) Bovine urine and dung deposited on Brazilian savannah pastures contribute differently to direct and indirect soil nitrous oxide emissions. **Agriculture, Ecosystems & Environment** 103:190–194.

Lima JE, Nascente AS, Leandro WM, Silveira PMD (2016) *Urochloa ruziziensis* responses to fertilizers and doses of urea. **Revista Brasileira de Engenharia Agrícola e Ambiental** 20:401-407.

Liu S, Wang JJ, Tian Z, Wang X, Harrison S (2017) Ammonia and greenhouse gas emissions from a subtropical wheat field under different nitrogen fertilization strategies. **Journal of Environmental Sciences** 57:196-210.

Longhini VZ, Cardoso AS, Berça AS, Boddey RM, Reis RA, Dubeux Jr,JCB, Ruggieri AC (2021) Nitrogen supply and rainfall affect ammonia emissions from dairy cattle excreta and urea apllied on warm-climate pastures. **Journal Environmental Quality** 49:1453-1466.

Lopes CM, Paciullo DSC, Araújo SAC, Gomide CAM, Morenz MJF, Villela SDJ (2017) Herbage mass, morphological composition and nutritive value of signal grass, submitted to shading and fertilization levels. **Arquivo Brasileiro de Medicina Veterinária e Zootecnia** 69:225–233.

MAPA. **Ministério de Agricultura, Pecuária e Abastecimento** (2017) Disponível em: http://www.agricultura.gov.br/noticias/valor-da-producao-agropecuaria-de-2017-estimado-em-r-548-milhoes-o-maior-em-30-anos Acesso em: outubro de 2018.

Marques DL, de Souza França AF, Oliveira LG, Arnhold E, Ferreira RN, Correa DS, Bastos DC; Brunes LC (2017) Production and chemical composition of hybrid *Brachiaria* cv. Mulato II under a system of cuts and nitrogen fertilization. **Bioscience Journal** 33(3).

McDonald IR, Bodrossy L, Chen Y, Murrell JC (2008) Molecular ecology techniques for the study of aerobic methanotrophs. **Applied Environmental Microbiology** 74:1305-1315.

McRoberts KC, Parsons D, Ketterings QM, Hai TT, Quan NH, Ba NX, Nicholson CF, Cherney DJR (2017) Urea and composted cattle manure affect forage yield and nutritive value in sandy soils of south-central Vietnam. **Grass and forage Science** 73:1–14.

MCTI. **Ministério da Ciência, Tecnologia e Inovação. Estimativas anuais de Revista emissões de gases de efeito estufa no Brasil** (2017) 4ª edição. MCTI, Brasília.

Meirelles GC, Heinrichs R, Ibãnez T.B, Ribeiro IV, Lira MVS, Matos MAS (2017) Volatilização de amônia de fertilizantes nitrogenadas com eficiência aumentada em condições de pastagem. In: IV Simpósio de fertilização e manejo de pastagens e iv de produção animal a pasto. **Anais...** Dracena, Unesp.

Moreira FS e Siqueira JS (2006) **Microbiologia e bioquímica do solo**. Lavras: Editora UFLA, p.729.

Morley N, Baggs EM, Dörsch P, Bakken L (2008) Production of NO, N_2O and N_2 by extracted soil bacteria, regulation by NO_2 - and O_2 concentrations. FEMS **Microbiology and Ecology** 65:102-112.

Nascimento CACD, Vitti,GC, Faria,LDA, Luz,PHC, Mendes,FL (2013) Ammonia volatilization from coated urea forms. **Revista Brasileira de Ciência do Solo** 37:1057-1063.

Nunes SG, Boock A, Pentead MIO (1985) ***Urochloa brizantha* cv. Marandu** (Campo Grande: EMBRAPA).

Pinheiro ÉFM (2018) Emissões de óxido nitroso sob cobertura vegetal de pastagem numa topossequência em Seropédica, RJ. **Revista Virtual de Química** 10(6).

Pires MV, da Cunha DA, Carlos SM, Costa MH (2015) Nitrogen-use efficiency, nitrous oxide emissions, and cereal production in Brazil: current trends and forecasts. **Plos One** 10:1-19.

Pulrolnik, K (2009) **Transformações do carbono no solo** (Embrapa Cerrados. Documentos 264). ISSN 1517-5111.

Raij BV (2017) **Fertilidade do solo e manejo de nutrientes.** 2ª ed. Piracicaba: International Plant Nutrition Institute.

Reetz, H. F Jr (2016) **Fertilizers and their Efficient Use**. International Fertilizer Industry Association - IFA. 1ª ed, IFA, Paris, França, 2016. ISBN 979-10-92366-04-4.

Ribeiro VJ, Andrade FV, de Souza CHE, Sa Mendonca E (2016) Volatilization of ammonia in stabilized slow-release nitrogen fertilizer under controlled conditions. **Australian Journal of Crop Science** 10:793.

Rodrigues LF, dos Santos AC, Junior OS, dos Santos JGD, de Faria AFG, Coelho BPL (2019) Morphogenic and structural characteristics of Marandu grass cultivated under grazing management and nitrogen fertilization. **Semina: Ciências Agrárias** 40:2331-2340.

Saggar S, Jha N, Deslippe J, Bolan NS, Luo J, Giltrap DL, Kim DG, Zaman M, Tillman RW (2013) Denitrification and N_2O: N_2 production in temperate grasslands: processes, measurements, modelling and mitigating negative impacts. **Science and Total Environment** 465:173-195.

Sales ECJ, dos Reis ST, Monção FP, Antunes AB, Alves DD, de Aguiar ACR, Antunes AP da S, Mota VAC (2014) Produção de forragem, características estruturais e eficiência de utilização de nitrogênio no capim-Marandu. **Agrarian** 7:434-446.

Santos ER, Carvalho BR, Rodrigues PM, Basso KC, de Carvalho NA (2018) Características estruturais do capim-marandu diferido com alturas e doses de nitrogênio variáveis. **Archivos de zootecnia** 67:420-426.

Silva DRG, Costa KADP, Faquin V, Oliveira ID, Souza MRFD, Souza MAS (2011) Eficiência nutricional e aproveitamento do nitrogênio pelo capim-marandu de pastagem em estágio moderado de degradação sob doses e fertilizantes de nitrogênio. **Ciência e Agrotecnologia** 35:242-249.

Silveira ML, Vendramini JMB, Sellers B, Monteiro FA, Artur AG, Dupas E (2013) Bahiagrass response and N loss from selected N fertilizer fertilizers. **Grass and Forage Science** 70:154-160.

Sommer SG, Schjorring JK, Denmead OT (2004) Ammonia volatilization from mineral fertilizers and plants in fields amended with ammoniacal fertilizers. **Advances in Agronomy** 82:557-622.

Souza TLD, Guelfi DR, Silva AL, Andrade AB, Chagas WFT, Cancellier EL (2017) Ammonia and carbon dioxide emissions by stabilized conventional nitrogen fertilizers and controlled release in corn crop. **Ciência e Agrotecnologia** 41: 494-510.

Stafanato JB, Goulart RDS, Zonta E, Lima E, Mazur N, Pereira CG, Souza HND (2013) Volatilização de amônia oriunda de ureia pastilhada com micronutrientes em ambiente controlado. **Revista Brasileira de Ciência do Solo** 37:726-732.

Su W, Lu J, Wang W, Li X, Ren T, Cong R (2014) Influence of rice straw mulching on seed yield and nitrogen use efficiency of winter oilseed rape (*Brassica napus* L.) in intensive rice–oilseed rape cropping system. **Field Crops Research** 159:53-61.

Tasca FA, Ernani PR, Rogeri DA, Gatiboni LC, Cassol PC (2011) Volatilização de amônia do solo após a aplicação de ureia convencional ou com inibidor de urease. **Revista Brasileira de Ciência do Solo** 35:493-502.

Telles EDCC, de Camargo PB, Martinelli LA, Trumbore SE, da Costa ES, Santos J., Higuchi N, Oliveira Jr RC (2003). Influência da textura do solo na dinâmica do carbono e no potencial de armazenamento em solos de floresta tropical da Amazônia. **Global Biogeochemical Cuts** 17(2) 1040.

Timilsena YP, Adhikari R, Casey P, Muster T, Gilla H, Adhikari B (2015) Enhanced efficiency fertilisers: a review of formulation and nutrient release patterns. **Journal of Science Food Agriculture** 95:1131-1142.

Tiritan CS, Bull LT, Crusciol CAC, Carmeis Filho ACA, Fernandes DM, Nascente AS (2016) Tillage system and lime application in a tropical region: soil chemical fertility and corn yield in succession to degraded pastures**. Soil & Tillage Research** 155:437-447.

Vasques IC, Souza AA, Morais EG, Benevenute PA, da Silva LDC, Homem BG, Casagrande DR, Silva BM (2019) Improved management increases carrying capacity of Brazilian pastures. **Agriculture, Ecosystems & Environment**

282:30-39.

Vieira RF (2017) **Ciclo do nitrogênio em sistemas agrícolas**. Embrapa Meio Ambiente-Livro científico (ALICE).

Zanatta JA, Bayer C, Vieira FC, Gomes J, Tomazi M (2010) Nitrous oxide and methane fluxes in South Brazilian Gleysol as affected by nitrogen fertilizers. **Revista Brasileira de Ciência do Solo** 34:1653-1665.

Zimmer AH, Macedo M.C.M, Kichel AN, de Almeida RG (2012) **Degradação, recuperação e renovação de patagens**. Embrapa Gado de Corte (INFOTECA-E Documentos 189). ISSN 1983-974X.

WMO - World Meteorological Organization (2019): **Greenhouse Gas Bulletin: The state of greenhouse gases in the atmosphere based on global observations through** 2018, 5. ISSN 2078-0796.

CAPÍTULO 2 - Ammonia volatilization, forage accumulation, and nutritive value of Marandu palisade grass pastures in different N fertilizers and doses[1]

ABSTRACT

The reduction in ammonia (NH_3) losses from volatilization has significant implications in forage production. The objective of this study was to evaluate the impact of N fertilizers (urea, ammonium nitrate, and ammonium sulfate) and four doses (0, 90, 180 and 270 kg N ha^{-1}) on N losses by NH_3 volatilization, accumulation, and forage chemical composition of *Urochloa brizantha* cv Marandu. Two field experiments was conduced to measure NH3-N losses using semi-open chambers. The forage accumulation and chemical composition were evaluated in the third experiment; the response variables included forage accumulation, crude protein (CP), and neutral detergent fiber (NDF). Compared to urea, ammonium nitrate and ammonium sulfate reduced NH_3-N losses by 84 and 87% and increased total forage accumulation by 14 and 23%, respectively. Forage accumulation rate and CP increased linearly with the N levels, while NDF contents decreased linearly with the N levels. In both experiments, NH_3-N losses and forage characteristics were different according to the rainfall pattern and temperature variations. Our results indicate that the use of nitric and ammoniacal fertilizers and the application of fertilizer in the rainy season constitute an efficient fertilizer management strategy to increase forage yield and decrease losses from volatilization of NH_3-N.

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[1] Este capítulo corresponde ao artigo científico submetido à revista Journal Environmental Quality e encontra-se em avaliação para publicação.

1. INTRODUCTION

Nitrogen (N) fertilization is one of the main strategies used to intensify the use of pastures to address the low natural availability of N in soils. However, the type, quantity, form, and timing of application of N fertilizers can have significant implications for N losses, mainly due to ammonia (NH_3) volatilization (Bruulsema, Lemunyon & Herz, 2009), affecting pasture productivity (Cardoso et al., 2020).

The ammonia volatilization is the main cause of low efficiency in using N fertilizers. Urea is the most used inorganic nitrogen fertilizer in the world (IFA and INPI, 2017), but it has the potential for NH_3 volatilization from up to 80% of the applied N, depending on the management practices adopted, soil type, and local environmental conditions mainly occurrence of rains (Lara-cabezas et al., 1997; Tian et al., 2015).

Nitrogen fertilization is known to increase forage dry matter yield and nutritional value, improving the chemical composition of the plant by increasing the crude protein content and decreasing the neutral detergent fiber (NDF) content (Dupas et al., 2016; McRoberts et al., 2017; Delevatti et al., 2019). However, NH_3-N losses after fertilization decreasing N use efficiency in plants present a threat to the environment; it can acidify the soil from ammonia oxidation (Liu et al., 2017; Pereira et al., 2017; Longhini et al., 2021). In addition, NH_3 acts as a secondary source of N_2O, an important greenhouse gas (Haynes & Sherlock, 1986; Cardoso et al., 2019).

Among the practices used to minimize NH_3-N volatilization is fertilization splitting (Liu et al., 2017), incorporating fertilizer into the soil (Rochette et al., 2009), and the use of N fertilizers in nitric and ammoniacal form, such as ammonium nitrate and ammonium sulfate (Souza et al., 2017). However, the results of research on NH_3-N emission factors (EF) obtained in different regions are often inconsistent and conflicting, generating the need to evaluate new strategies to mitigate NH_3 losses for regions and specific crop systems (Cardoso et al., 2019; Martha Jr et al., 2004; Tian et al., 2015).

The use of NH_3-N EF from other countries, mainly in temperate climates, leads to uncertainties in Brazilian national inventories, requiring more studies to develop country-specific EF (de Morais et al., 2013; Cardoso et al., 2020; Longhini et al., 2021). Furthermore, the potential for NH_3 losses from different nitrogen fertilizers in tropical pastures has not yet been clearly determined.

Urochloa brizantha cv Marandu is one of the most used species in regions with different soil and climate conditions in tropical Latin America, particularly in Brazil (Jank et al., 2014; Pagano et al., 2017; Pontes et al., 2017), which indicates more regional variation in response to fertilizer management practices. However, in Marandu palisade grass, the potential N loss from volatilization and the characteristics of the forage in response to three main N fertilizers used in the country are still unknown.

Furthermore, to evaluate different fertilization strategies for crop yields, it is important to study the environmental effects of this fertilization to contribute to the development of more sustainable systems. Therefore, the objective of this study was to investigate the effect of three N fertilizers (urea, ammonium nitrate, and ammonium sulfate) and four doses of N (0, 90, 180, and 270 kg N ha^{-1}) on forage accumulation and chemical composition, and NH_3 emissions in tropical Marandu grass pastures in the Brazil’s Cerrado region.

2. MATERIALS AND METHODS

2.1 Experimental Site

The field study was carried out in a Marandu grass pasture (*Urochloa brizantha* cv. Marandu), established in 2001, and located in the Forage and Grassland sector of São Paulo State University - UNESP, Jaboticabal, São Paulo, Brazil (21º15’22” S and 48º18’58” W; 595 m altitude). According to the Köppen climatic classification, the climate in the region is of the Aw type (tropical, characterized by dry winters). The annual rainfall is 1424 mm, and the average air temperature is 22.3 °C. The soil is an Oxisol (USDA, 2014). Soil properties (0-20 cm depth) were bulk density of 1.41 g cm^{-3}, contains 340 g kg^{-1} sand, 140 g kg^{-1} silt and 520 g kg^{-1} clay (Claessen, 1997), pH ($CaCl_2$) 5.4, organic matter 31 g kg^{-1}, cation exchange capacity 85 mmolc dm^{-3}, P (ion-exchange resin extraction method) 16.5 mg dm^{-3}, $Mehlich^{-1}$ extractable Ca 36.5 mmolc dm^{-3}; $Mehlich^{-1}$ extractable Mg 14 mmolc dm^{-3}, Mehlich-1 extractable K 4.2 mmolc dm^{-3}, base saturation 550 g kg^{-1}.

Meteorological data were measured throughout the experimental period, including temperature, rainfall and water balance data being obtained from the Agrometeorological Station, Department of Exact Sciences, FCAV / UNESP, located 1.5 km from the experiment site.

2.2 Experimental Design and Treatments

Three experiments were performed on Marandu grass pastures: the first and second for the evaluation of volatilized NH_3, and the third for the evaluation of forage accumulation and chemical composition. The experimental area during the evaluation period was not allowed to grazing to avoid disturbance or influence of animal excretions. In each experiment, 40 experimental plots were used.

The experiment 1 was conducted from December 13, 2017 to January 3, 2018, and experiment 2 was from November 27, 2018 to March 9, 2019. The experiment was arranged in a randomized block design, with 4 repetitions, in a 3 x 3 + 1 factorial scheme. The treatments were three N fertilizers: urea, ammonium nitrate, and ammonium sulfate; three doses of nitrogen: 90, 180, and 270 kg ha^{-1} $year^{-1}$, and one treatment without nitrogenous fertilization (control).

In experiment 1, the N doses were applied in a single fertilization (December 13, 2017). In experiment 2, conducted in another area, the doses were split into three applications (November 27, 2018, January 12, 2019, and February 16, 2019), representing 30, 60, and 90 kg N $application^{-1}$, distributed manually after the standardization cuts, carried out to a residue of 15 cm from the soil.

The experiment 3 was held from November 27, 2018 to November 28, 2019. The doses of N were divided into three applications, and applied on the same dates, similar to experiment 2. The experimental design was randomized blocks, with 4 repetitions, in a 3 x 4 x 4 factor scheme. Three N fertilizers were used: urea, ammonium nitrate, and ammonium sulfate, in four N doses: 0, 90, 180, and 270 kg N ha^{-1} $year^{-1}$, and four experimental cuts.

In the experimental 3, the pasture was managed in a cutting regime. Therefore, the experimental cuts refer to the cutting of forage, whenever the experimental plot reaches 30 cm in canopy height, with the cut being made to a residue of 15 cm from the soil. The management of pasture under a cutting regime at a height of 30 cm canopy (when marandu grass intercepts 95% of the light) and 15 cm of residue, refers to the most favorable growth pattern (crop growth rates, relative growth and net assimilation) for this cultivar (Carneiro et al., 2007, Giacomini et al., 2009).

2.3 Soil Ammonia Volatilization Measurement

After the application of fertilizers in 21 days, evaluations of N losses by volatilization of NH_3 were carried out on the samples 1, 3, 5, 9, 14, and 21 day after application (DAA) of treatment, with the plots that did not receive fertilization as reference. Volatilized N quantification was performed according to the methodology described by Araújo et al. (2009) and Longhini et al. (2021). NH_3 was captured by a semi-open chamber that consists of a transparent polyethylene terephthalate bottle (PET, soda bottle 2 L) with no bottom.

To absorb the volatilized NH_3, a foam strip (3 mm thick, 2.5 cm wide, and 25 cm long) was moistened in an acidic solution of 1 M H_2SO_4 ± 2% glycerin, and hung inside the flask, with its lower end inserted in a plastic jar (100 mL) containing the same solution of H_2SO_4. Samples were evaluated using ammonia analysis by steam distillation (Keeney and Nelson, 1982). The amount of N recovered in the foam and plastic jar was multiplied by a factor of 1.74 calculated from the recovery of NH_3-N (1 / 0.63), according to the calibration of the technique by Araújo et al. (2009).

Ammonia emission for treatment in each sampling interval was calculated following Eq. (1)

$$Ammonia\ emission\ (\%) = \frac{\text{NH3 (treatment)} - \text{NH3 (soil background)}}{\text{N (applied)}} \quad (1)$$

Where $NH_{3\ (Treatment)}$ is total cumulative NH_3 emission (% total N applied lost as NH_3) for the fertilizers treatments, $NH_{3\ (Soil\ background)}$ is total cumulative NH_3

emission (% total N applied lost as NH_3) for the air + soil + palisade grass without N addition, and $N_{(applied)}$ is N application in the area covered by the chamber (kg N ha^{-1}).

2.5 Forage Chemical Composition

To determine the chemical composition of forage, the samples of the portion kept intact were oven-dried for 72 hours at 55 °C weighed and ground in a 1 mm sieve in a mill (Thomas-Wiley Laboratory Mill Model 4, H. Thomas Co.), and taken to the laboratory for analysis. The samples were submitted to dry matter (DM) analysis (AOAC 934.01), crude protein (CP) content was estimated using a LECO® FP 528 device (Leco Corporation, Michigan, USA). The neutral detergent fiber (NDF) and acid detergent fiber (ADF) were determined using the procedures described by ANKOM Technology (ANKON, 2006).

2.6 Statistical Analysis

The data of NH_3-N volatilization, forage accumulation, and chemical composition were submitted to analysis of variance (ANOVA). In experiments 1 and 2, the statistical model included effects of N fertilizers, doses, and their interaction according to the statistical model:

Model: μ + ßi + Fj + Dk + (FD)jk + εjki

In experiment 3, the statistical model included the effects of N fertilizers, doses, cuts, and interactions:

Model: μ + ßi + Fj + Dl + Cj + (FD)kl + (FC)kl + (DC)kl + (FDC)kl + εijkl

Where, μ was the mean; ßi were the effects of the blocks; Fj, Dk + (FD)jk were the effects of N fertilizers, dose, and dose and N fertilizers interaction, respectively; F_j, D_l and C_j were the effects of N fertilizers, dose, and curt, respectively; and $(FD)_{kl}$ + $(FC)_{kl}$ + $(DC)_{kl}$ + $(FDC)_{kl}$ were the effects of interactions, while ε_{ijkl} was the random error.

When significant, the N fertilizers and doses were compared by Tukey-HSD test at 5% probability and orthogonal polynomial contrasts, respectively. The analyses were conducted using the R program (Version 3.4.5).

3 RESULTS

3.1 Environmental Factors

Meteorological data were measured throughout the experimental period; the distribution of rainfall after fertilization differed between experiments (Fig. 1a,b,c). In experiment 1, the accumulated amount of rainfall was 138 mm, and the average air temperature varied from 21.1 to 26.1 ºC (Fig. 1a). There was no accumulated rainfall greater than 5 mm until the 8th DAA, an event that during the rainy season is considered veranico (i.e. lack of rainfall), according to Sansigolo (1989).

In experiment 2, within 21 days of evaluation after each fertilization, the accumulated rainfall were 39.6, 102.5, and 202.7 mm in the first, second, and third fertilization, respectively, and the average temperatures were 25.2. 25.8, and 23.6 ºC, respectively (Fig. 1b). In experiment 2 and 3, one veranico occurred after the first fertilization (from December 2 to December 12, 2018), while two veranico occurred between the second and third fertilizations (from January 15 to January 24, 2019, and from January 27 to February 2, 2019).

In experiment 3, the total annual rainfall was 994.8 mm, of which 39.6, 572.3, 157.2, 48.1, and 177.6 mm fell during the late spring of 2018, and summer, fall, winter, and spring of 2019, respectively. The average temperatures of those periods were 25.3, 24.7, 22.3, 21.6, and 25.2 ºC (Fig. 1c), respectively. The average annual rainfall during the experimental period was lower than the historical average in the period from 1956 to 2015, which was 1398 mm (André & Anunciação, 2017). In curts 1, the period of growth until the cutting of forage included the months of December and January; the cuts 2 were made in February and March; March, April, and May in cuts 3, and May to November in cuts 4.

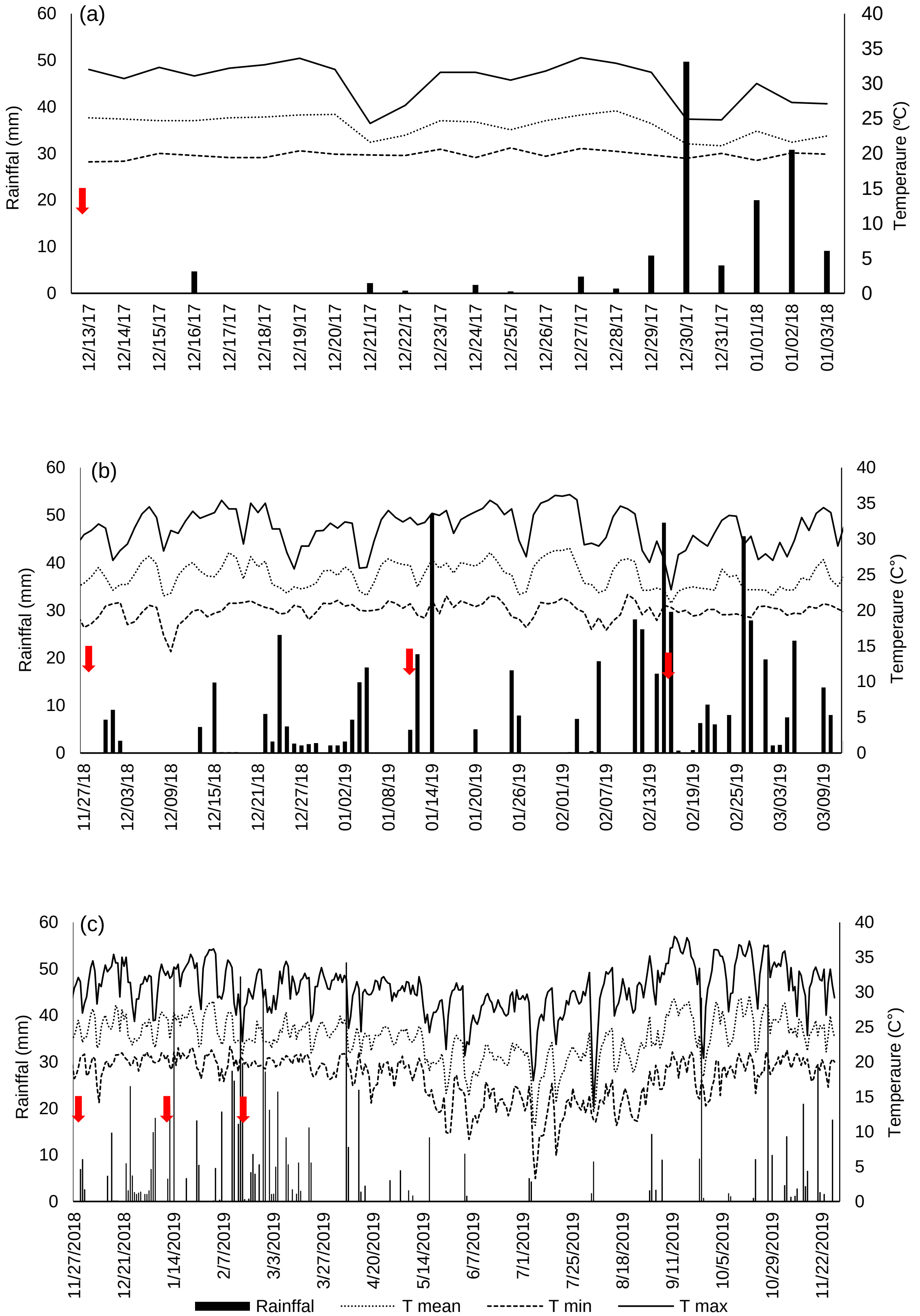

Fig. 1. Daily air temperature (minimum, medium, and maximum T; ºC) and daily rainfall (R; mm). Data from the Agrometeorological Station, Department of Exact Sciences, FCAV / UNESP. (a) Experiment 1, (b) Experiment 2, and (c) Experiment 3. Arrows indicate fertilization events.

In the water balance of experiment 3, the water deficit and excess water values were 0 and 163 mm in November, -10 and 0 mm in December 2018, 0 and 0 mm in January, 0 and 171 mm in February, 0 and 0 mm in March, 0 and 0 in April, -16 and 0 mm in May, -29 and 0 mm in June, -32 and 0 mm in July, -53 and 0 mm in August, -27 and 0 mm in September, -58 and 0 mm in October and -20 and 0 mm in November 2019, respectively (UNESP / FCAV Agroclimatologic Station, 2019).

3.2 Ammonia Volatilization

In both experiments, the NH_3-N volatilization varied according to N fertilizers ($p < 0.0001$) and nitrogen doses ($p < .0001$), and the interaction between fertilizers and doses had significant effect in experiment 1 ($p = .0003$) and experiment 2 ($p < .0001$) (Table 1). The N doses had linear positive effect on NH_3-N volatilization in all fertilizers evaluated in experiment 1 ($p < .0265$) and experiment 2 ($p < .0025$).

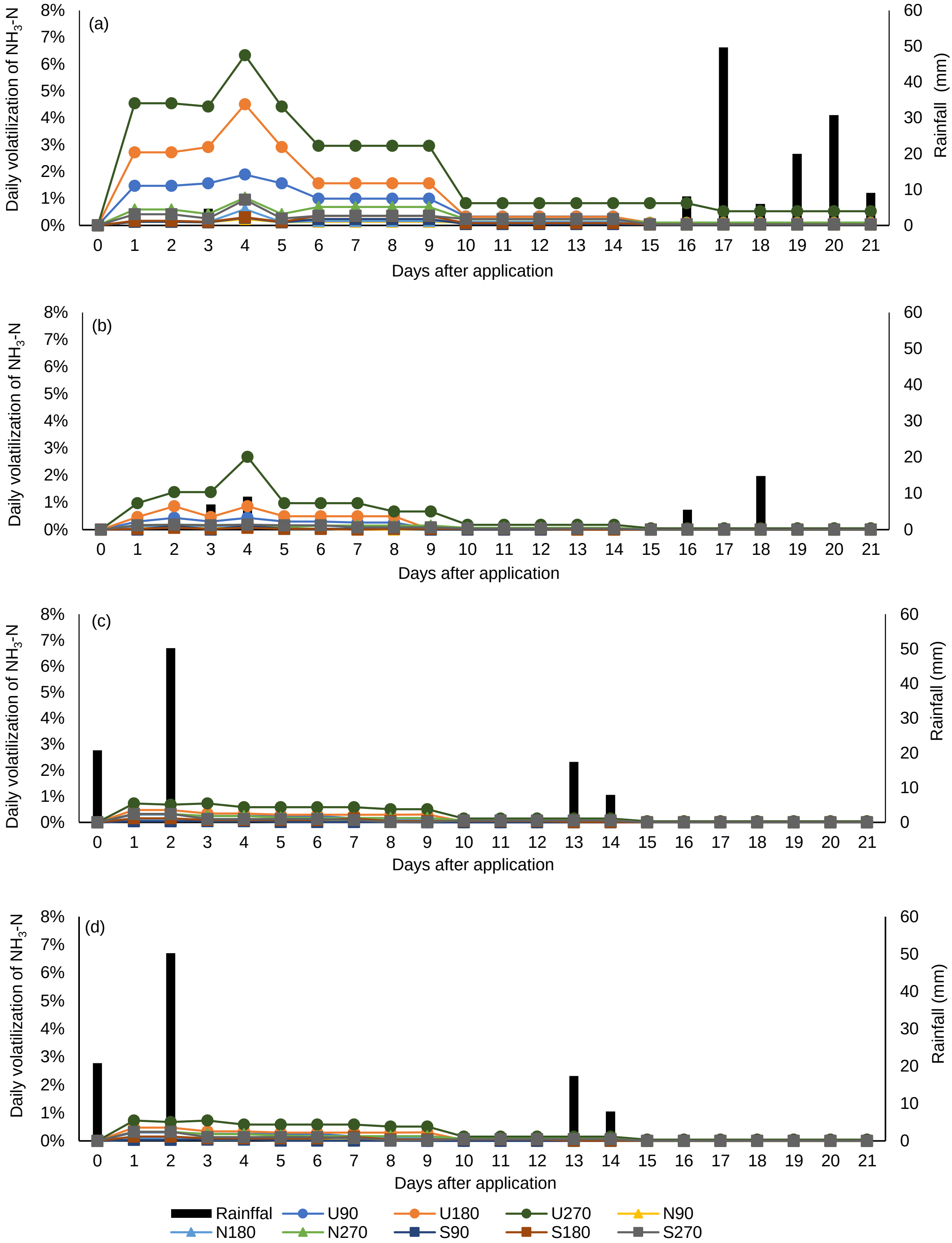

Fig. 2. Daily ammonia volatilization in marandu palisade grass pastures under fertilization with fertililizers and doses of N. (a) experiment 1, single application (b) experiment 2, 1st fertilization, (c) experiment 2, 2nd fertilization, and (d) experiment 2, 3rd fertilization. U: urea, N: ammonium nitrate, S: ammonium sulfate.

Table 1. Emission factor (EF) in marandu palisade grass pastures in fertilization with different N sources and doses in two experiments.

		Experiment 1	Experiment 2
N Fertilizers (F)	*Doses (kg ha^{-1}) (D)*	---- % NH_3-N ----	
Urea	90	13.92	6.30
	180	24.37	10.87
	270	44.58	24.10
	Mean	27.62	13.76
Ammonium nitrate	90	2.02	1.05
	180	3.17	2.58
	270	7.71	5.67
	Mean	4.30	3.10
Ammonium sulfate	90	2.22	0.78
	180	3.10	1.88
	270	5.27	3.65
	Mean	3.53	2.10
	SEM	0,04	0,03
P-value			
F		<.0001	<.0001
D		<.0001	<.0001
F x D		0.0003	<.0001

Abbreviations: SEM, standard error of the mean. Experiment 1: N applied in a single dose. Experiment 2: N applied in three doses.

The decreasing sequence of the accumulated loss of N was: urea > ammonium nitrate = ammonium sulfate, in both experiments. When N fertilizers were applied in a single dose (experiment 1), the highest percentages of losses was observed in urea, which reached almost 45% of total N loss as NH_3 at a rate of 270 kg N ha^{-1} (Table 1).

In experiments 1 and 2, the greatest NH_3-N losses occurred until the 9th DAA, referring to the 4th collecting (Fig. 2a,b,c,d), which gradually decreased until the 15th DAA; the losses were negligible after that period. In experiment 1, there was a similar pattern of daily NH_3-N losses in all treatments, varying only in quantity of volatilized NH_3-N. The maximum peak of volatilization occurred on the 4th DAA. In experiment 2, peak emissions occurred in the 4th DAA in the first fertilization (Fig. 2b); the peak was not observed in the second and third fertilization (Fig. 2c,d).

The EF of NH_3-N obtained in this study were differentiated according to N doses and sources, which ranged from 6.30 to 44.58% in urea, 1.05 to 7.71% in ammonium nitrate, and 0.78 to 5.27% in ammonium sulfate (Table 1).

3.3 Forage Accumulation

Cuts ($p < .001$), N fertilizers ($p < .001$), and N doses ($p < .001$) had a significant effect on FAR (Fig. 3a,b,c). The FAR in ammonium sulfate was significantly higher by 36% than in urea (Fig. 3a). The FAR had a linear increase in response to N application, so the treatments with 90, 180, and 270 kg N ha^{-1} increased the FAR by 46, 102, and 106%, respectively, in relation to the control treatment (Fig. 3b), with a quadratic effect of the experimental cuts, with lower accumulation rates observed in cuts 1 and 4 (Fig. 3c).

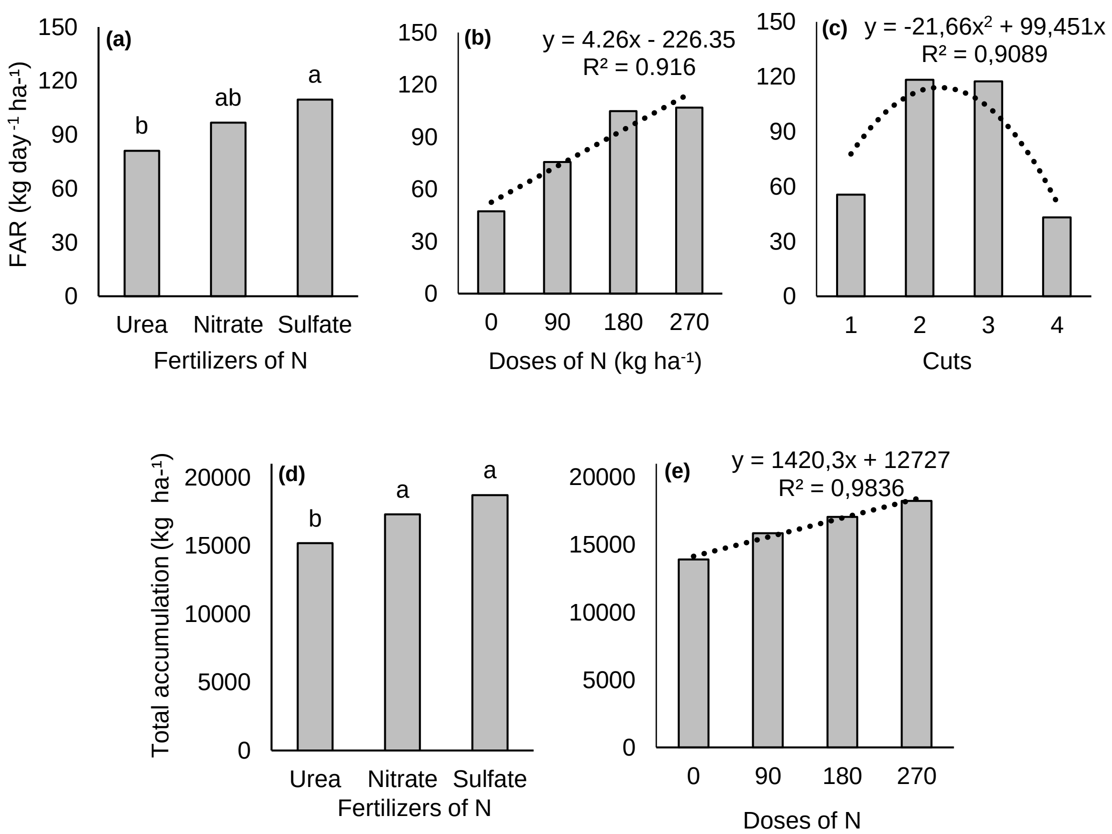

Fig. 3. Forage accumulation rate (FAR, kg ha^{-1} DM day^{-1}) and total forage accumulation (kg ha^{-1}) of marandu palisade grass pasture in fertilization with N fertilizers and doses. (a) effect of N fertilizers on the FAR, (b) effect of doses of N on the FAR, (c) effect of cuts on the FAR, (d) effect of N fertilizers on the total accumulation, (e) effect of doses of N on the total accumulation.

Total forage accumulation was affected by N fertilizerrs and doses (p< .05); the ammonium nitrate and ammonium sulfate provided significantly higher mean TFA of 17299 and 18713 kg DM ha^{-1} year, respectively, than urea, with a mean of 15178 kg DM ha^{-1} year (Fig. 3d). TFA had a positive linear increase in response to the N doses, with percentage increases of 14, 23, and 32% at doses 90, 180, and, 270 kg N ha^{-1}, respectively, compared to the control treatment (Fig. 3e).

3.4 Chemical Composition of Forage

The effect of N fertilizers (p= .001) and doses (p= .0027) on CP content was dependent on the cuts; the means of cut 4 were the lowest, differing significantly from cut 2, which had the highest CP content (Table 2). There was a positive linear increase in CP content with N levels in cuts 1, 2, and 3. In cut 4, a cubic increase was observed (Table 2).

The effect of N fertilizers and doses on NDF and ADF concentration were dependent on the cuts (p< .01). The N dose decreased linearly the NDF concentration in all cuts except in cut 4, which increased linearly. The N doses had a quadratic effect on ADF in cuts 2 and 4, with no significant effect in cuts 1 and 3. Within each experimental cuts, no significant difference was observed between the N fertilizers for the variables CP, NDF, and ADF.

Table 2. Crude protein (CP), neutral detergent fiber (NDF), acid detergent fiber (ADF) of marandu palisade grass pastures in fertilization with different N fertilizers and doses.

	Crude Protein (g kg^{-1} DM)			
Factors				
Cuts	1	2	3	4
N fertilizers				
Urea	132.0^{abcd}	147.1^{ab}	121.9^{cde}	105.9^{e}
Nitrate	142.1^{abc}	142.5^{abc}	130.5^{bcd}	111.1^{de}
Sulfate	145.3^{ab}	153.2^{a}	140.4^{abc}	108.4^{e}
Doses of N (kg ha^{-1})				
0	126.0	100.3	99.4	119.4
90	133.3	133.2	111.1	103.2
180	141.0	146.7	137.0	112.8
270	145.1	163.0	144.8	109.3
Mean	136.3	135.8	123.1	111.2
Effect	Linear	Linear	Linear	Cubic
	Neutral Detergent Fiber (g kg^{-1} DM)			
N fertilizers				
Urea	634.4^{ab}	634.4^{ab}	638.6^{ab}	657.8^{a}
Nitrate	630.6^{ab}	625.5^{ab}	629.1^{ab}	644.9^{ab}
Sulfate	634.3^{ab}	624.5^{b}	624.2^{b}	650.4^{ab}
Doses of N (kg ha^{-1})				
0	643.3	658.0	657.3	601.1
90	638.4	641.8	656.2	643.8
180	633.5	621.0	619.0	653.3
270	627.4	621.6	616.7	655.9
Mean	635.6	635.6	637.3	638.5
Effect	Linear	Linear	Linear	Linear
	Acid Detergent Fiber (g kg^{-1} DM)			
N fertilizers				
Urea	305.4^{a}	288.0^{abc}	299.4^{abc}	295.4^{abc}
Nitrate	302.7^{ab}	280.2^{c}	296.9^{abc}	285.6^{abc}
Sulfate	297.0^{abc}	283.0^{bc}	290.6^{abc}	301.2^{abc}
Doses of N (kg ha^{-1})				
0	301.7	298.3	299.5	263.5
90	302.8	286.2	299.4	280.8
180	300.5	278.4	292.2	304.9
270	301.7	286.5	295.3	296.6
Mean	301.7	287.4	296.6	286.4
Effect	NS	Quadratic	NS	Quadratic

Abbreviation: SEM, standard error of the mean. NS, not significant. CP: SEM = 7.9 (g kg^{-1} DM). NDF: SEM = 9.1 (g kg^{-1} DM). ADF: SEM = 3.9 (g kg^{-1} DM). Means not followed by the same letter differ based on Tukey-HSD test at 5% probability (comparisons between the 12 means).

4. DISCUSSION

4.1 Ammonia volatilization

In the interaction between N fertilizers and doses, there was an increasing linear effect of N doses on NH_3 losses by volatilization in both experiments, showing that the increase in amount of fertilizer applied to the soil favors losses by volatilization. According to Vlek & Stumpe (1978), NH_3 loss was a first order reaction, which was directly related to N concentration in the soil solution. This reaction also explains the lower losses by volatilization observed in experiment 2, because the amount of NH_4^+ in the soil available for hydrolysis was less when the fertilization was done (Timilsema et al., 2015).

Reduction of volatilization losses observed in ammonium nitrate and ammonium sulfate occur essentially by the difference between the physical-chemical reactions of fertilizer volatilization. Higher losses were observed in urea, because, according to Fenn & Hosnner (1985), fertilizers that produce ammonium carbonate ($(NH_4)2CO_3$) were more susceptible to NH_3 loss. Hydrolysis of urea by the enzyme urease results in $(NH_4)2CO_3$, which decomposes rapidly into bicarbonate (HCO_3^-), hydroxyl (OH-), and ammonium ($2NH_4^+$), and pH elevation due to increased HCO_3^- concentration (Harrison & Webb, 2001).

The losses from volatilization of different fertilizers depend mainly on NH_4^+ and HCO_3^- concentrations, inducing an increase in pH; thus, due to the acidity of ammonium nitrate and ammonium sulphate, NH_4^+ ions remained stable and were not converted to NH_3, and the losses in these fertilizers were lower than in urea, which depends on soil alkalinity (Fenn & Hossner, 1985). The significant reduction in NH_3-N emissions from nitric and ammonia fertilizers was similar to that reported for sugarcane in tropical regions (Otto et al., 2017), ryegrass (Benardini et al., 2013), and subtropical maize in Brazil (Viero et al., 2014).

In both experiments, the greatest losses occurred until the 9th DAA, referring to the 4th collection (Fig. 2a,b,c,d), because of the higher concentration of ammoniacal nitrogen in soil solution (Sommer, Schjorring & Denmead, 2004). In contrast, the difference in rainfall between fertilization events (Fig. 1a,b) caused varied results in volatilization peak and accumulated NH_3-N emissions. This was the main variable that regulated the volatilization potential in both experiments, demonstrating the large influence of climatic conditions on NH_3-N emissions (Sommer, Schjorring & Denmead, 2004).

In experiment 1 and first fertilization in experiment 2, there was no occurrence of rain on the day of fertilization, which occasionally led to a peak volatilization on the 4th DAA, one day after the first rainfall, which were 4.7 and 7 mm respectively (Fig. 2a,b). This was because under dry soil conditions, volatilization increases when a small amount of water of around 3 mm, was added to the soil (Sanz-Cobena et al., 2011; Longhini et al. 2021). According to Kissel et al. (2004), low rainfall may stimulate urea volatilization, because it was not sufficient to incorporate the fertilizer. According to Sanz-Cobena et al. (2011), adding 14 mm of water to the soil after fertilization can reduce volatilization losses by up to 89%, which justifies the absence of volatilization peaks in the second and third fertilizations of experiment 2, where there were rainfalls greater than 20 mm until the 2nd DAA (Fig. 2c,d).

The mean EF values in experiment 1 and 2 were 27.62% and 13.76% in urea, 4.30 and 3.10% in ammonium nitrate, and 3.53 and 2.10% in ammonium sulfate, respectively. According to the IPCC (2019), the standard EF for the respective fertilizers are 14.2, 3.0, and 9.5%, indicating that there was divergence between the EF obtained under experimental conditions and the standard established by the IPCC, which was calculated in temperate climate.

Although there was a large database with estimates of NH_3 volatilization based on the types of N fertilizers and their uses, most of these studies were conducted under temperate and subtropical conditions (Forrestal et al., 2016; Li et al., 2017; Liu et al., 2017). Because NH_3 emissions after fertilizer application vary with soil type, pH, and temperature, inventories should assign emission factors for different fertilizers in different countries according to the prevailing soil and climate category in order to obtain reliable estimates of nitrogen fertilizer impact analysis for different crops.

Studies conducted in the state of São Paulo pointed out the differences between the EF obtained in pastures and the IPCC default EF. Cardoso et al. (2019) obtained EF of 16.9% in Marandu grass pastures fertilized with 80 kg of N from urea and at similar conditions Longhini et al. (2021) found EF varying from 11.2 to 20.5% (mean 14.8%)., While Morais et al. (2013) reported a mean EF of 49% in elephant grass (*Pennisetum purpureum* Schum.) fertilized with 80 and 100 kg of N ha^{-1} from urea. Thus, the results of this study are important for the development of specific EF for gas emissions according to the climatic conditions and characteristics of ruminant production systems, especially in tropical regions.

4.2 Forage Accumulation

Compared to urea, higher FAR (Fig. 3a) and TFA (Fig. 3d) observed in ammonium sulfate was due to the intrinsic factors of this source, since plants treated with fertilizers containing (sulfur) S use N more efficiently, and the balance between the amounts of N and S has a direct impact on forage growth (Artur & Monteiro, 2014; De Bona & Monteiro, 2010). De Bona, Schmidt & Monteiro (2013) highly recommended the use of fertilizers containing NH_4^+ and NO_3^- for cultivation of *U. brizantha* or similar species due to increased absorption of N and S, improving growth, nutritional value, and dry matter accumulation. We observed higher FAR (Fig. 3b) and TFA (Fig. 3e) with the increase in the amount of fertilizer used which was expected when N demands of grasses was met, since N fertilization is known to increase plant productivity and growth (Dupas et al., 2016; McRoberts et al., 2017; Cardoso et al., 2020).

The effect of cuts in the FAR (Fig. 3c) is due to the rainfall pattern throughout the experiment, which can be exemplified by the water balance, for this variable, we observed that cuts 2 and 3, which had the highest FAR, were performed between February and May, which corresponded to the period with better water conditions, with greater water excess and low water deficit; while the opposite was observed for cuts 1 and 4, which, consequently, had the lowest FAR. According to Lima et al., (2016), the availability of water in the soil has a significant effect on the rate of development of *Urochloa* forage, with less plant development being observed in the period of lower precipitation and lower temperatures, corroborating the results of the lowest FAR in the cut 4, which was performed in the coldest months and with greater water deficit.

4.3 Chemical Composition of Forage

The CP, NDF and FDA contents were affected by the interaction between N fertilizers, N doses and cuts (Table 2). It was observed that the effect of fertilization was dependent on climatic conditions, mainly rainfall and temperature, resulting in high availability of forage of good nutritional value during rainy season, and decrease in quantity and quality during dry season, as noted by other authors (Pinho Costa et al., 2014; Lima et al., 2016; Avelino et al., 2019).

It should be noted that, in addition to the amount of nutrient in the soil, intrinsic aspects of forage species, management factors and environmental factors also regulate the chemical composition of the plant (Benett et al., 2008; Avelino et al., 2019). In the tropics, temperature and water deficit are the main limiting factors for forage production (Van Soest, 1994), thus environmental fluctuations modify the morphology, development rate and alter the chemical composition of the plant.

The effect of N doses on the linear increase in CP contents and on the linear decrease in NDF contents in cuts from 1 to 3 are due to the more favorable conditions for plant development in the cutting period (December to May), where it is observed higher temperatures, higher rainfall occurrence (Fig.1) and low water deficit. On the contrary, in cut 4 (May to November), all the evaluation months had water deficit and days with minimum temperatures below 15 ºC. Similar results were reported by Campos et al. (2016), where N fertilization caused linear increase in CP content and linear decrease in NDF content, stimulating cell wall formation with better quality fibers, resulting to greater digestibility of the forage, depending on the climatic conditions.

The temperature regulates the meristematic activity and, in effect, the plant growth, the ideal temperature for the growth of tropical grasses varies from 30 ºC to 35 ºC while from 10 ºC to 15 ºC photosynthesis decreases and the growth practically ceases (McWilliam, 1978). Likewise, rainfall is a key factor for grass development, considering that N is a nutrient absorbed by mass flow (Malavolta et al., 1997), rainier months, which consequently increase the amount of water in the soil, favor the absorption of this nutrient by the plant.

Nitrogen fertilization in periods with favorable climatic conditions promotes significant increases in dry matter yield (Costa et al., 2005; Lima et al., 2016) and affects the chemical composition and nutritional value of pastures (Campos et al., 2016 ; Cardoso et al., 2020) as observed in this work. Climatic factors also impact the morphological and chemical composition of the plant. During the period of better plant growth, N fertilization promotes acceleration in tissue renewal and an increase in the proportion of leaves, due to N increasing the elongation rate and leaf area of grasses (Lopes et al., 2017, Marques et al. ., 2017).

Environmental stresses such as water deficit and low temperatures cause growth arrest and death of the aerial part of forages, as a result of the lack of organ and tissue renewal, there is an increase in structural compounds characterized by the fiber and, in parallel, a decrease in cell content levels, as protein. These factors explain the higher NDF and lower CP contents in cut 4 (Table 2). The environmental conditions did not intensely impact the ADF levels, which had smaller variations in the mean, while the effect of fertilization with N on this variable is diverse, being able to increase (Avelino et al., 2019), decrease (Carvalho et al., 2019), cause a quadratic effect (Marques et al., 2017) or have no effect (Dupas et al., 2016; Delevatti et al., 2019).

5. CONCLUSION

This study is new in reporting the agronomic and chemical variables of forage and the losses due to volatilization of NH_3-N as a function of the main commercial sources of N in tropical pastures. Our results reveal that plant responses and N losses in the system vary not only due to the amount and type of fertilizer applied, but mainly due to climatic fluctuations related to precipitation and temperature. The NH_3 emission factors of the fertilizers differed from the IPCC standards, being on average 68% lower in ammonium sulphate, and 97% higher in urea with single fertilization, so that the IPCC standard EFs show little adequate depending on of fertilization management in tropical pastures. As a fertilization strategy for lower volatilization losses and higher forage productivity, we suggest fertilization in the rainy season and the use of ammonium sulfate fertilizer.

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Declaration of conflict of interest

We declare we have not conflict of interest.

6. REFERENCES

André, R. G. B., & Anunciação, Y. M. T. (2017). A precipitação pluvial provável em Jaboticabal, São Paulo. *Agrometeoros*, *25*(2), 347-359.

ANKOM Acid detergent fiber in feeds (2006). Filter bag technique (for A200, A200I). Ankom Technology Method 8. Ankom Technology Corp.

AOAC (1990). Official methods of analysis of the Association of Official Analytical Chemists 15th ed. (Association of Official Analytical Chemists 1990).

Araújo, E. S., Marsola, T., Miyazawa, M., Soares, L. H. B, Urquiaga, S., Oddey, R. M., & Alves, B. J. R. (2009). Calibração de Câmara Semiaberta Estática para Quantificação de Amônia Volatilizada do Solo. *Pesquisa agropecuária brasileira, 44*(7), 769-776. https://doi.org/10.1590/S0100-204X2009000700018.

Artur, A. G., & Monteiro, F. A. (2014). Marandu palisade grass growth and nutrient accumulation as affect by nitrogen and sulfur fertilizations. *Australian Journal of Crop Science, 8*(3), 422-429.

Avelino, A. C. D., de Faria, D. A., Penso, S., Lima, D. D. O. S., Rodrigues, R. C., de Abreu, J. G., Cabral, L. S., & Peixoto, W. M. (2019). Agronomic and bromatological traits of *Brachiaria brizantha* cv. Piatã as affected by nitrogen rates and cutting heights. *Journal of Experimental Agriculture International, 36*(6), 1-11. https://doi.org/10.9734/jeai/2019/v36i630253.

Baumont, R., Lewis, E., Delaby, L., Prache, S., & Horan, B. (2014). Sustainable intensification of grass-based ruminant production. *Grassland Science In Europe, 19*, 521-532.

Benett, C. G. S., Buzetti, S., Silva, K. S., Bergamaschine, A. F., & Fabricio, J. A. (2008). Yield and bromatologic composition of marandu grass as function of sources and doses of nitrogen. (In Portuguese, with English abstract.) *Ciência e Agrotecnologia, 32*(5), 1629-1636. https://doi.org/10.1590/S1413-70542008000500041.

Bourscheidt, M. L. B., Pedreira, B. C., Pereira, D. H., Zanette, M. C., & Devens, J. (2019). Nitrogen input strategies in pastures: Mineral fertilizer, bacterial inoculant and consortium with forage peanuts. (In Portuguese, with English abstract). *Scientific Electronic Archives, 12*(3), 137–147. http://dx.doi.org/10.36560/1232019784.

Bruulsema, T., Lemunyon, J., & Herz, B. (2009). Know your fertilizer rights. *Crops & Soils, 42*, 13-18.

Campos, F. P., Nicácio, D. R. O., Sarmento, P., Cruz, M. C. P., Santos, T. M., Faria, A. F. G., Ferreira, M. E., Conceição, M. R. G., & Lima, C. G. (2016). Chemical composition and in vitro ruminal digestibility of hand-plucked samples of Xaraes palisade grass fertilized with incremental levels of nitrogen. *Animal Feed Science Technology, 215*, 1-12. https://doi.org/10.1016/j.anifeedsci.2015.12.013.

Cardoso, A. S., Oliveira, S. C., Janusckiewicz, E. R., Brito, L. F., da Silva Morgado, E., Reis, R. A., & Ruggieri, A. C. (2019). Seasonal effects on ammonia, nitrous oxide, and methane emissions for beef cattle excreta and urea fertilizer applied to a tropical pasture. *Soil & Tillage Research, 194*, 104341. https://doi.org/10.1016/j.still.2019.104341.

Cardoso, A. S., Barbero, R. P., Romanzini, E. P., Teobaldo, R. W., Ongaratto, F., Fernandes, M. H. M. R., Ruggieri, A.C., & Reis, R. A. (2020). Intensification: A Key Strategy to Achieve Great Animal and Environmental Beef Cattle Production Sustainability in *Brachiaria* Grasslands. *Sustainability, 12*, 6656.

https://doi.org/10.3390/su12166656.

Carvalho, Z. G., Sales, E. C. J. D., Monção, F.P ., Vianna, M. C. M., Silva, E. A., & Queiroz, D. S. (2019). Morphogenic, structural, productive and bromatological characteristics of Braquiária in silvopastoral system under nitrogen doses. *Acta Scientiarum. Animal Sciences, 41*, e39190. http://dx.doi.org/10.4025/actascianimsci.v41i1.39190.

Claessen, M. E. C. (1997). *Manual de métodos de análise de solo/Centro Nacional de Pesquisa de Solos (Manual of soil analysis methods/National Soil Research Center)*. (2nd ed.). Rio de Janeiro, EMBRAPA-CNPS.

De Bona F. D. & Monteiro F. A., (2010). Marandu palisade grass growth under nitrogen and sulphur for replacing signal grass in degraded tropical pasture. (In Portuguese, with English abstract.) *Scientia Agricola, 67*(5), 570-578. https://doi.org/10.1590/S0103-90162010000500011.

De Bona, F. D., Schmidt, F., & Monteiro, F. A. (2013). Importance of the nitrogen source in the grass species *Brachiaria brizantha* responses to sulfur limitation. *Plant Soil, 373*(1), 201-216. https://doi.org/10.1007/s11104-013-1789-7.

De Morais, R. F., Boddey, R. M., Urquiaga, S., Jantalia, C. P., & Alves, B. J. (2013). Ammonia volatilization and nitrous oxide emissions during soil preparation and N fertilization of elephant grass (*Pennisetum purpureum* Schum.). *Soil Biology and Biochemistry, 64*, 80-88. https://doi.org/10.1016/j.soilbio.2013.04.007.

Delevatti, L. M., Cardoso, A. S., Barbero, R. P., Leite, R. G., Romanzini, E. P., Ruggieri, A. C., & Reis, R. A. (2019). Effect of nitrogen application rate on yield, forage quality, and animal performance in a tropical pasture. *Science*

Reports, 9(1), 7596. https://doi.org/10.1016/j.soilbio.2013.04.007.

Dominiano, L. F., Santos, M. L., Boote, K. J., Santos, P. M., Pereira, D. H., & Pedreira, B. C. (2020). Physiological responses and forage accumulation of Marandu palisade grass and Mombaça guinea grass to nitrogen fertilizer in the Brazilian forage-based systems. *Grassland Science*, 2020;00: 1-9. https://doi.org/10.1111/grs.12291.

Dupas, E., Buzetti, S., Rabêlo, F. H. S., Sarto, A. L., Cheng, N. C., Galindo, F. S., Dinalli, R. P., & de Niro Gazola, R. (2016). Nitrogen recovery, use efficiency, dry matter yield, and chemical composition of palisade grass fertilized with nitrogen sources in the Cerrado biome. *Australian Journal Crop Science 10*(9), 1330-1338. https://doi.org/10.21475/ajcs.2016.10.09.p7854.

Fenn, L. B., & Hossner, L. R. (1985). Ammonia volatilization from ammonium or ammonium-forming nitrogen fertilizers. In: B. A. Stewart (ed), *Advances in Soil Science* (pp. 123-169). Springer, New York.

Forrestal, P. J., Harty, M., Carolan, R., Lanigan, G. J., Watson, C. J., Laughlin, R. J., McNeill, G., Chambers, B. J., & Richards, K. G. (2016). Ammonia emissions from urea, stabilized urea and calcium ammonium nitrate: insights into loss abatement in temperate grassland. *Soil use Manage*, *32*(1), 92-100. https://doi.org/10.1111/sum.12232.

Galindo, F. S., Buzetti, S., Teixeira Filho, M. C. M., Dupas, E., & Carvalho, F. C. (2018). Management of nitrogen fertilization in the Mombaça grass in function of sources and nitrogen doses. (In Portuguese, with English abstract.) *Revista de Ciências Agrárias, 41*(4), 900-913. http://dx.doi.org/10.19084/RCA18131.

Harrison, R., & Webb, J. (2001). A review of the effect of N fertilizer type on gaseous emissions. *Advances in Agronomy, 73*, 65–108. https://doi.org/10.1016/S0065-2113(01)73005-2.

Haynes, R. J., & Sherlock, R. R. (1986). Gaseous losses of nitrogen. In: R.J. Haynes (ed.) *Mineral Nitrogen in the Plant–Soil System* (pp. 242–302). Academic Press, Nova York.

IFA e IPNI (2017) Assessment of Fertilizer Use by Crop at the Global Level. International Fertilizer Association (IFA) and International Plant Nutrition Institute (IPNI). Disponível em: < https://www.ifastat.org/plant-nutrition > Acesso em: outubro de 2019.

IPCC (2019). Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Guidelines for National Greenhouse Gas Inventories. P. International Panel on Climate Change (IPCC). pp. 546-554.

Jank, L., Barrios, S. C., do Valle, C. B., Simeão, R. M., & Alves, G. F. (2014). The value of improved pastures to Brazilian beef production. *Crop and Pasture Science, 65*(11), 1132-1137. https://doi.org/10.1071/CP13319.

Keeney, D. R., & Nelson, D. W. (1982). Nitrogen: inorganic forms. In: A.L. Page, R. H. Miller & D. R. Keeney (Eds.), *Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties* (2nd ed., pp. 643-698). Madison, WI, Agron. Monogr. https://doi.org/10.2134/agronmonogr9.2.2ed.c33.

Kissel, D. E., Cabrera, M. L., Vaio, N., Craig, J. R., Rema, J. A., & Morris, L. A. (2004). Rainfall timing and ammonia loss from urea in a loblolly pine plantation. *Soil Science Society of America Journal, 68*(5), 1744-1750. https://doi.org/10.2136/sssaj2004.1744.

Lara Cabezas, W. A. R., Korndörfer, G. H., & Motta, S. A. (1997). Volatilização de N-NH_3 na cultura de milho: I. Efeito da irrigação e substituição parcial da ureia por sulfato de amônio. *Revista Brasileira de Ciência do Solo, 21*, 481-487. https://doi.org/10.1590/S0100-06831997000300018.

Li, Y., Huang, L., Zhang, H., Wang, M., & Liang, Z. (2017). Assessment of ammonia volatilization losses and nitrogen utilization during the rice growing season in alkaline salt-affected soils. *Sustainability, 9*(1), 132. https://doi.org/10.3390/su9010132.

Lima, J. E., Nascente, A. S., Leandro, W.M., & Silveira, P. M. D. (2016). *Urochloa ruziziensis* responses to sources and doses of urea. *Revista Brasileira de Engenharia Agrícola e Ambiental, 20*(5), 401-407. https://doi.org/10.1590/1807-1929/agriambi.v20n5p401-407.

Liu, S., Wang, J. J., Tian, Z., Wang, X., & Harrison, S., 2017. Ammonia and greenhouse gas emissions from a subtropical wheat field under different nitrogen fertilization strategies. *Journal Environmental Science, 57*, 196-210. https://doi.org/10.1016/j.jes.2017.02.014.

Longhini, V. Z., Cardoso, A. S., Berça, A. S., Boddey, R. M., Reis, R. A., Dubeux Jr, J. C. B., & Ruggieri, A. C. (2021). Nitrogen supply and rainfall affect ammonia emissions from dairy cattle excreta and urea apllied on warm-climate pastures. *Jounal Environmental Quality* (just acepeted).

Marques, D. L., de Souza Franca, A. F., Oliveira, L. G., Arnhold, E., Ferreira, R. N., Correa, D. S., Bastos, D. C., & Brunes, L. C. (2017). Production and chemical composition of hybrid *Brachiaria* cv. Mulato II under a system of cuts and nitrogen fertilization. *Bioscience Journal, 33*(3), 685-696. https://doi.org/10.14393/BJ-v33n3-32956.

Martha Jr, B. G., Corsi, M., Trivelin, P. C. O., Vilela, L., Pinto, T. L. F., & Barioni, L. G. (2004). Ammonia volatilization loss in Tanzânia grass pasture fertilized with urea in the summer. (In Portuguese, with English abstract.) *Revista Brasilleira de Zootecnia, 33*(6), 2240-2247. https://doi.org/10.1590/S1516-35982004000900009.

McWilliam, J. R. (1978). Response of pasture plants to temperature. In: Wilson, J. R. (Ed.). Plant relation in pasture. Melbourne: CSIRO, p. 17-34.

McRoberts, K. C., Parsons, D., Ketterings, Q. M., Hai, T. T., Quan, N. H., Ba, N. X., Nicholson, C. F., & Cherney, D. J. R. (2017). Urea and composted cattle manure affect forage yield and nutritive value in sandy soils of south-central Vietnam. *Grass and forage Science, 73*, 1–14. https://doi.org/10.1111/gfs.12289.

Mertens, D. R. (1994). Regulation of forage intake. In: G. C. Fahey Jr (ed.), *Forage quality, evaluation and utilization* (pp. 450-493). American Society of Agronomy, Madison. https://doi.org/10.2134/1994.foragequality.c11.

Otto, R., Zavaschi, E., Netto, S., Machado, B. D. A., & Mira, A. B. D. (2017). Ammonia volatilization from nitrogen fertilizers applied to sugarcane straw. *Revista Ciência Agronômica, 48*(3), 413-418. https://doi.org/10.5935/1806-6690.20170048.

Pagano, M. C., Correa, E. J. A., Duarte, N. F., Yelikbayev, B., O'Donovan, A., & Gupta, V. K. (2017). Advances in eco-efficient agriculture: the plant-soil mycobiome. *Agriculture, 7*(2), 14. https://doi.org/10.3390/agriculture7020014.

Pereira, E. I., Nogueira, A. R., Cruz, C. C., Guimarães, G. G., Foschini, M. M., Bernardi, A. C., & Ribeiro, C. (2017). Controlled urea release employing nanocomposites increases the efficiency of nitrogen use by forage. *ACS Sustainable Chemistry & Engineering, 5*(11), 9993-10001.

https://doi.org/10.1021/acssuschemeng.7b01919.

Pinho Costa, K. A., Severiano, E. C., Simon, G. A., Epifanio, P. S., Silva, A. G., Costa, R. R. G., Santos, C. B., & Rodrigues, C. R. (2014). Nutritional Characteristics of *Brachiaria brizantha* Cultivars Subjected to Different Intensities Cutting. *American Journal of Plant Sciences, 5*, 1961-1972. https://doi.org/10.4236/ajps.2014.513210.

Pontes, L. D. S., Baldissera, T. C., Giostri, A. F., Stafin, G., dos Santos, B. R. C., & Carvalho, P. D. F. (2017). Effects of nitrogen fertilization and cutting intensity on the agronomic performance of warm-season grasses. *Grass and Forage Science, 72*(4), 663-675. https://doi.org/10.1111/gfs.12267.

Rochette, P., Angers, D. A., Chantigny, M. H., Macdonald, J.D ., Gasser, M. O., & Bertrand, N., 2009. Reducing ammonia volatilization in a no-till soil by incorporating urea and pig slurry in shallow bands. *Nutrient Cycling in Agroecosystems, 84*(1), 71-80. https://doi.org/10.1007/s10705-008-9227-6.

Sansigolo, A. S. (1989). Variabilidade Interanual da estação chuvosa em São Paulo. *Climanálise, 4*(9), 40-43.

Sanz-Cobena, A., Misselbrook, T., Camp, V., & Vallejo, A. (2011). Effect of water addition and the urease inhibitor NBPT on the abatement of ammonia emission from surface applied urea. *Atmospheric Environment, 45*(8), 1517-1524. https://doi.org/10.1016/j.atmosenv.2010.12.051.

Sarmadi, B., Rouzbehan, Y., & Rezaei, J. (2016). Influences of growth stage and nitrogen fertilizer on chemical composition, phenolics, in situ degradability and in vitro ruminal variables in amaranth forage. *Animal Feed Science and Technology, 215*, 73-84. https://doi.org/10.1016/j.anifeedsci.2016.03.007.

Sommer, S. G., Schjorring, J. K., & Denmead, O. T. (2004). Ammonia emission from mineral fertilizers and fertilized crops. *Advances in agronomy*, *82*, 557-622.

Souza, T. L. D., Guelfi, D. R., Silva, A. L., Andrade, A. B., Chagas, W. F. T., & Cancellier, E. L. (2017). Ammonia and carbon dioxide emissions by stabilized conventional nitrogen fertilizers and controlled release in corn crop. (In Portuguese, with English abstract.) *Ciência e agrotecnologia, 41*(5), 494-510. https://doi.org/10.1590/1413-70542017415003917.

Tian, Z., Wang, J. J., Liu, S., Zhang, Z. Q., Syam, K. D., & Gerald, M. (2015). Application effects of coated urea and urease and nitrification inhibitors on ammonia and greenhouse gas emissions from a subtropical cotton field of the Mississippi delta region. *Science Total Environmental, 533*, 329–338. https://doi.org/10.1016/j.scitotenv.2015.06.147.

United States Department of Agriculture (USDA), Soil Survey Staff. (2014). *Keys to Soil Taxonomy*. (12th ed) United States Department of Agriculture-Natural Resources Conservation Service, Washington, DC.

Viero, F., Bayer, C., Fontoura, S. M. V., & Moraes, R. P. de (2014). Ammonia volatilization from nitrogen fertilizers in no-till wheat and maize in southern Brazil. *Revista Brasileira de Ciência do Solo, 38*(5), 1515-1525. https://doi.org/10.1590/S0100-06832014000500017.

Vlek, P. L. G., & Stumpe, J. M. (1978). Effects of solution chemistry and environmental conditions on ammonia volatilization losses from aqueous systems. *Soil Science Society of America Journal, 42*(3), 416-421. https://doi.org/10.2136/sssaj1978.03615995004200030008x.

Article

Are CH_4, CO_2, and N_2O Emissions from Soil Affected by the Sources and Doses of N in Warm-Season Pasture?[1]

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Abstract: The intensification of pasture production has increased use of nitrogen N fertilizers, a practice that can alter soil greenhouse gas (GHG) fluxes. The objective of this present study was to evaluate the fluxes of CH_4, CO_2, and N_2O 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 N_2O and CO_2 emissions compared to the control treatment. The N_2O 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

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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 (N_2O), fluxes.

Methane (CH_4), carbon dioxide (CO_2), andN_2O are the three major GHGs that play important roles in regulating the global climate. Although CO_2 is cycled in greater quantities through root and rhizomicrobial respiration and soil organic matter (OM) decomposition, the warming potential of CH_4 and N_2O is respectively 25 and 298 times greater than that of CO_2 [4]. CH_4 is produced by methanogenic archaea during anaerobic OM digestion, while N_2O is mainly produced via two microbial processes, namely nitrification and denitrification [5,6].

N addition to the pasture system markedly increase in N_2O emissions [7-10], increases the efficiency of soil carbon sequestration [11] and reduces the atmospheric concentrations of CO_2 [12]. Although the effects of soil N deposition on CH_4 fluxes,

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remain debatable, fertilization may increase the rates of CH_4 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_2O 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_2O emissions from Marandu pastures as well as to determine the applicability of the standard N_2O EF under tropical conditions. We hypothesized that the use of ammonium sulfate as the N source would reduce GHG emissions and that N_2O 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.

Table 1. Soil chemical attributes of the experimental area at the depth of 0 – 20 cm, Jaboticabal– SP.

Experiment	P resin	$S\text{-}SO_4^{2-}$	MO	pH $CaCl_2$	K^+	Ca^{2+}	Mg^{2+}	H+Al	Al^{3+}	CEC	V%
	mg/dm³		g/dm³			mg/dm³					
1	12	16	25	5,6	2,6	36	11	22	0	72	69
2	21	11	37	5,1	5,8	37	17	38	0	98	61

2.2. *Experimental Design and Treatments*

Two experiments were performed on Marandu pastures to evaluate CH_4, CO_2, and N_2O 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 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_2O 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 m3. 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 (t0), 20 minutes (t20) and 40 minutes (t40) 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_2O 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 (μg CH_4 m^{-2} h^{-1}), CO_2 (mg C m^{-2} h^{-1}), and N_2O (μg N_2O 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 of the 0–20 cm depth 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 50 mm in diameter and 50 mm in height. The WFPS was calculated from the gravimetric water content and bulk density using 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

CH_4, CO_2, and N_2O 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, NH_4–N, NO_3–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 mm) 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).

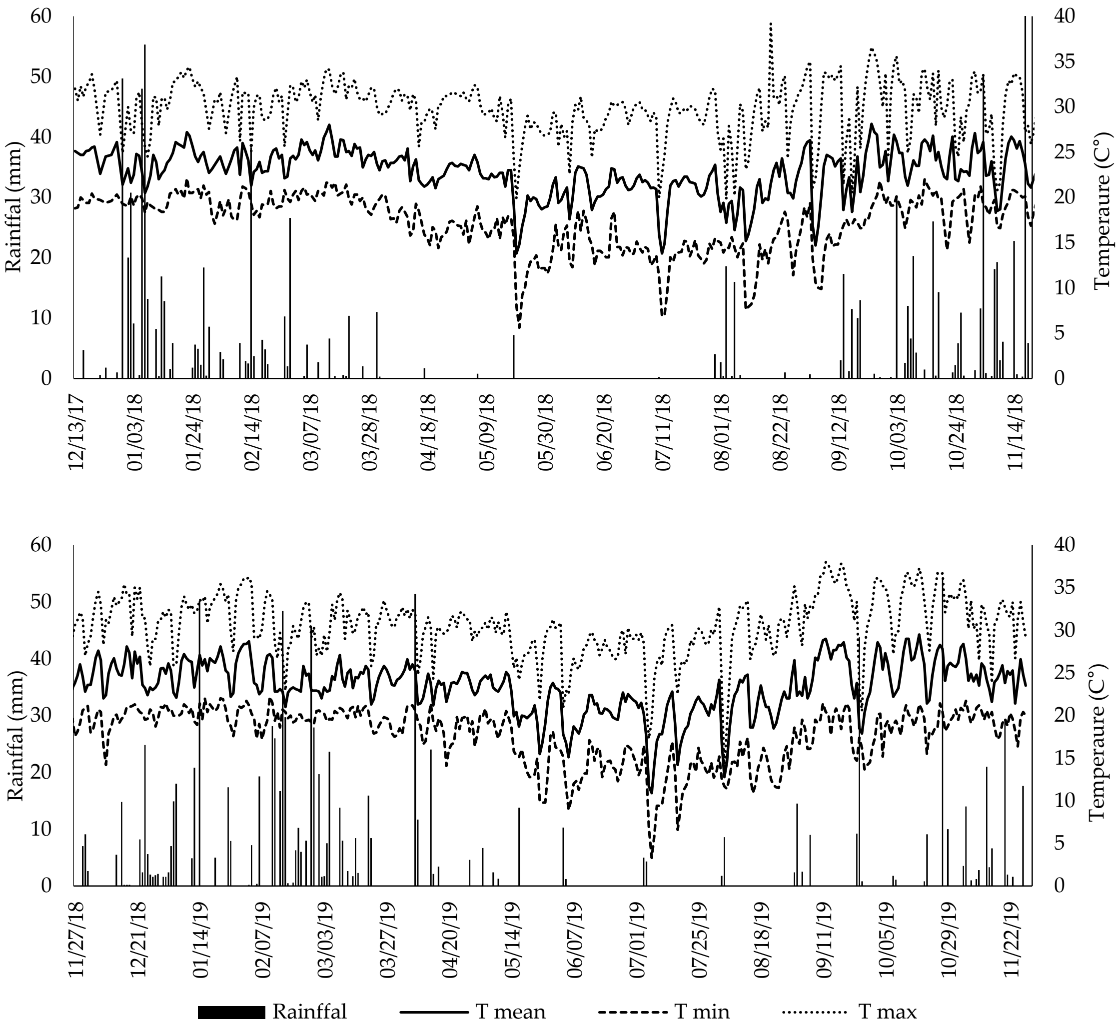

Figure 1. Daily air temperature (minimum, medium and maximum) and daily rainfall. Data were obtained from the Agrometeorological Station, Department of Exact Sciences, FCAV / UNESP, located 1.5 km from the experiment site. Experiment 1 (a) and 2 (b).

3.2. CH_4 flux

In the first experiment, CH_4 production was higher in spring and uptake rates were higher in winter (Figure 3a–c). In the second experiment, CH_4 emissions were higher in summer but CH_4 consumption was higher in the spring of 2018 and summer of 2019 (Figure 3d–f). In both experiments, the peak CH_4 emissions were higher using ammonium sulfate as the N source (387, 404, and 523 μg CH_4 m^{-2} h^{-1} in September 2018 and 149, 671, and 745 μg CH_4 m^{-2} h^{-1} in January 2019 at doses of 90, 180, and 270 kg N ha^{-1}, 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).

The CH_4 fluxes were correlated with NH_4–N content, ambient temperature, and CO_2 emissions in both experiments. In addition, CH_4 flux was positively correlated with soil temperature in the first experiment but negatively correlated with %WFPS in the second experiment (Table 2).

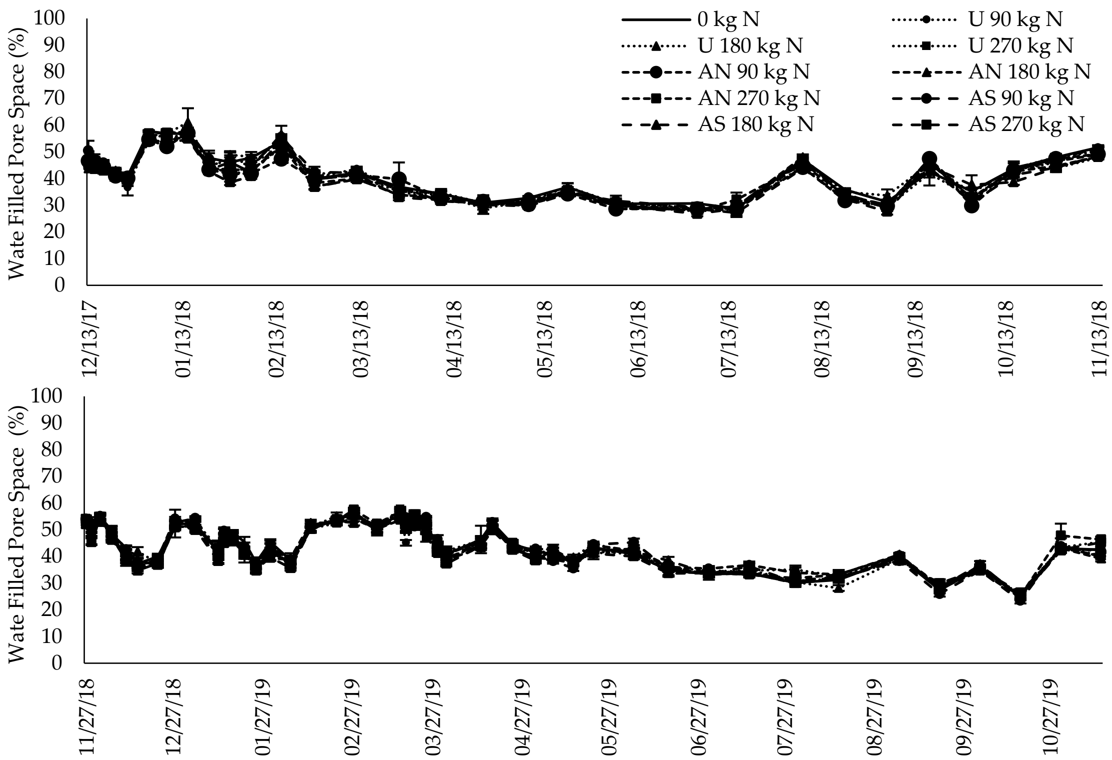

Figure 2. Descriptive averages of water–filled pore space (%) in experiment 1 (a) and 2 (b).

3.3. CO_2 flux

In both experiments, the highest CO_2 fluxes occurred in summer and the lowest in winter (Figure 4). The highest emission peaks of 1149, 1444, and 1185 mg CO_2 m^{-2} h^{-1} were recorded in December 2017 (Figure 4a–c) and of 1563, 1860, and 1574 mg CO_2 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, CO_2 flux was positively correlated with soil NH_4–N and NO_3–N levels and ambient temperature but negatively correlated with soil temperature. In the second experiment, CO_2 flux was positively correlated with %WFPS and ambient temperature (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)[a]	**N_2O**	**CH_4**	**CO_2**	**N_2O**	**CH_4**	**CO_2**
Air T°	+ (<0.01)	+ (<0.001)	+ (<0.001)	- (<0.001)	- (<0.01)	+ (<0.001)
Soil T°	- (<0.001)	+ (<0.001)	- (<0.001)	+ (<0.001)	NS	NS
% WFPS	NS	NS	NS	- (<0.001)	- (<0.01)	+ (<0.001)
Moisture	NS	NS	NS	+ (<0.001)	NS	NS
NH_4-N	+ (<0.01)	+ (<0.001)	+ (<0.05)	- (<0.05)	- (<0.01)	NS
NO_3-N	NS	NS	+ (<0.01)	NS	NS	NS
CO_2	+ (<0.001)	+ (<0.001)		+ (<0.001)	+ (<0.001)	

[a] Positive, negative, or not significant; p values within brackets for the factor in the best fitted model selected by Akaike Information Criterion. T° - Temperature. WFPS - Wate Filled Pore Space.

3.4. N_2O flux

Peak N_2O 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 μg N_2O m^{-2} h^{-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 μg N_2O m^{-2} h^{-1} (Figure 5c). Peaks N_2O emissions were also recorded after precipitation events following a long dry period (Figure 1a) in August and September 2018 (Figure 5a–c).

Negative N_2O fluxes were observed in approximately 32% of all sampling events, particularly in winter, when %WFPS was the lowest (Figure 2a,b). The highest N_2O consumption rate was recorded on 13 November 2018, with mean values of 77, 98, and 58 μg N_2O m^{-2} h^{-1} using urea, ammonium nitrate, and ammonium sulfate as the N sources, respectively (Figure 5a–c).

In the second experiment, N_2O emissions were higher in summer, with peak mean fluxes of 257, 340, and 273 μg N_2O m^{-2} h^{-1} recoded in November 2018 and of 265, 134, and 157 μg N_2O 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_2O m^{-2} h^{-1} were observed throughout the experiment, mainly in November 2018 and May and July 2019 (Figure 5d–f).

N_2O flux was significantly correlated with ambient and soil temperature and NH_4–N content. In both experiments, N_2O fluxes were positively correlated with CO_2 fluxes. In the second experiment, N_2O fluxes were negatively correlated with %WFPS and positively correlated with soil moisture (Table 2).

The effects of ambient and soil temperature on N_2O fluxes were dependent on fertilization management. At high N doses, N_2O fluxes increased with temperature; however, when fertilization was fractioned, N_2O fluxes were negatively correlated with temperature. The correlation between soil temperature and N_2O flux was positive under single fertilization and negative under fertilization fractionation.

3.5. N-inorganic

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}, 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_2O, CH_4, and CO_2 fluxes in the first experiment and with N_2O 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).

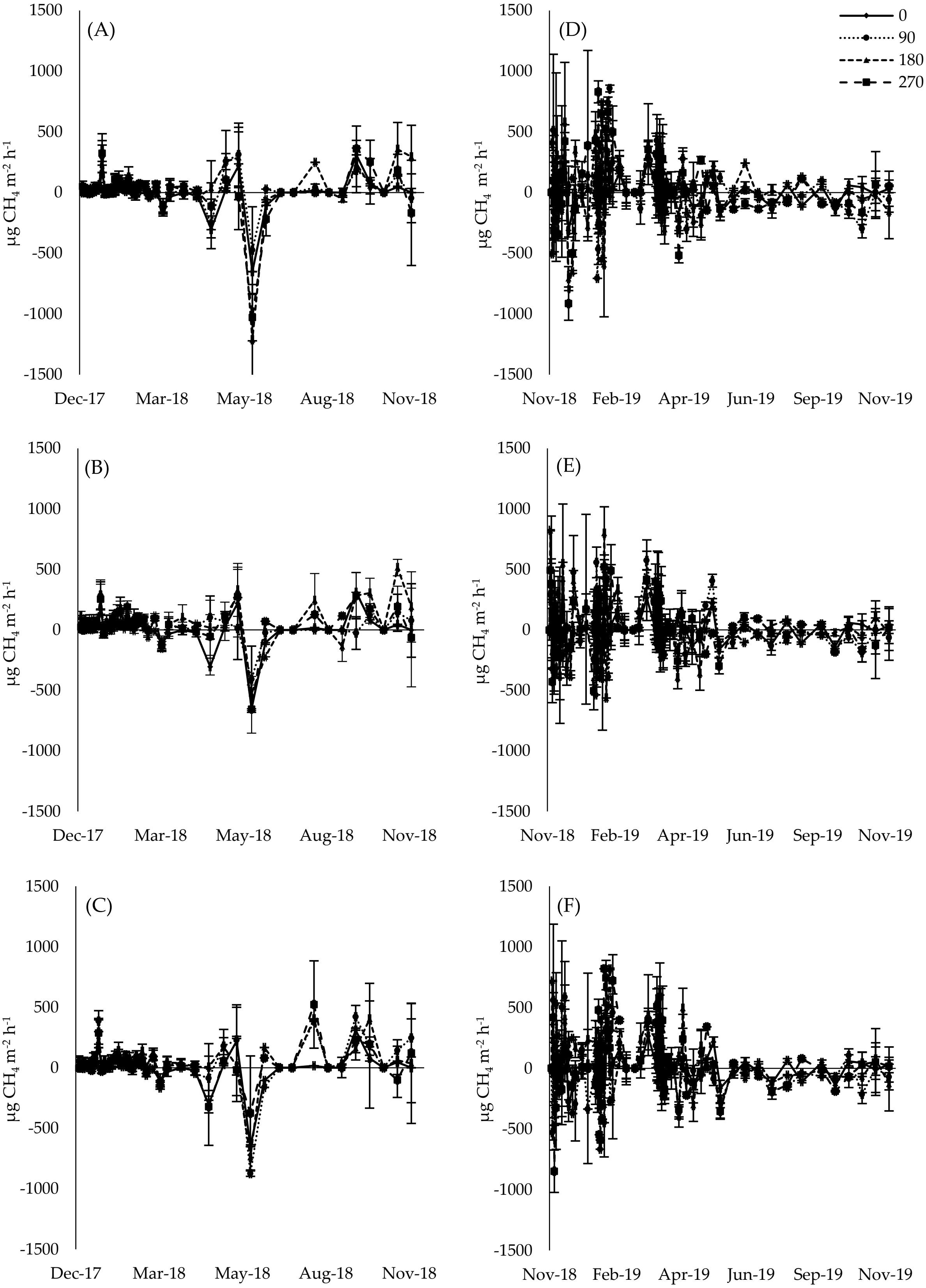

Figure 3. Descriptive of average CH_4 fluxes (μg m^{-2} h^{-1}) from pastures managed with N fertilizers in two experiments. (A) Urea, (B) ammonium nitrate, and (C) ammonium sulfate in experiment 1. (D) Urea, (E) ammonium nitrate, and (F) ammonium sulfate in experiment 2.

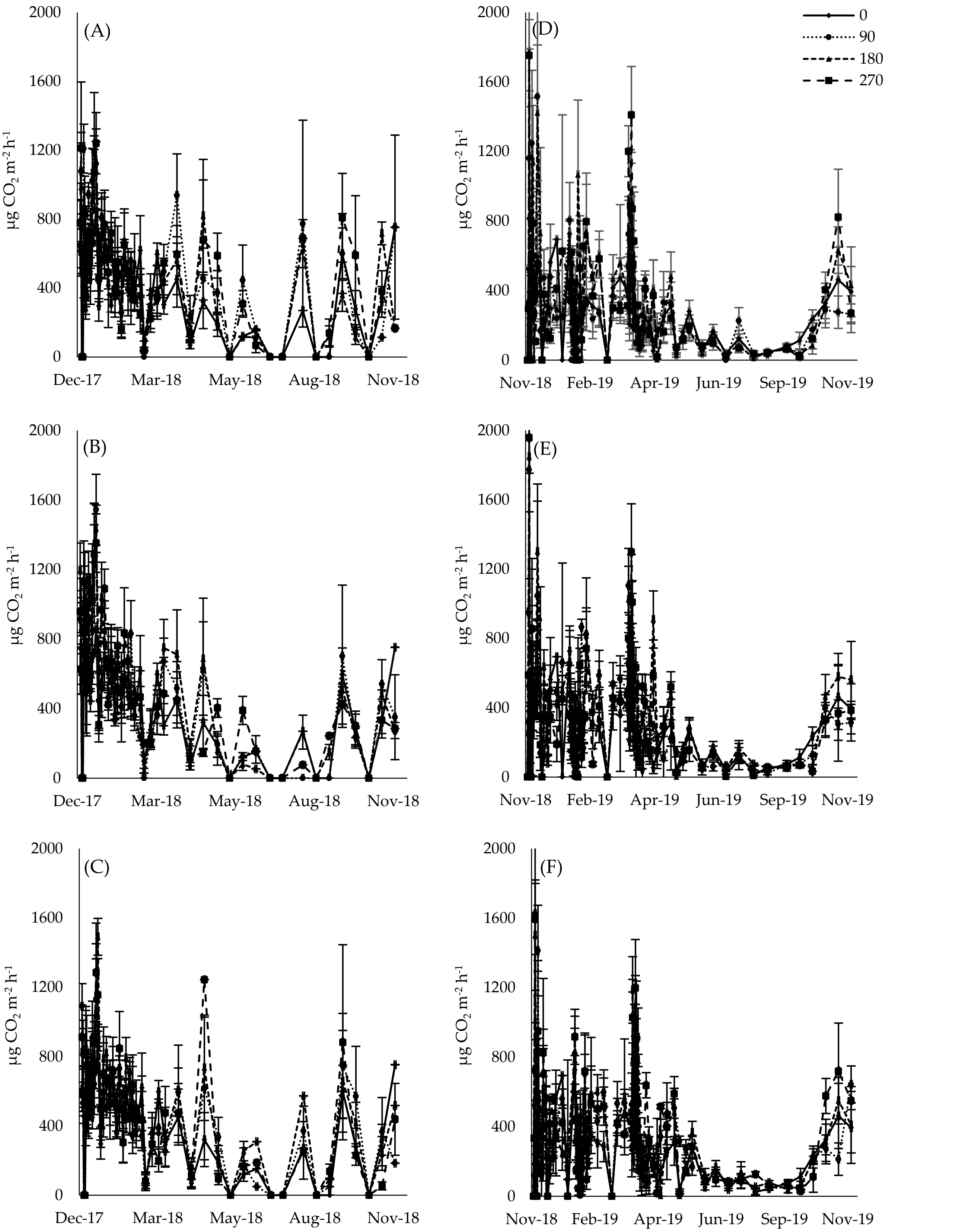

Figure 4. Descriptive average of CO_2 fluxes (mg m^{-2} h^{-1}) of pastures fertilized with N fertilizers in two experiments: experiment 1: (A) urea, (B) ammonium nitrate, (C) ammonium sulfate; experiment 2: (D) urea, (E) ammonium nitrate, (F) ammonium sulfate.

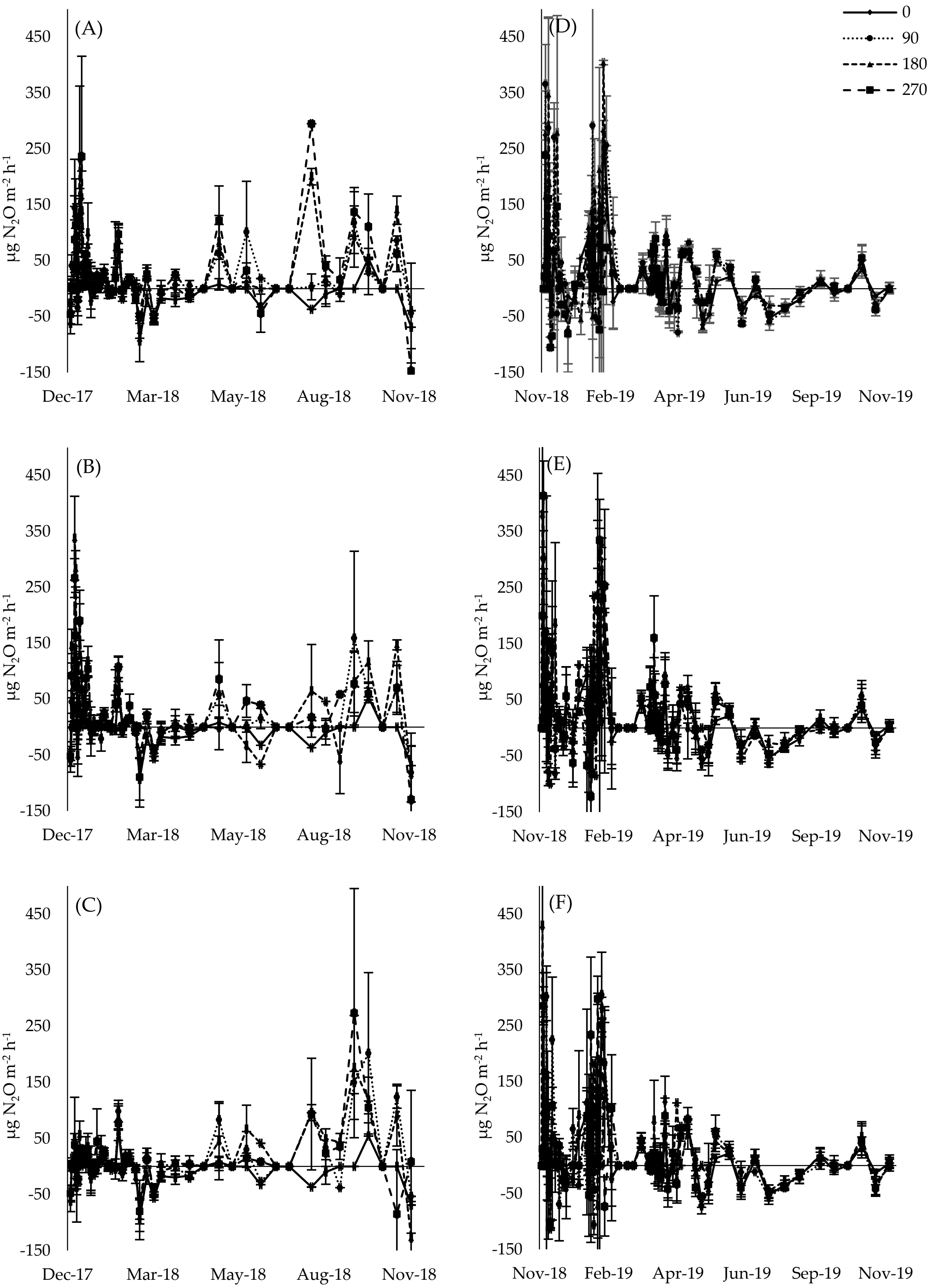

Figure 5. Descriptive averages of N_2O fluxes (μg m^{-2} h^{-1}) from pastures managed with N fertilizers in two experiments. (A) Urea, (B) ammonium nitrate, and (C) ammonium sulfate in experiment 1. (D) Urea, (E) ammonium nitrate, and (F) ammonium sulfate in experiment 2.

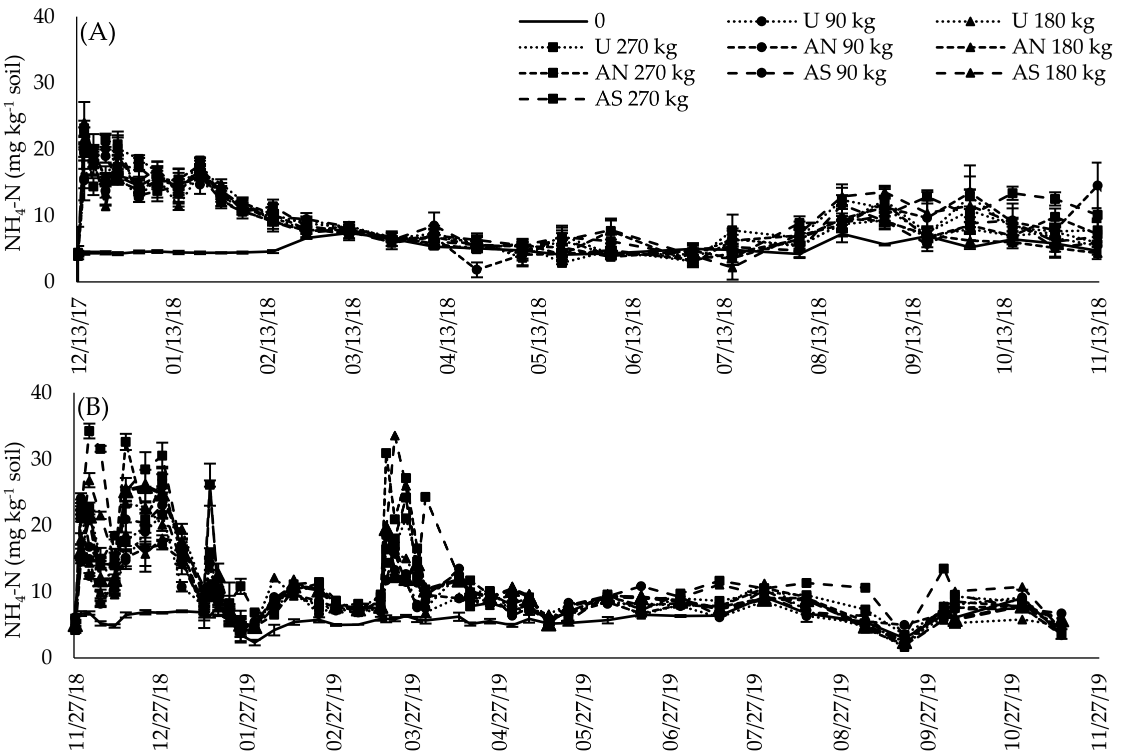

Figure 6. Descriptive averages of NH_4–N content of soil (mg NH_4–N kg^{-1} dry soil). Experiment 1 (A) and 2 (B).

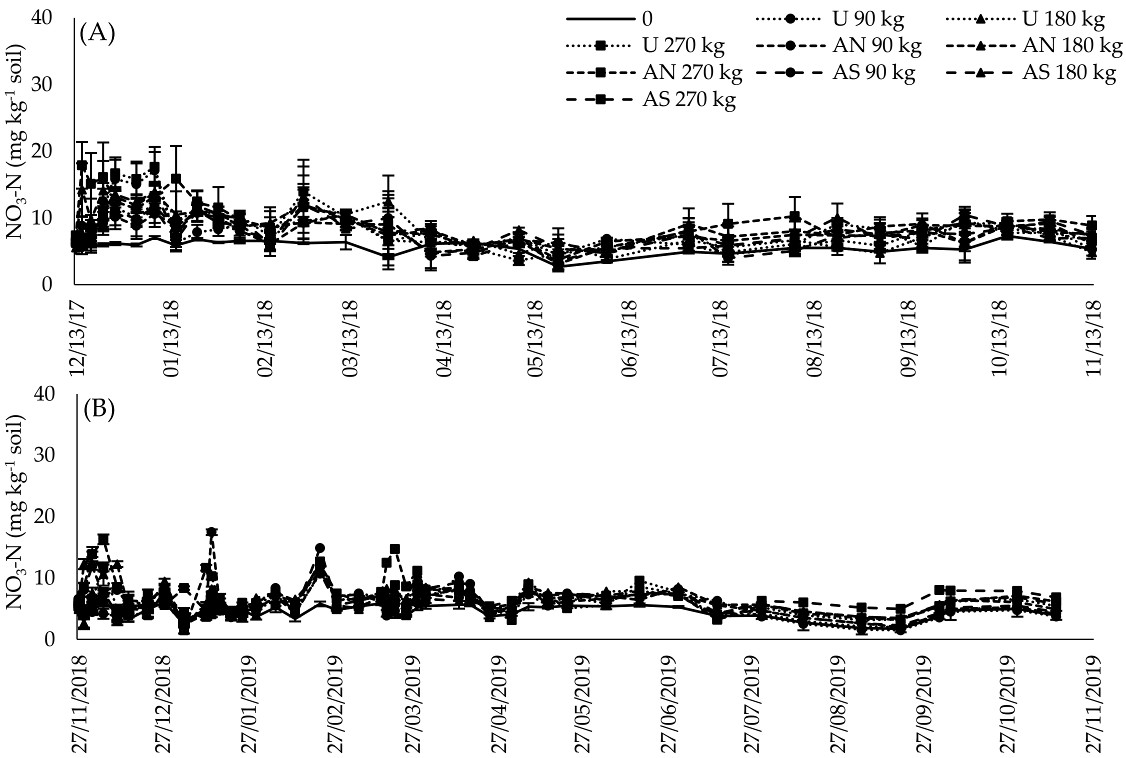

Figure 7. Descriptive averages of NO_3–N content of soil (mg NO_3–N kg^{-1} dry soil). Experiment 1 (A) and 2 (B).

3.6. *Cumulative GHG Emissions*

N sources and doses did not significantly affect CH_4, CO2, and N_2O cumulative emissions in either experiment ($p > 0.05$). In contrast, N applied as single fertilization, regardless of the source, promoted CO_2 and N_2O 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_2O emissions under N fertilization were 1909.0 mg CO_2 m^{-2} and 79.6 mg N_2O m^{-2}, respectively. In the second experiment, the mean CO_2 and N_2O 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_2O emissions by 28% and 151%, respectively, compared with the control treatment.

The N_2O EF did not differ among the evaluated fertilizer sources and was lower in the second experiment when the fertilization was fractionated (Table 4).

Table 3. Cumulative CH_4 (mg CH_4 m^{-2}), CO_2 (mg CO_2 m^{-2}) and N_2O (mg N_2O m^{-2}) emissions from Marandu pastures fertilized with different N sources and doses in two experiments.

GHG	Source	Emission	
		Experiment 1	Experiment 2
CH_4	Urea	25.5±82.4[a]	20.4±83.6[a]
	Ammonium nitrate	177.4±90.4[a]	-3.9±88.4[a]
	Ammonium sulfate	162.6±109.2[a]	2.6±134.8[a]
	Control	-99.8±40.8[a]	-77.4±33.5[a]
CO_2	Urea	2208.9±102.8[a]	1796.2±132.3[a]
	Ammonium nitrate	2206.5±77.6[a]	1887.7±99.6[a]
	Ammonium sulfate	2115.6±113.4[a]	2043.5±170.3[a]
	Control	1523.4±66.6[b]	1486.6±170.3[a]
N_2O	Urea	153.4±27.7[a]	94.7±20.0[a]
	Ammonium nitrate	122.0±33.7[ab]	75.3±14.9[a]
	Ammonium sulfate	158.9±28.9[a]	68.7±16.1[a]
	Control	-26.6±4.2[b]	31.7±22.9[a]

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

Table 4. Anual N_2O emission fator (g N per 100 g N applied).

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

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

4. Discussion

4.1. *CH_4 flux*

In the present study, the highest CH_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_4 production, with temperatures around 35 °C being the most suitable for CH_4 formation in soil [33–35].

Throughout the experimental period, CH_4 fluxes were correlated with ambient temperature. In 2018, soil temperature also strongly affected CH_4 fluxes (Table 2), with higher CH_4 consumption during the coldest period (Figure 3a–c). CH_4 consumption in grasslands is significantly correlated with ambient temperature and soil temperature and moisture [8,36], which are the key factors determining CH_4 uptake; as such, moisture content around 21–24% and temperatures near 10 °C are conducive to CH_4 consumption [37,38].

In the present study, we noted a positive correlation between ambient temperature and CH_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_4 emissions and temperature in Marandu pastures using conventional urea, and Jiang et al. [40] observed a positive correlation between CH_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_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_2/CO_2 and acetate as precursors to produce CH_4; meanwhile, at low temperatures, methanogens of the Methanosaetaceae family are dominant, which can only use acetate as the CH_4 precursor [42–44]. This explains the higher CH_4 emission observed in summer (Figure 3) and its positive relationship with CO_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 CH_4 and CO_2 fluxes.

The effects of mineral fertilization on soil CH_4 emissions reported in the literature are complex and sometimes contradictory [10,17,46]. In the present study, the NH_4–N content of soil was closely related to CH_4 emissions (Table 2), and the largest variations in fluxes occurred after fertilization in the second experiment, when the NH_4–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 CH_4 fluxes were greater following N application and CH_4 emissions were closely and directly related to soil NH_4–N content.

The positive relationship between CH_4 fluxes and NH_4–N content is attributed to the inhibitory effect of NH_4–N on methanotrophy, during which CH_4 in the soil is oxidized; thus, when a large amount of NH_4–N is available, methanotrophic bacteria oxidize NH_4–N at the expense of CH_4 [47,48], leading to higher net CH_4 emissions from the soil.

In the present study, the relationship between NH_4–N and CH_4 fluxes was dependent on the amount of N applied. At lower N doses under fertilization fractionation, there was a negative correlation between NH_4–N and CH_4 fluxes, while at higher N doses under single fertilization, CH_4 fluxes increased with NH_4–N content. Consistent with our results, Zhang et al. [13] have reported a negative correlation between CH_4 consumption and NH_4–N content, resulting in positive CH_4 emission from the soil.

4.2. CO_2 flux

In the present study, CO_2 fluxes were higher during summer, similar to N_2O and CH_4 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 CO_2 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 CO_2

production by roots and organisms and, consequently, the gaseous exchange between the soil and the atmosphere.

Precipitation events drive the seasonal variations in CO_2 fluxes; thus, increased CO_2 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 CO_2 release [50,53].

Another factor that can increase CO_2 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 CO_2 fluxes [39,49].

CO_2 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 $N–NH_4$ and $NO_3–N$ 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 CO_2 flux [10].

According to Fang et al. [56], CO_2 emissions were positively correlated with $N–NH_4$ content and aboveground biomass, highlighting the relevance of autotrophic respiration. Moreover, the authors proposed that N addition to the soil affects CO_2 fluxes by altering plant growth and renewing soil C reserves. N fertilization likely alters the major pathways related to CO_2 fluxes since it also increases forage accumulation [57]; therefore, the response of CO_2 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_2O flux

The higher N_2O 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_2O 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_2O 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_2O flux and %WFPS in the first experiment and their negative correlation in the second experiment (Table 2), as N_2O emission via nitrification was favored under the conditions of lower %WFPS.

The correlation between soil moisture and N_2O emissions (Table 2) was comparable to that observed in other experiments on grasslands reporting greater variations in N_2O emissions coinciding with the periods of higher precipitation [10,36,39,62,63].

The N_2O fluxes recorded in the present study were similar to those reported previously for tropical soils. Low N_2O emissions [9,64–67] are attributed to denitrification as the main process of N_2O 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_2O 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_2O 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_2O emissions [68].

Likewise, Jantalia et al. [64] reported that N_2O 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_2O 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_2O 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_2O 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_2O emissions from soils by stimulating microbial activity. This explains the positive correlation between NH_4–N content and N_2O fluxes at high N doses under single fertilization as opposed to that at low N doses under fertilizer fractionation (Table 2).

The High availability of mineral N in the soil combined with high moisture can induce N2O fluxes [68], provided that no other important limiting factor operates in the system; thus, increased N2O emissions during the rainy season in the present study can be explained by elevated NH4–N levels after fertilization. Similarly, Campanha et al. [66] observed that higher mineral N content immediately after fertilization promoted N2O 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_2O 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_2O emission was reduced and N_2O consumption was enhanced.

Changes in soil moisture and temperature could explain up to 95% of the temporal variation in soil N_2O emissions [72]. In both experiments, soil and ambient temperatures were the key drivers of variations in N_2O fluxes (Table 2), with emission peaks occurring in warmer months (Figures 1 and 5).

Increases in N_2O 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_2O 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_2O production is mediated by soil microbial communities, specifi- cally 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_2O fluxes may be ex- plained 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_2O production [73], even though denitrification was not the main pathway of N_2O 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_2O 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 monooxygenase 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_2O emissions.

In the present study, N_2O 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_2O emissions following N fertilization [10,39,82]. However, the factors involved in N_2O production and consumption in soils are complex and may generate different results, although N addition does not significantly affect N_2O 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_2O 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_2O emissions from the soil. For instance, amidic and ammoniacal sources are expected to increase emissions by affecting N_2O formation through nitrification and denitrification [86], while in nitric and nitrate fertilizers, which only produce N_2O through denitrification, are expected to reduce emissions (Table 3).

4.5 *EFs of N_2O*

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_2O. In the present study, only the EFs of N_2O 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_2O 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_2O emissions from soil.

In another study on Marandu pastures near our experimental area, Cardoso et al. reported EFs of N_2O 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_2O 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_2O 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 pro- moted CO_2 and N_2O emissions and seasons regulated changes in GHG fluxes throughout the year.

Under fertilization fractionation, N_2O 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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References

1. Dupas, E.; Buzetti, S.; Rabêlo, F.H.S.; Sarto, A.L.; Cheng, N.C.; Galindo, F.S.; Dinalli, R.P.; de Niro Gazola, R. Nitrogen recovery, use efficiency, dry matter yield, and chemical composition of palisade grass fertilized with nitrogen fertilizers in the Cerrado biome. *Aust. J. Crop Sci.* **2016**, *10(9)*, 1330. https://doi.org/10.21475/ajcs.2016.10.09.p7854.
2. Pires, M.V.; da Cunha, D.A.; Carlos, S.M.; Costa, M.H. Nitrogen-use efficiency, nitrous oxide emissions, and cereal production in Brazil: current trends and forecasts. *Plos One* **2015**, *10*, 1-19. https://doi.org/10.1371/journal.pone.0135234.
3. Tiritan, C.S.; Bull, L.T.; Crusciol, C.A.C.; Carmeis Filho, A.C.A.; Fernandes, D.M.; Nascente, A.S. Tillage system and lime application in a tropical region: soil chemical fertility and corn yield in succession to degraded pastures. *Soil Till. Res*. **2016,** 155, 437-447. https://doi.org/10.1016/j.still.2015.06.012.
4. Intergovernmental Panel on Climate Change – IPCC, 2013. Climate Change 2013: the physical Science basis - Contribution of working group I to the fifth assessment report of the intergovernamental panel on climate change. New York: Cambridge University Press.
5. Firestone, M.K.; Davidson E.A. Microbiological basis of NO and N_2O production and consumption in soil. Exchange of trace gases between terrestrial ecosystems and the atmosphere **1989,** *47*, 7-21.
6. Kreuzer, M.; Hindrichen, I.K. Methane mitigation in ruminants by dictary means: The role of their methane emission from manure. *Int Congr* **2006**, *1293*, 199– 208. https://doi.org/10.1016/j.ics.2006.01.015.
7. De Morais, R.F.; Boddey, R.M.; Urquiaga, S.; Jantalia, C.P.; Alves, B.J. Ammonia volatilization and nitrous oxide emissions during soil preparation and N fertilization of elephant grass (*Pennisetum purpureum Schum*.). *Soil Biol Biochem* **2013,** *64*, 80-88. https://doi.org/10.1016/j.soilbio.2013.04.007.
8. Cardoso, A.S.; Oliveira, S.C.; Janusckiewicz, E.R.; Brito, L.F.; Morgado, E.S.; Reis, R.A.; Ruggieri, A.C. Seasonal effects on ammonia, nitrous oxide, and methane emissions for beef cattle excreta and urea fertilizer applied to a tropical pasture. *Soil Tillage Res* **2019,** *194*, 104341. https://doi.org/10.1016/j.still.2019.104341.
9. Nascimento, A.F.; de Oliveira, C.M.; Pedreira, B.C.; Pereira, D.H.; Rodrigues, R.R.A., Nitrous oxide emissions and forage accumulation in the Brazilian Amazon forage-livestock systems submitted to N input strategies. *Grassl. Sci* **2020**. https://doi.org/10.1111/grs.12287.
10. Raposo, E.; Brito, L.F.; Janusckiewicz, E.R.; Oliveira, L.F.; Versuti, J.; Assumpção, F.M.; Cardoso, A.S., Sinischalchi, D.; Delevatti, L.M.; Malheiros, E.B.; Ruggieri, A.C.; Reis, R.A., Greenhouse gases emissions from tropical grasslands affected by nitrogen fertilizer management. *Agron. J.* **2020.** https://doi.org/10.1002/agj2.20385.
11. Li, X.G.; Jia, B.; LV, J.; Ma, Q.; Kuzyakov, Y.; Li, F.M. Nitrogen fertilization decreases the decomposition of soil organic matter and plant residues in planted soils. *Soil Biol Biochem* **2017,** *112*, 47-55. https://doi.org/10.1016/j.soilbio.2017.04.018.
12. Skinner, R.H. Nitrogen fertilization effects on pasture photosynthesis, respiration, and ecosystem carbon content. *Agric. Ecosyst. Environ* **2013**, *172*, 35-41. https://doi.org/10.1016/j.agee.2013.04.005.
13. Zhang, L.; Hou, L.; Guo, D.; Li, L.; Xu, X., Interactive impacts of nitrogen input and water amendment on growing season fluxes of CO_2, CH_4, and N_2O in a semiarid grassland, Northern China. *Sci. Total Environ*. **2017**, *578*, 523-534. https://doi.org/10.1016/j.scitotenv.2016.10.219.
14. Vilarrasa-Nogué, M.; Teira-Esmatges, M.R.; Pascual, M.; Villar, J.M.; Rufat, J. Effect of N dose, fertilisation duration and application of a nitrification inhibitor on GHG emissions from a peach orchard. *Sci. Total Environ*. **2020**, *699*, 134042. https://doi.org/10.1016/j.scitotenv.2019.134042.
15. Liu, L.; Greaver, T.L.A. Review of nitrogen enrichment effects on three biogenic GHGs: the CO_2 sink may be largely offset by stimulated N_2O and CH_4 emission. *Ecol. Lett*. **2009**, *12*(10), 1103-1117. https://doi.org/10.1111/j.1461-0248.2009.01351.x.
16. Hawthorne, I.; Johnson, M.S.; Jassal, R.S.; Black, T.A.; Grant, N.J.; Smukler, S.M. Application of biochar and nitrogen influences fluxes of CO_2, CH_4 and N_2O in a forest soil. *J. Environ. Manage*. **2017**, *192*, 203-214. https://doi.org/10.1016/j.jenvman.2016.12.066.
17. Cardoso, A. S.; Quintana, B.G.; Janusckiewicz, E.R.; Brito, L.F.; da Silva Morgado, E.; Reis, R.A.; Ruggieri, A.C. How do methane rates vary with soil moisture and compaction, N compound and rate, and dung addition in a tropical soil?. *Int. J. Biometeorol.* **2018**, *63*(11), 1533-1540. https://doi.org/10.1007/s00484-018-1641-0.
18. Peters, M.; Rao, I.M.; Fisher, M.J., Subbarao, G., Martens, S., Herrero, G., Hyman, G. et al. Tropical forage-based systems to mitigate greenhouse gas emissions. 2012. In C.H. Hershey (Ed.), Eco-Efficiency: From vision to reality. Valle del Cauca, Colombia: Centro Internacional de Agricultura Tropical (CIAT).
19. IPCC (2019). Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Guidelines for National Greenhouse Gas Inventories. P. International Panel on Climate Change (IPCC). Chapter 11_Volume 4.
20. Bruulsema, T.; Lemunyon, J.; Herz, B. Know your fertilizer rights. *Crops and Soils* **2009**, *42*(2), 13-18.
21. Del Grosso, S.J.; Ojima, D.S.; Parton, W.J.; Stehfest, E.; Heistemann, M.; DeAngelo, B.; Rose, S. Global scale DAYCENT model analysis of greenhouse gas emissions and mitigation strategies for cropped soils. *Glob Planet Change* **2009,** *67*(1-2), 44-50. https://doi.org/10.1016/j.gloplacha.2008.12.006.
22. Signor, D.; Cerri, C. E. P. Nitrous oxide emissions in agricultural soils: a review. *Pesqui. Agropecu. Trop*. **2013**, *43*(3), 322-338. https://doi.org/10.1590/S1983-40632013000300014.
23. Tan, I. Y.; van Es, H. M.; Duxbury, J. M.; Melkonian, J. J.; Schindelbeck, R. R.; Geohring, L. D.; Moebius, B. N. et al. Single-event nitrous oxide losses under maize production as affected by soil type, tillage, rotation, and fertilization. *Soil Tillage Res* **2009**, *102*(1), 19-26. https://doi.org/10.1016/j.still.2008.06.005.

24. Viard, A.; Hénault, C.; Rochette, P.; Kuikman, P.; Flénet, F.; Cellier, P. Le protoxyde d'azote (N_2O), puissant gaz à effet de serre émis par les sols agricoles: méthodes d'inventaire et leviers de réduction. *OCL* **2013**, *20*(2), 108-118. https://doi.org/10.1051/ocl.2013.0501.
25. IUSS. 2006. World reference base for soil refertilizers 2006. World Soil Refertilizers Reports. FAO, Rome, Italy.
26. Mosier, A.R., 1989. Chamber and isotope techniques. In: Andreae, M.O., Schimel, D.S. (Eds.), Exchange of Traces Gases between Terrestrial Ecosystems and the Atmosphere: Report of the Dahlem Workshop. Wiley, Germany, pp. 175–187.
27. Alves, B. J.; Smith, K. A.; Flores, R. A.; Cardoso, A. S.; Oliveira, W. R.; Jantalia, C. P.; Boddey, R. M. et al. Selection of the most suitable sampling time for static chambers for the estimation of daily mean N_2O flux from soils. *Soil Biol Biochem* **2012**, *46*, 129-135. https://doi.org/10.1016/j.soilbio.2011.11.022.
28. Cardoso, A.S.; Alves B.J.R.; Urquiaga, S.; Boddey, R.M. Effect of volume of urine and mas of feces on N_2O and CH_4 emissions of dairy cow excreta in a tropical pasture. *Anim. Product. Sci.* **2016**. https://doi.org/10.1071/AN15392.
29. Kempers, A.J., Zweers, A. Ammonium determination in soil extracts by the salicylate method. *Commun Soil Sci Plant Anal* **1986**, *17*, 715–723.
30. Miyazawa, M.; Pavan, M.A.; Block, M.F.M. Spectrophotometry determination of nitrate in soil extracts without chemical reduction. *Pesqui. Agropecu. Bras.* **1985**, *20*, 29–133.
31. Olsen, K.K. Multiple wavelength ultraviolet determinations of nitrate concentration, method comparisons from the preakness brook monitoring project, October 2005 to October 2006. *Water Air Soil Pollut*. **2008**, *187*, 195–202. https://doi.org/10.1007/s11270-007-9508-8.
32. André, R.G.B.; da Anunciação, Y.M.T. A precipitação pluvial provável em Jaboticabal, São Paulo. *Agrometeoros* **2018**, *25*(2). http://dx.doi.org/10.31062/agrom.v25i2.26201.
33. Boon, P.I.; Mitchell, A. Methanogenesis in the sediments of an Australian freshwater wetland, Comparison with aerobic decay, and factors controlling methanogenesis. *FEMS Microbiol Ecol*. **1995**, *18*, 175–190, https://doi.org/10.1111/j.1574-6941.1995.tb00175.x.
34. Miyajima, T.; Wada, E.; Hanba, Y.T.; Vijarnsorn, P., Anaerobic mineralization of indigenous organic matters and methanogenesis in tropical wetland soils. *Geochim Cosmochim Acta* **1997**, *61*, 3739–3751. https://doi.org/10.1016/S0016-7037(97)00189-0.
35. Rath, A K., Ramakrishnan, B., Sethunathan, N. Temperature dependence of methane production in tropical rice soils. *Geomicrobiol. J*. **2002**, *19*, 581–592. https://doi.org/10.1080/01490450290098595.
36. Mazzetto, A.M.; Barneze, A.S.; Feigl, B.J.; Van Groenigen, J.W.; Oenema, O.; Cerri, C.C. Temperature and moisture affect methane and nitrous oxide emission from bovine manure patches in tropical conditions. *Soil Biol. Biochem*. **2014**, *76*, 242–248. https://doi.org/10.1016/j.soilbio.2014.05.026.
37. Castro, M.S.; Steudler, P.A.; Melillo, J.M.; Aber, J.D.; Bowden, R.D. Factors controlling atmospheric methane consumption by temperate forest soils. *Global Biogeochem Cuts* **1995**, *9*(1), 1–10. https://doi.org/10.1029/94GB02651.
38. Dasselaar, P.A.; Beusichem, M.V.; Oenema, O. Effects of soil moisture content and temperature on methane uptake by grassland on sandy soils. *Plant and Soil* **1998**, *204*(2), 213–222. https://doi.org/10.1023/A:1004371309361.
39. Cardoso, A. S.; Brito, L.F.; Janusckiewicz, E.R.; Morgado, E.S.; Barbero, R.P.; Koscheck, J.F.W.; Reis, R.A.; Ruggieri, A.C. Impact of grazing intensity and seasons on greenhouse gas emissions in tropical grassland. *Ecosystems* **2016**, *20*(4), 845-859. https://doi.org/10.1007/s10021-016-0065-0.
40. Jiang, C.; Yu, G.; Fang, H.; Cao, G.; Li, Y. Short-term effect of increasing nitrogen deposition on CO_2, CH_4 and N_2O fluxes in an alpine meadow on the Qinghai-Tibetan Plateau, China. *Atmos. Environ*. **2010**, *44*(24), 2920-2926. https://doi.org/10.1016/j.atmosenv.2010.03.030.
41. Agostinetto, D.; Fleck, N.G.; Rizzardi, M.A.; Balbinot Jr., A.A. Potencial de emissão de metano em lavouras de arroz irrigado. *Cienc. Rural* 2002, *32*(6), 1073-1081. https://doi.org/10.1590/S0103-84782002000600026.
42. Westermann, P. Temperature regulation of methanogenesis in wetlands. *Chemosphere* **1993**, *26*, 321–328. https://doi.org/10.1016/0045-6535(93)90428-8.
43. Wagner, D.; Pfeiffer, E.M., Two temperature optima of methane production in a typical soil of the Elbe river marshland. *FEMS Microbiol. Ecol*. **1997**, *22*, 145–153. https://doi.org/10.1111/j.1574-6941.1997.tb00366.x.
44. Chin, K.; Lukow, T.; Conrad, R. Effect of temperature on structure and function of the methanogenic archaeal community in an anoxic rice field soil. *Appl Environ Microbiol* **1999**, *65*(6), 2341-2349. https://doi.org/10.1128/AEM.65.6.2341-2349.
45. Chu, H.; Hosen, Y.; Yagi, K. NO, N_2O, CH_4 and CO_2 fluxes in winter barley field of Japanese Andisol as affected by N fertilizer management. *Soil Biol Biochem* **2007**, *39*(1), 330-339. https://doi.org/10.1016/j.soilbio.2006.08.003.
46. Liu, L.; Greaver, T.L.A. Review of nitrogen enrichment effects on three biogenic GHGs: the CO_2 sink may be largely offset by stimulated N_2O and CH_4 emission. *Ecol. Lett*. **2009**, *12*(10), 1103-1117. https://doi.org/10.1111/j.1461-0248.2009.01351.x.
47. Hütsch, B.W. Methane oxidation in arable soil as inhibited by ammonium, nitrite and organic manure with respect to soil pH. *Biol. Fertil. Soils* **1998**, *28*, 27–35. https://doi.org/10.1007/s003740050459.
48. Hütsch, B.W. Methane oxidation in non-flooded soils as affected by crop production - invited paper. *Eur. J. Soil Sci*. **2001**, *14*, 237–260. https://doi.org/10.1016/S1161-0301(01)00110-1.
49. Brito, L.de F.; Azenha, M.V.; Janusckiewicz, E.R.; Cardoso, A.S.; Morgado, E.S.; Malheiros, E.B.; La Scala, N.; Reis, R.A.; Ruggieri, A.C. Seasonal fluctuation of soil carbon dioxide emission in differently managed pastures. *Agron. J*. **2015**, *107*(3), 957-962. https://doi.org/10.1590/S0100-06832010000500018.
50. Moreira, F.S.; Siqueira, J.S. 2006. Microbiologia e bioquímica do solo. Lavras: Editora UFLA, 729.

51. Epron, D.; Bosc, A.; Bonal, D.; Freycon, V. Spatial variation of soil respiration across a topographic gradient in a tropical rain forest in French Guiana. *J. Trop. Ecol*. **2006**, *22*(5), 565-574. https://doi.org/10.1017/S0266467406003415.
52. Lal, R. Challenges and opportunities in soil organic matter research. *Eur. J. Soil Sci*. 2009, *60*(2), 158–169. https://doi.org/10.1111/j.1365-2389.2008.01114.x.
53. Pulrolnik, K. Transformações do carbono no solo. Embrapa Cerrados, **2009**, Documentos 264. ISSN 1517-5111.
54. Neff, J.C.; Townsend, A.R.; Gleixner, G.; Lehman, S.J.; Turnbull, J.; Bowman, W.D. Variable effects of nitrogen additions on the stability and turnover of soil carbon. *Nature* **2002**, *419*, 915-917. https://doi.org/10.1038/nature01136.
55. Potthoff, M.; Dyckmans, J.; Flessa, H.; Muhs, A.; Beese, F.; Joergensen, R.G. Dynamics of maize (Zea mays L.) leaf straw mineralization as affected by the presence of soil and the availability of nitrogen. *Soil Biol Biochem* 2005, *37*(7), 1259-1266. https://doi.org/10.1016/j.soilbio.2004.11.022.
56. Fang, H.; Cheng, S.; Yu, G.; Zheng, J.; Zhang, P.; Xu, M.; Yang, X. et al. Responses of CO_2 efflux from an alpine meadow soil on the Qinghai Tibetan Plateau to multi-form and low-level N addition. *Plant and Soil* **2012**, *351*(1), 177-190. https://doi.org/10.1007/s11104-011-0942-4.
57. Corrêa, D. C. C.; Cardoso, A. da S.; Siniscalchi, D.; Ruggieri, A. C.; Reis, R. A. Influência de fertilizantes nitrogenados no acúmulo de forragem em pastos de Capim-Marandu no noroeste paulista. IX Simpósio sobre Manejo Estratégico de Pastagens e VI Simpósio Internacional sobre Produção Animal em Pastejo. 2019, Viçosa - MG.
58. Tian, Z.; Wang, J. J.; Liu, S.; Zhang, Z.; Dodla, S. K.; Myers, G. Application effects of coated urea and urease and nitrification inhibitors on ammonia and greenhouse gas emissions from a subtropical cotton field of the Mississippi delta region. *Sci. Total Environ*. **2015**, *533*, 329-338. https://doi.org/10.1016/j.scitotenv.2015.06.147.
59. Song, L.; Tian, P.; Zhang, J.; Jin, G. Effects of three years of simulated nitrogen deposition on soil nitrogen dynamics and greenhouse gas emissions in a Korean pine plantation of northeast China. *Sci. Total Environ*. **2017**, *609*, 1303-1311. https://doi.org/10.1016/j.scitotenv.2017.08.017.
60. Grant, B.; Smith, W. N.; Desjardins, R.; Lemke, R.; Li, C. Estimated N_2O and CO_2 emissions as influenced by agricultural practices in Canada. *Climatic Change*, **2004,** *65*, 315– 332. https://doi.org/10.1023/B:CLIM.0000038226.60317.35.
61. Dobbie, K.E.; Smith, K.A. The effects of temperature, water-filled pore space and land use on N_2O emissions from an imperfectly drained gleysol. *Eur. J. Soil Sci*. **2001**, *52*(4), 667-673. https://doi.org/10.1046/j.1365-2389.2001.00395.x.
62. Nogueira, A.K.D.S.; Rodrigues, R.D.A.; Castro, B.S.; Nogueira, T.F.; da Silva, J.J.; Behling, M.; Mombacha, M.; Armacoloa, N.; Silveira, J.G. Emissões de óxido nitroso e metano do solo em áreas de recuperação de pastagens na Amazônia matogrossense. *Química Nova* **2015**, *38*(7), 937-943. https://doi.org/10.5935/0100-4042.20150109.
63. Van Der Weerden, T.J.; Luo, J.; Di, H.J.; Podolyan, A.; Phillips, R.L.; Saggar, S.; Klein, C.A.M.; Cox, N.; Ettema, P.; Rys, G. Nitrous oxide emissions from urea fertiliser and effluent with and without inhibitors applied to pasture. *Agric. Ecosyst. Environ*. **2016**, 219, 58-70. https://doi.org/10.1016/j.agee.2015.12.006.
64. Jantalia, C.P.; dos Santos, H.P.; Urquiaga, S.; Boddey, R.M.; Alves, B.J., Fluxes of nitrous oxide from soil under different crop rotations and tillage systems in the South of Brazil. *Nutr. Cycling Agroecosyst*. **2008**, *82*(2), 161-173. https://doi.org/10.1007/s10705-008-9178-y.
65. Piva, J.T.; Dieckow, J.; Bayer, C.; Zanatta, J.A.; de Moraes, A.; Tomazi, M.; PAuletti, V.; Barth, G.; de Cassia Piccolo, M. Soil gaseous N_2O and CH_4 emissions and carbon pool due to integrated crop-livestock in a subtropical Ferralsol. *Agric. Ecosyst. Environ*. **2014**, 190, 87-93. https://doi.org/10.1016/j.agee.2013.09.008.
66. Campanha, M.M.; de Oliveira, A.D.; Marriel, I.E.; Neto, M.M.G.; Malaquias, J.V.; Landau, E.C.; Albuquerque Filho, M.R.de; Ribeiro, F.P.; de Carvalho, A.M. Effect of soil tillage and N fertilization on N_2O mitigation in maize in the Brazilian Cerrado. *Sci. Total Environ*. **2019**, *692*, 1165-1174. https://doi.org/10.1016/j.scitotenv.2019.07.315.
67. Nascimento, A.F.; Rodrigues, R.D.A.R.; Silveira, J.G.D.; Silva, J.J.N.D.; Daniel, V.D.C.; Segatto, E.R. Nitrous oxide emissions from a tropical Oxisol under monocultures and an integrated system in the Southern Amazon–Brazil. *Rev. Bras. Cienc. Solo*, **2020**, *44*. https://doi.org/10.36783/18069657rbcs20190123.
68. Smith, K.A.; Ball, T.; Conen, F.; Dobbie, K.E.; Massheder, J.; Rey, A. Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *Eur. J. Soil Sci*. **2003**, *54*, 779–791. https://doi.org/10.1046/j.1351-0754.2003.0567.x.
69. Bento, C.B.; Filoso, S., Pitombo, L.M.; Cantarella, H.; Rossetto, R.; Martinelli, L.A.; do Carmo, J.B. Impacts of sugarcane agriculture expansion over low-intensity cattle ranch pasture in Brazil on greenhouse gases. *J. Environ. Manage* **2018**, *206*, 980-988. https://doi.org/10.1016/j.jenvman.2017.11.085.
70. Bouwman, A.F. 1990. Exchange of greenhouse gases between terrestrial ecosystems and the atmosphere. In: Bouwman, A.F.(Ed.), Soils and the Greenhouse Effect. John Wiley, New York, pp.61– 127.
71. Ryden, J.C. Denitrification loss from a grassland soil in the field receiving different rates of nitrogen as ammonium nitrate. *J. Soil Sci* **1983**, *34*, 355-365. https://doi.org/10.1111/j.1365-2389.1983.tb01041.x.
72. Kirschbaum, M.U.F. The temperature dependence of organic-matter decomposition: still a topic of debate. *Soil Biol Biochem* **2006**, *38*, 2510–2518. https://doi.org/10.1016/j.soilbio.2006.01.030.
73. Burton, D.L.; Li, X.; Grant, C.A. Influence of fertilizer nitrogen source and management practice on N_2O emissions from two Black Chernozemic soils. *Can. J. Soil Sci*. **2008**, *88*(2), 219-227.2008. https://doi.org/10.4141/CJSS06020.
74. Bédard, C.; Knowles, R. Physiology, biochemistry, and specific inhibitors of CH_4, NH_4^+, and CO oxidation by methanotrophs and nitrifiers. *Microbiol Mol Biol Rev* **1989**, *53*(1), 68-84.
75. Veldkamp, E.; Weitz, A.M.; Keller, M. Management effects on methane fluxes in humid tropical pasture soils. *Soil Biol Biochem* **2001**, 33(11), 1493-1499. https://doi.org/10.1016/S0038-0717(01)00060-8.

76. Hawthorne, I.; Johnson, M.S.; Jassal, R.S.; Black, T.A.; Grant, N.J.; Smukler, S.M. Application of biochar and nitrogen influences fluxes of CO_2, CH_4 and N_2O in a forest soil. *J. Environ. Manage*. **2017**, *192*, 203-214. https://doi.org/10.1016/j.jenvman.2016.12.066.
77. Mohanty, S. R.; Bodelier, P. L.; Floris, V.; Conrad, R. Differential effects of nitrogenous fertilizers on methane-consuming microbes in rice field and forest soils. *Appl Environ Microbiol* **2006**, *72*(2), 1346-1354. doi:10.1128 / AEM.72.2.1346-1354.2006.
78. Tao, B.; Liu, C.; Zhang, B.; Dong, J. Effects of inorganic and organic nitrogen additions on CO_2 emissions in the coastal wetlands of the Yellow River Delta, China. *Atmos. Environ*. **2018**, *185*, 159-167. https://doi.org/10.1016/j.atmosenv.2018.05.009.
79. Chi, Y.; Yang, P.; Ren, S.; Ma, N.; Yang, J.; Xu, Y. Effects of fertilizer types and water quality on carbon dioxide emissions from soil in wheat-maize rotations. *Sci. Total Environ*. **2020**, *698*, 134010. https://doi.org/10.1016/j.scitotenv.2019.134010.
80. Liu, S.; Wang, J.J.; Tian, Z.; Wang, X.; Harrison, S. Ammonia and greenhouse gas emissions from a subtropical wheat field under different nitrogen fertilization strategies. *J Environ Sci* **2017**, *57*, 196-210. https://doi.org/10.1016/j.jes.2017.02.014.
81. Li, K.; Gong, Y.; Song, W.; He, G.; Hu, Y.; Tian, C.; Liu, X. Responses of CH_4, CO_2 and N_2O fluxes to increasing nitrogen deposition in alpine grassland of the Tianshan Mountains. *Chemosphere* **2012**, *88*(1), 140-143. https://doi.org/10.1016/j.chemosphere.2012.02.077.
82. Liyanage, A.; Grace, P. R.; Scheer, C.; de Rosa, D.; Ranwala, S.; Rowlings, D. W. Carbon limits non-linear response of nitrous oxide (N_2O) to increasing N inputs in a highly-weathered tropical soil in Sri Lanka. *Agric Ecosyst Environ* **2020**, *292*, 106808. https://doi.org/10.1016/j.agee.2019.106808.
83. Barton, L.;Kiese, R.; Gatter, D.; Butterbach-Bahl, K.; Buck, R.; Hinz, C.; Murphy, D.V. Nitrous oxide emissions from a cropped soil in a semi-arid climate. *Glob. Change Biol*. **2008**, *14*(1), 177-192. https://doi.org/10.1111/j.1365-2486.2007.01474.x.
84. Zebarth, B.J.; Rochette, P.; Burton, D.L.; Price, M. Effect of fertilizer nitrogen management on N_2O emissions in commercial corn fields. *Can. J. Soil Sci*. **2008**, *88*(2), 189-195. https://doi.org/10.4141/CJSS06010.
85. Vanderzaag, A.C.; Jayasundara, S.; Wagner-Riddle, C. Strategies to mitigate nitrous oxide emissions from land applied manure. *Anim. Feed Sci. Technol*. **2011**, *166*, 464-479. https://doi.org/10.1016/j.anifeedsci.2011.04.034.
86. Bayer, C.; Gomes, J.; Zanatta, J.A.; Vieira, F.C.B.; de Cássia Piccolo, M.; Dieckow, J.; SIX, J. Soil nitrous oxide emissions as affected by long-term tillage, cropping systems and nitrogen fertilization in Southern Brazil. *Soil Tillage Res* **2015**, *146*, 213-222. https://doi.org/10.1016/j.still.2014.10.011.
87. Cardoso, A.S.; Junqueira, J.B.; Reis, R.A.; Ruggieri, A.C. How do greenhouse gas emissions vary with biofertilizer type and soil temperature and moisture in a tropical grassland? *Pedosphere* **2020**, *30*(5), 607-617. https://doi.org/10.1016/S1002-0160(20)60025-X.
88. Dos Santos, C.A.; de Rezende, C.P.; Boddey, R.M.; Jantalia, C.P.; Urquiaga, S.; Alves, B.J.R. Nitrous oxide emissions from fertiliser and cattle excreta applied to a palisade grass pasture with and without urea fertilisation or mixed with the forage legume *Desmodium heterocarpon*. *Nutr. Cycling Agroecosyst*. (Manuscript in preparation).