UNIVERSIDADE DE SÃO PAULO
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PAUL LINEKER AMARAL DE MELO

Greenhouse gas emissions (CO_2, CH_4 and N_2O) in saline-alkaline systems of the Pantanal of Nhecolândia/MS, Brazil.

Piracicaba
2022

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Marilia Ribeiro Garcia Henyei

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To my grandmother Jacira Sebastiana for so much love and affection dedicated to me.
May life keep us together wherever it may be.
Keep blessing me from above, Bazinha. (in memory)

I DEDICATE

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ABSTRACT

MELO, P. L. A. **Greenhouse gas emissions (CO_2, CH_4 and N_2O) in saline-alkaline systems of the Pantanal of Nhecolândia/MS.** 2022. 69 p. Tese (Doutorado em Ciências) - Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Piracicaba, 2022.

The Pantanal is recognized as one of the largest wetlands on the planet, one of the main Brazilian biomes and represents an important study environment regarding the emission of Greenhouse Gases (GHG) due to the relatively constant and high temperature of the environment. Given the reality of mitigation and the need to limit global warming to 1.5°C, greenhouse gas emissions in already impacted natural environments have been studied, especially in wetlands. In this work, GHG emissions were evaluated in saline-alkaline systems (lakes and lakes margins - soil) to identify, in two campaigns (2018 and 2019), the behavior and the main processes of formation of CO_2, CH_4, and N_2O gases. For this, four lakes and their margins were selected according to their characteristics identified a priori and classified as black lakes (01SR and 06SR), green lake (04SR), and crystalline lake (07SR). The flow of emissions from the soil of margins was based on different points of saturation by the water of the lakes, with a saturated zone (ZS), an intermediate zone (ZI) and an unsaturated zone (ZI). For this, we also evaluated the carbon stock up to 50 cm depth in the soil. Through principal component analysis (PCA), the chemical variables of the lakes were grouped with the greenhouse gases emitted from the water, while the emissions from the soil in different saturation zones were evaluated by comparing averages. In general, black lakes (01SR and 06SR) were important CO_2 emitters, but weak CH_4 emitters, both behaviors were more prominent in the second campaign. The green lake (04SR), for the first campaign, was an important CO_2 consumer and CH_4 emitter, especially due to the presence of methanogenic organisms. However, the behavior of this lake was changed in the second campaign in response to the reduction in the volume of water and the high concentration of nutrients. For this, the consumption of CO_2 was impaired and higher emission of CH_4 was observed. The Crystalline Lake is the lake that presented the smallest alteration between the campaigns, in both, high emissions of both CO_2 and CH_4 were observed. For this, the presence of macrophytes is the main vector of gas production. No consistent trend was observed for N_2O emission from all lakes. On the margins of the lakes, higher CH_4 emission was observed at points of lower oxygenation (saturated zone) with a reduction in their emissions and higher CO_2 and N_2O emissions when sampling points of higher oxygenation (intermediate and unsaturated zones).

Likewise, it was possible to observe that the margins of lakes with a greater presence of grasses were responsible for a greater stock of carbon in the soil.

Keywords: Climate change. Wetlands. Greenhouse gas emissions. Global warming. Lakes. Soils. Carbon sequestration.

RESUMO

MELO, P. L. A. **Emissões de gases de efeito estufa (CO_2, CH_4 e N_2O) em sistemas salino-alcalinos do Pantanal da Nhecolândia/MS.** 2022. 69 p. Tese (Doutorado em Ciências) - Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Piracicaba, 2022.

O Pantanal é reconhecido como uma das maiores áreas úmidas do planeta, um dos principais biomas brasileiros e representa um importante ambiente de estudo quanto a emissão de Gases de Efeito Estufa (GEE) em função da temperatura relativamente constante e elevada do ambiente. Diante da realidade de mitigação e a necessidade de limitação do aquecimento global a 1,5°C, as emissões de gases de efeito estufa em ambientes naturais já impactados tem sido alvos de estudo, em especial, em áreas úmidas. Neste trabalho, foram avaliadas emissões de GEE em sistemas salino-alcalinos (lagoa e solo da borda) a fim de identificar, em duas campanhas (2018 e 2019), o comportamento e os principais processos de formação dos gases CO_2, CH_4 e N_2O. Para isso, quatro lagoas e suas margens foram selecionadas mediante suas características identificadas a priori, e classificadas como: lagoas pretas (01SR e 06SR), lagoa verde (04SR) e lagoa cristalina (07SR). Os fluxos de emissões a partir do solo de suas margens se baseou em diferentes pontos de saturação pela água das lagoas, com uma zona saturada (ZS), uma zona intermediária (ZI) e uma zona não saturada (ZI). Para esta, também se avaliou o estoque de carbono no solo até 50 cm de profundidade. Por meio de análises de componentes principais (PCA), as variáveis químicas da lagoa foram agrupadas com os gases de efeito estufa emitidos a partir da água em duas amostragens, enquanto as emissões a partir do solo em diferentes zonas de saturação foram avaliadas por comparação de médias. De modo geral, lagoas de cor preta (01SR e 06SR) se apresentaram como importantes emissores de CO_2, mas fracos emissores de CH_4, ambos comportamentos foram mais proeminentes na segunda campanha. A lagoa de cor verde (04SR), na primeira amostragem, se apresentou como um importante consumidor de CO_2 e emissor de CH_4 especialmente pela presença de organismos metanogênicos. No entanto, o comportamento desta lagoa foi alterado na segunda campanha em resposta à redução do volume de água e a alta concentração de nutrientes. Para esta, o consumo de CO_2 foi prejudicado e foi observado maior emissão de CH_4. A Lagoa cristalina é a lagoa que apresentou menor alteração entre as campanhas, em ambas, foram observadas elevadas emissões tanto de CO_2 quanto de CH_4. Para esta, a presença de macrófitas é o principal vetor de produção de gases. Não foi observada uma tendência consistente sobre a emissão de N_2O por essas lagoas. Nas margens das lagoas observou-se maior emissão de CH_4 em pontos de menor oxigenação (zona saturada) com redução de suas emissões e maior emissão de CO_2 quando amostrados pontos de maior oxigenação (zonas intermediárias e não saturadas). Da mesma forma, foi possível observar que margens de lagoas com maior presença de gramíneas foi responsável por maior estoque de carbono no solo.

Palavras-chave: Mudanças climáticas. Áreas úmidas. Gases de Efeito Estufa. Aquecimento Global. Lagoas. Solos. Sequestro de carbono.

SUMÁRIO

1. INTRODUCTION

As it constitutes a potentially irreversible threat to humanity, the global climate change has been the subject of intense research efforts. Combating climate change is one of the Sustainable Development Goals (SDGs) of the 2030 Agenda of the UN, where it warns of its risks and impacts on society, in addition to the need for significant actions to mitigate greenhouse gas emissions (GHG) (UN, 2015).

GHGs are present in the atmosphere, and it is produced from natural or anthropogenic sources. Such gases absorb and emit radiation at specific wavelengths across the Earth's surface, the atmosphere, and clouds. This property causes the greenhouse effect. Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are the main greenhouse gases in the atmosphere capable of causing climate change. Based on their radioactive properties, these gases have different global warming potentials (GWP): CH_4 and N_2O, respectively, have a GWP 28 and 273 times greater than CO_2. Since 1850, increases in CO_2, CH_4 and N_2O were about 47%, 156%, and 23%, respectively (IPCC, 2021).

According to the Intergovernmental Panel on Climate Change (IPCC, 2021), for the year 2019, the atmospheric concentration of CO_2 was 410 ppm, while for CH_4 and N_2O they were 1866 ppbv and 332 ppbv, respectively. The increase in their concentrations in the atmosphere results in an increase in global temperature. Also, according to a report (IPCC, 2021), human activities were the main responsible for the increase in global temperature. In the first two decades of the 21st century (2001-2020) it was 0.99 [0.84-1.10] °C higher than in 1850-1900. Following this pace, it is estimated that by 2050 this warming will reach 1.5ºC. Recognizing the urgency of the matter, the Paris agreement negotiated in 2015 during the Conference of the Parties (COP-21), determined by global leaders to limit global warming to 1.5˚C, in relation to the pre-industrial period, having as its main objective to reach zero net CO_2 emissions by mid-2050, and between 2060 and 2070 for total net GHG emissions. The report warns that significant climate impacts will occur with an increase of 1.5˚C, but the risks of warming are substantially lower than those arising from the 2˚C limit initially proposed under the Paris Agreement. Among the highlighted impacts is the loss of about 7% of ecosystems, which will be transformed into another biome. This percentage will reach 13% in case of an increase of around 2°C in global temperature.

Among these ecosystems, wetlands are key environments that provide services for climate regulation. These areas represent permanently or periodically flooded environments, comprising about 7 million km² of land surface area (around 4 to 6%). Naturally, wetlands are responsible for contributing around 20-39% of global methane emissions (IPCC, 2007).

Only seasonally frozen wetlands account for about 10% of the global source of methane (IPCC, 2013). Permafrost wetlands can contribute a significant portion of global methane emissions. The potential additional release of carbon from future thawing and the release of methane from wetlands tend to alter the natural concentration of gases in the atmosphere, as it stores large amounts of organic carbon, almost twice as much carbon in the atmosphere (IPCC, 2018). Likewise, wetlands are potentially large sinks for CO_2 during anaerobic periods, depending heavily on the processes by hydrologic variations (Dalmagro et al., 2019).

The Pantanal is the world's largest wetland and has one of the most biodiverse places on Earth. This environment represents a large and heterogeneous of interconnected aquatic, terrestrial, and wetland ecosystems. It also plays an important role in biological diversity, in addition to many essential ecosystem services including carbon storage, flood control and aquifer recharge (Alho, 2008). However, despite this importance, the Pantanal is in danger. Events of high temperatures and low precipitation have been causing prolonged extreme drought conditions and severe impacts on its hydrology (Marengo et al., 2021). As rainfall and flood pulse are the main processes that maintain these landscapes, these extreme events can drastically alter the landscape and also the biogeochemical functionality of the environment (Ivory et al., 2019).

Faced with the reality of mitigation and the adaptation of plans and targets to limit global warming to 1.5°C, uncertainties turn to greenhouse gas emissions from these natural environments already impacted by global warming in the current temperature patterns and that have no forecast of the impact of temperature rise. According to Mitsch et al. (2010), climate change can affect tropical wetlands in four different ways: changes in hydrological pulses; changes in local rainfall patterns; changes in temperature/humidity, subsequent evapotranspiration patterns; and influences of sea level and coastal storms on coastal wetlands.

There are few studies that evaluate GHG emissions from the landscape-atmosphere system in undisturbed natural environments. Despite its considerable area (155.000 km^2), there are few data on GHG production and emissions for this zone (Marani; Alvalá, 2007; Bastviken et al., 2010). In general, among the studies found for the Pantanal biome, most are focused on anthropogenic changes such as land-use change, use of fertilizers, and especially livestock. In this context, the aim of our study was to seek an understanding of the multiple factors and processes that together affect the emission of greenhouse gases in the Pantanal of Nhecolândia.

This research is part of the project entitled “Climate change and environmental impacts in wetlands of the Pantanal (Brazil): quantification, control factors and long-term forecast” (FAPESP Nº 2016/14227-5) and is part of the second action of research “Genesis and dynamics of the soil-pond system in the Pantanal”.

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2. DYNAMICS OF GHG'S EMISSIONS IN THE SALINE-ALKALINE LAKES OF THE PANTANAL, BRAZIL

Abstract

The Pantanal of Nhecolândia is surrounded by tens of thousands of saline and nonsaline lakes due to the complex fluvium-lake system. There are three primary types of lakes: green water, black water, and crystalline water, with biogeochemical differences that can alter the landscape's gas exchange with the atmosphere. Here, we synthesized the CO_2, CH_4, and N_2O emission data from two campaigns in the three lake groups in this ecosystem to: (1) estimate GHG emissions from lakes and (2) identify best predictors of these emissions. Aiming to accomplish these goals, we used a principal component analysis (PCA) to characterize the types of lake characteristics. The results highlight important variations in daily and seasonal gas fluxes. In the first campaign, the standard emissions revealed that green lakes are CH_4 and N_2O sources and CO_2 sinks; black lakes are CO_2 sources with lower CH_4 emissions; and crystalline lakes are CH_4 and CO_2 sources. For these last two lakes, the N_2O behavior was not significant. However, during hot extreme events, such as the second campaign, the GHG emissions increased in magnitude. The lakes' functionality was altered as a result of the high temperatures, lower water levels, and nutrient enrichment. The green lake exhibited no CO_2 consumption and CH_4 emissions increased; black and crystalline lakes exhibited increases in CO_2 and CH_4 emissions, respectively. Our findings indicated that the effects of global warming and climate change on this ecosystem might alter the biological function of some lakes and increase the gas production. As greenhouse gas concentration rise, their effects become more pronounced.

Keywords: Greenhouse gas emission; Alkaline lakes; Pantanal wetland

2.1 Introduction

Scientific research demonstrates the importance of wetlands environments for global warming. These ecosystems cover approximately 7 million km² and play an important role in regulating flooding cycles, immobilization of toxic compounds by redox processes (Barbiero et al., 2008), sedimentation control (Martins, 2012), and support for high biodiversity (Pott et al., 2011). It is also an important source of greenhouse gases (GHG: i.e., CO_2, CH_4 and N_2O) in very different proportions (Barbiero et al., 2018).

Pantanal is one of the world's largest wetlands (with a surface area of approximately 155.000 km²) and one of the most important Brazilian biomes (Gomide, 2014) due to its significant influence on regional and local climate. This region has a number of distinct characteristics due to the relatively constant and high temperature (~ 30°C), which causes a considerable increase in the rate of production and emission of GHGs in a vast different proportion (Barbiero et al., 2018).

The Pantanal of Nhecolândia (approximately 26,000 km²) is characterized by the presence of a complex fluvium-lake system, with approximately 15.000 saline and non-saline lakes coexisting nearby. There are three main types of lakes: green water lakes that have permanent or seasonal cyanobacterial blooms, phytoplankton and archaea, black water with high organic matter (OM) content and dispersed clay particles, and crystalline waters, which present an important presence of aquatic vegetation (Barbiero et al., 2018). In contrast to black or crystalline water lakes, green water lakes are known as important sites of organic matter production (Andreote et al., 2014; Vaz et al., 2015; Genuário et al., 2017).

In addition to strong interactions between biotic and abiotic processes, humid alkaline environments are characterized by a high pH that favors the solubilization, transport and accumulation of organic matter, the easy transport of metals and trace elements, and the formation of specific clay neoformations for these environments (Barbiero et a., 2002; Furquim et al., 2010; Martins, 2012; Barbiero et al., 2016). The OM transported can be decomposed and remain in the water column or precipitate until it is stored in sediment. Lastly, gases can be released back into the water column as CO_2 by respiration or, under anoxic conditions, utilized to produce CH_4 via methanogens (Bastviken, 2009).

Respiration is the primary source of CO_2 in an unaltered natural environment, whereas photosynthesis by vegetation, phytoplankton and microorganisms is the main source of CO_2 sink (Dalal; Allen, 2008; Chapman et al., 2019). Due to the limited distribution of oxygen within sediments in aquatic ecosystems, anaerobic metabolism, whether respiratory or fermentative, predominates in sediments (King; Foster; Graham, 2016). The CH_4 production (methanogenesis) by methanogenic organisms in anaerobic environments occurs in two major pathways: hydrogen dependent (Hydrogenotrophic) and acetate dependent methanogenesis (Acetotrophic). However, the relative contributions of these two pathways may vary depending on the specific conditions (Cui et al., 2015). The N_2O emissions can occur both aerobically and anaerobically. The N_2O is produced by a product of nitrification, in which ammonium (NH_4^+) is oxidized to nitrate (NO_3^-) by nitrifying bacteria and archaea (Löscher et al., 2012). Under anoxic conditions, N_2O is produced by incomplete denitrification, a process in which nitrate (NO_3^-) and nitrite (NO_2^-) are reduced to N_2 gas (Ji et al., 2019; Nutanong et al., 2019).

Considering that the production or consumption of gases will be directly related to the physical-chemical characteristics of the soil and water, these will also select the organisms capable of playing an important role in modifying the gas exchange with the atmosphere (Ventura, 2014; Attermeyer et al., 2016). The assessment of these emissions has been limited by the complexity of the environment and the need for a multidisciplinary strategy. To improve the assessment of the global GHG cycle, it is necessary to comprehend the production, storage, consumption, and the distribution of greenhouse gases. In this regard, the purpose of this study was to describe the wide range of greenhouse gas flux (CO_2, CH_4 and N_2O) and the associated processes in the saline-alkaline system of the Pantanal of Nhecolândia.

2.2 Material and Methods

2.2.1 Study area

The Pantanal of Nhecolândia is located between the Taquari River and Negro River. Our study area is in the São Roque Reserve (19º22'17.97"S and 56°20'47.85"W) in the municipality of Aquidauana, MS, Brazil. The region is characterized by an abundance of shallow lakes with round to irregular shapes. The lakes in this region are regularly supplied with rainwater and exceptionally with water from the Taquari River. Saline-alkaline and freshwater lakes coexist side by side. The physical-chemical characteristics of saline-alkaline lakes are controlled by intense evaporation processes together with specific topography, which block the entry and exit of water.

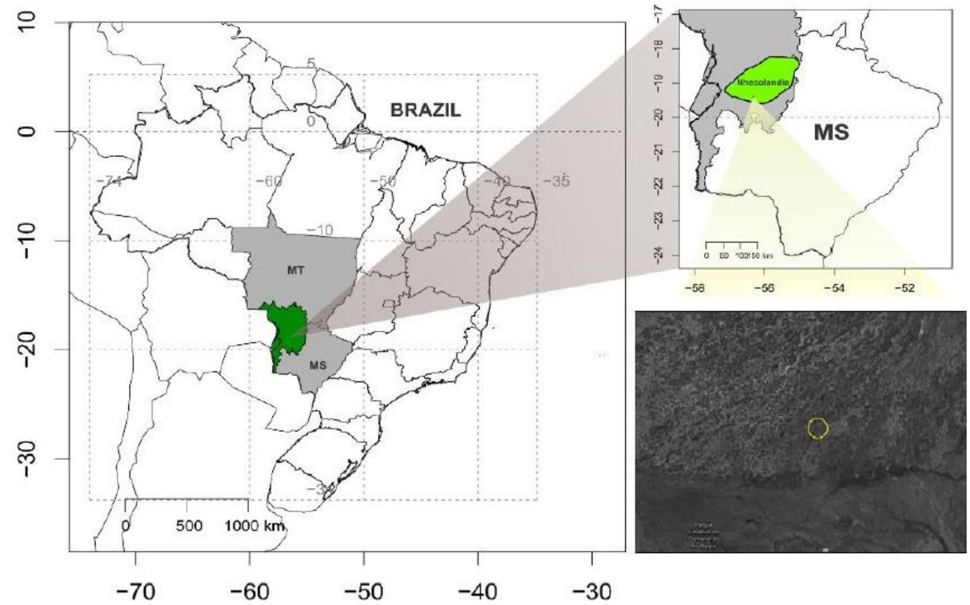

Figure 1. Nhecolândia sub-region in the southern portion of the Taquari River. On the right, the detail shows the landscape consisting of lakes with rounded contours characteristic of this sub-region of the Pantanal

2.2.2 Climate characterization

The climate of the region is classified as Awa according to the Köppen classification, with marked dry (from April to September), and wet (from October to March) seasons, with dry winter and rainy summer (Oliveira et al., 2011). This behavior was partially observed during the evaluation years of our study. During 2018, the region had accumulated rainfall of 793 mm with an average temperature of 27.67°C. As for the year 2019, the accumulated precipitation was around 702 mm and an average temperature of 29.10 °C (Figure 2). For the second campaign, the climatic characterization promoted a lower water column in the lakes, and a greater enrichment of nutrients in concentration.

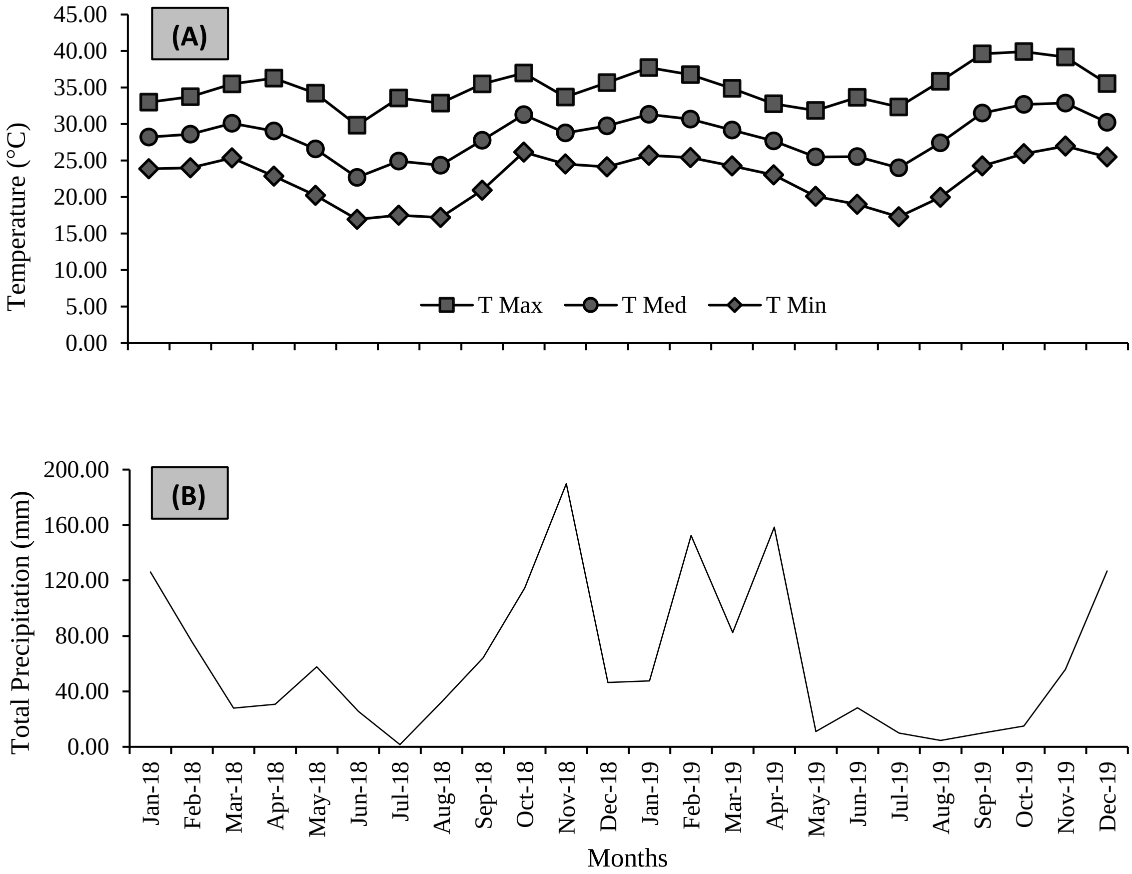

Figure 2. Climatic characterization with the maximum, mean and minimum temperatures (A) and total precipitation (B) for the local study São Roque Farm in the sampling period: first campaign (2018) and second campaign (2019).

2.2.3 Lakes selection

As mentioned, this project is part of a Thematic Project, which has been studying eleven (11) lakes in total with different physicochemical characteristics among them. Of these, four (4) lakes were selected based on the physicochemical characteristics of the alkaline-saline lakes sampled at the study site: one with green water (identified as 04SR); two with black water (01SR and 06SR), and one crystalline water (07SR) in order to characterize the biogeochemical variation between them (Figure 3).

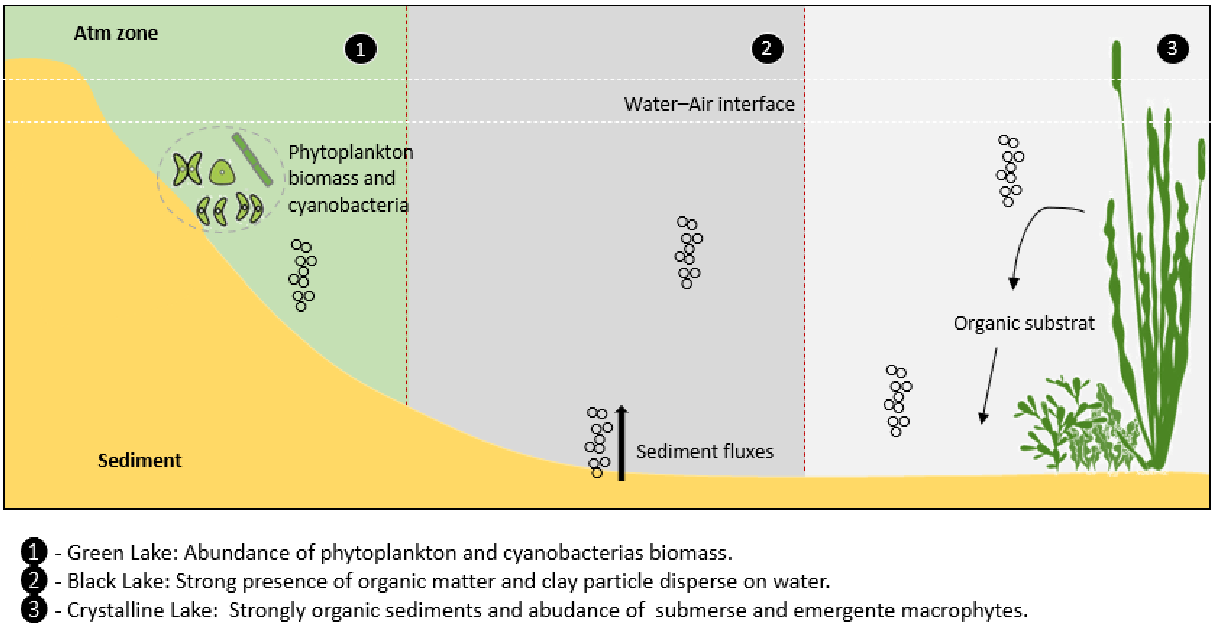

Figure 3. Selection of the study lakes and their main characteristics for greenhouse gas emissions study in the Pantanal of Nhecolândia

The denomination used "SR" refers to the collection site (São Roque farm) and the numbering corresponds to the number of each pond chosen from the field. Sampling was carried out in two campaigns: the first in September 2018, the second in September 2019. Samplings were carried out in 1 day for each laked studied. The month of September was selected because it is the month in which, historically, the Pantanal lakes are more stationary, that is, neither too full nor too dry.

2.2.4 Physical-chemical water characterization

The collected water samples were divided into three sub-samples for chemical analysis: unfiltered, filtered through a glass microfiber with a pore size of 0.7 µm (Whatman GF/F, Sigma-Aldrich, St. Louis, MO, USA) and filtered through a 0.45 µm pore size ester-cellulose membrane (Merck Millipore, Billerica, MA, USA). Unfiltered sub-samples were used to determine total nitrogen (TN) and total phosphorus (TP); Filtered GF/F sub-samples were used to analyze dissolved organic and inorganic carbon (DOC and DIC, respectively) and total dissolved nitrogen (TDN); Sub-samples filtered were used to determine the concentration of the following ions: NH_4^+, NO_3^-, NO_2^-, by flow injection analyses; Alkalinity, water salinity and concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} were also analyzed. All methods used for physical-chemical water determination were described in Pellegrinetti et al. (2022).

2.2.5 GHG lake emissions samples

Five polyethylene floating chambers (volume: 32L; base area: 0.195 m^2) separated by approximately 10m were used to sample gas fluxes at the air-water interface of the lakes. This was accomplished by traversing the set of chambers along a 150-meter-long transect from one lake shore to the other. The collections were conducted four times each day. The fluxes are represented by two times: T0, the initial time of departure of the set of chambers (ambient atmospheric air), and T30, the accumulation 30 minutes after the passage of chambers along the entire transect (final time). In order to monitor the temperature, thermometers were placed within the floating chambers. Using a 60 mL syringe (Becton Dickinson Ind. Surgical Inc.) with a check valve, duplicate gas samples were collected for each chamber (approximately 2 minutes apart per chamber) using a Becton Dickinson Ind. Surgical Inc. The gases were transferred into 30 mL glass bottles with gas-tight caps and evacuated at 0.75 kPa with a hand vacuum pump.

Gas concentrations in the liquid phase were estimated indirectly using the headspace displacement technique (Hamilton; Sippel; Melack, 1995) with a 140 mL syringe and a 1:3 air-to-water ratio (volume: 35:105 mL). The water samples were collected five centimeters beneath the surface and approximately thirty meters from the lake's shoreline. To balance the headspace with the liquid phase, the syringe was shaken by hand for two minutes prior to injecting the headspace into 30 mL glass bottles that had been previously gas-tightly sealed and evacuated with a hand vacuum pump at 0.75 kPa.

2.2.6 Measurements

GHG concentrations were measured by gas chromatography (SRIGC-110®, Torrance, USA) with a packaged HAYESP ™ column (80-100 mesh) maintained at 82°C to separate the molecular gases. The concentration of N_2O was quantified using an electron capture detector (ECD), and the concentrations of CO_2 and CH_4 through a flame ionization detector (FID). The GHG flows were calculated by linear variation in the amount of each gas in the chambers (obtained by the Clapeyron equation) as a function of the incubation time (30 minutes). Cumulative GHGs were calculated after extrapolating hourly flows to daily.

2.2.7 Data analysis

R statistical software was used for all statistical analyses (R Core Team, 2017). After confirming the results' normality (Shapiro-Wilk test, p 0.05 - *Package 'rstatix'*), principal component analysis (PCA) (*Package* "*factoextra"* and *"factomineR"*) was applied via the correlation matrix to identify and classify the primary variability factors and how they affect the formation of greenhouse gas emissions in the environment.

2.3 Results

2.3.1 Physical-chemical properties

The results of the water physico-chemical analyses (Supplementary Table 1) revealed that, among the campaigns studied, the second campaign had a lower water volume and a nutrient enrichment (by concentration) in the majority of elements. The greater proportion of dissolved organic carbon in the cyanobacterial bloom-characterized green lake's (04SR) total dissolved solids results in greater amounts of total dissolved solids. Also in this lake, macronutrient concentrations in nitrogen source fractions were higher than in other lakes studied (01SR, 06SR and 07SR). Terminal electron acceptors (TEAs), particularly SO_4^{2-} and Fe^{2+}, were abundant in black lakes (01SR and 06SR), whereas their concentration was negligible in the other lakes.

2.3.2 GHG lake emissions

Our findings corroborated earlier evidence for the distinct functioning of these lakes, particularly due to biogeochemical variations between campaigns with notable exceptions. Changes in GHG fluxes (Figure 4) must be due in large part to variations in ambient temperature throughout the day (between 8 am and 8 pm) during the two studied campaigns (Supplementary Table 2).

CO_2 emissions demonstrated different behavior in relation to lakes, particularly the green lake (04SR), which was formerly recognized as significant CO_2 sinks. This trend is evident in the initial campaign. However, the second campaign revealed changes in the functioning of green lake, revealing the behavior of CO_2 producers and emitters, instead of consumers. During our campaigns, crystalline and black lakes proved to be significant CO_2 sources, especially for the second campaign, without undergoing significant change.

For the first campaign, the sequence of accumulated daily CO_2 fluxes was 07SR (97.7 mmol m^2 day^{-1}), 06SR (94.4 mmol m^2 day^{-1}), 01SR (43.9 mmol m^2 day^{-1}), and 04SR (-25.0 mmol m^2 day^{-1}) (Figure 4A). Therefore, only the 04SR lake exhibited CO_2 consumption daily. For the second campaign, the sequence was 07SR (98.8 mmol m^2 day^{-1}), 06SR (69.4 mmol m^2 day^{-1}), 01SR (60.3 mmol m^2 day^{-1}) and 04SR were presented in the following order for the year 2019: (17.3 mmol m^2 day^{-1}) (Figure 4D). In this instance, the 04SR lakes emitted CO_2, in contrast to the previous year's observations.

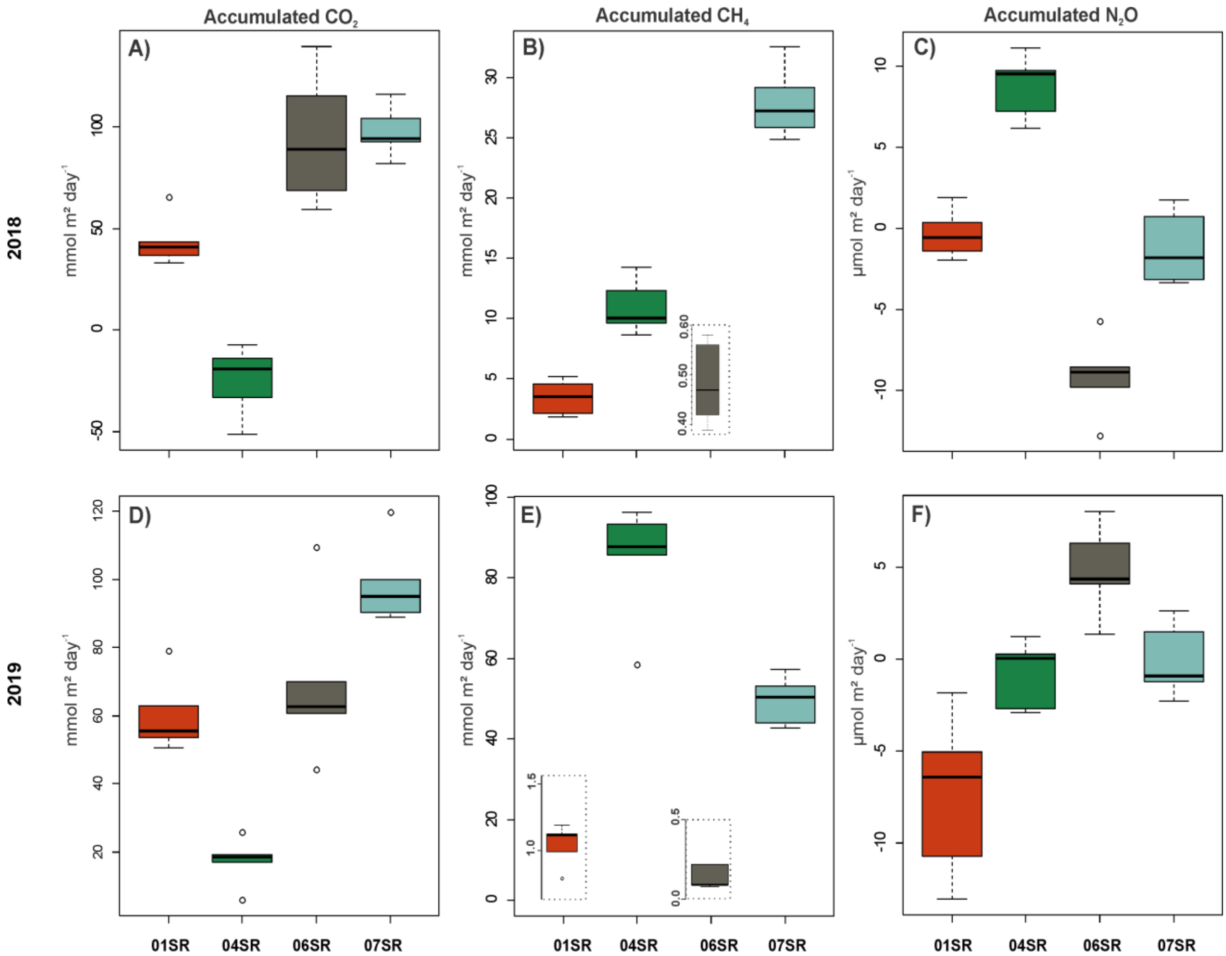

Figure 4. Accumulated greenhouse gases emissions from saline-alkaline lakes of Pantanal of Nhecolândia, Brazil. n=4.

Black lakes (01SR and 06SR) were found to be poor producers of CH_4 with values of approximately 4 mmol m^2 day^{-1}, whereas green and crystalline lakes were found to be significant sources of CH_4 with constant values between 11 and 84 mmol m^2 day^{-1} between campaigns. The accumulated daily CH_4 emissions for the first campaign were as follows: 07SR (27.9 mmol m^2 day^{-1}), 04SR (11.0 mmol m^2 day^{-1}), 01SR (3.5 mmol m^2 day^{-1}) and 06SR (0.5 mmol m^2 day^{-1}) (Figure 4B), indicating higher emissions for the crystalline and green lakes and low CH_4 emission from the black lakes (01SR and 06SR). For the subsequent campaign, there were few variations in accumulated emissions, with 04SR having the greatest emission (84.3 mmol m^2 day^{-1}), followed by 07SR lake (49.6 mmol m^2 day^{-1}), 01SR (1.0 mmol m^2 day^{-1}) and 06SR (0.1 mmol m^2 day^{-1}) (Figure 4E).

Despite exhibiting the same trend in accumulated methane emission throughout the campaigns, the flows of the green lake exhibited distinct behaviors. First, our results demonstrated a decrease in methane emissions throughout the day, particularly when high temperatures were present (12:00 h). In the second campaign, however, the behavior was observed to be the opposite. Again, green, and crystalline lakes were significant sources of CH_4, and their emissions followed the same daily pattern. Nonetheless, during the most recent campaign, Green Lake was the primary source of methane emissions with values exceeding 3.5 mmol m^2 per hour (Supplementary Table 2).

For the first campaign, the highest N_2O emissions were observed at 8 a.m., particularly in the green and crystalline lakes (04SR and 07SR) and decreased throughout the day until they were practically null (Supplementary Table 2). The most significant value was observed in a green lake at 8:00 a.m. (50.5 mol m^2 day^{-1}). In contrast, black lake 01SR showed an increase in N_2O emissions throughout the day, followed by a decrease as the sun set. For the second campaign, 06SR lake produced the highest observed value (16 mol m^2 day^{-1} - 16:00h) with a trend very similar to that of crystalline lake (07SR). Nonetheless, the second campaign for the black lake (01SR) and green lake (04SR) did not reveal any clear emission or consumption trends for N_2O.

The accumulated daily emissions for N_2O, as observed, are of a much smaller magnitude than those for CO_2 and CH_4, and similarly exhibited large variations and distinct behaviors throughout the study years. In 2018, emission sequences 04SR (8.79 mmol m^2 day^{-1}), 01SR (-0.31 mmol m^2 day^{-1}), 07SR (-1.14 mmol m^2 day^{-1}) and 06SR (-9.12 mmol m^2 day^{-1}) accumulated the most (Figure 4C). For the year 2019, the sequence was 06SR (4.81 mmol m^2 day^{-1}), 07SR (-0.07 mmol m^2 day^{-1}), 04SR (-0.82 mmol m^2 day^{-1}) and 01SR (-7.40 mmol m^2 day^{-1}) (Figure 4F).

Figure 5 depicts the calculated CH_4 concentration in lake water based on headspace measurements from two campaigns. For the first campaign, the crystalline lake (07SR), values ranged from 24 to 44 µmol L^{-1} (mean: 35 µmol L^{-1}). The mean value found for the green lake (04SR) was 19 µmol L^{-1}. In contrast, the concentrations of CH_4 in the black water lakes' gas flow were lower, with a mean of 1.4 and 5.5 µmol L^{-1} for lakes 06SR and 01SR, respectively. Similarly, except for black lakes, samples in the liquid phase exhibited greater emission intensities during the second campaign. The mean value found for this parameter in the green lake was 66 µmol L^{-1}. Very close to the observed value of 52 µmol L^{-1} for the crystalline lake. Lakes 01SR and 06SR had mean values of 0.72 µmol L^{-1} and 0.21 µmol L^{-1}, respectively, which were lower than the values from the initial campaign.

The methane concentration in the water column exhibits the same trend as the hourly methane emission for each campaign. For the first campaign, the concentration of methane decreases, particularly during periods of higher water temperature, whereas for the second campaign, the concentration rises.

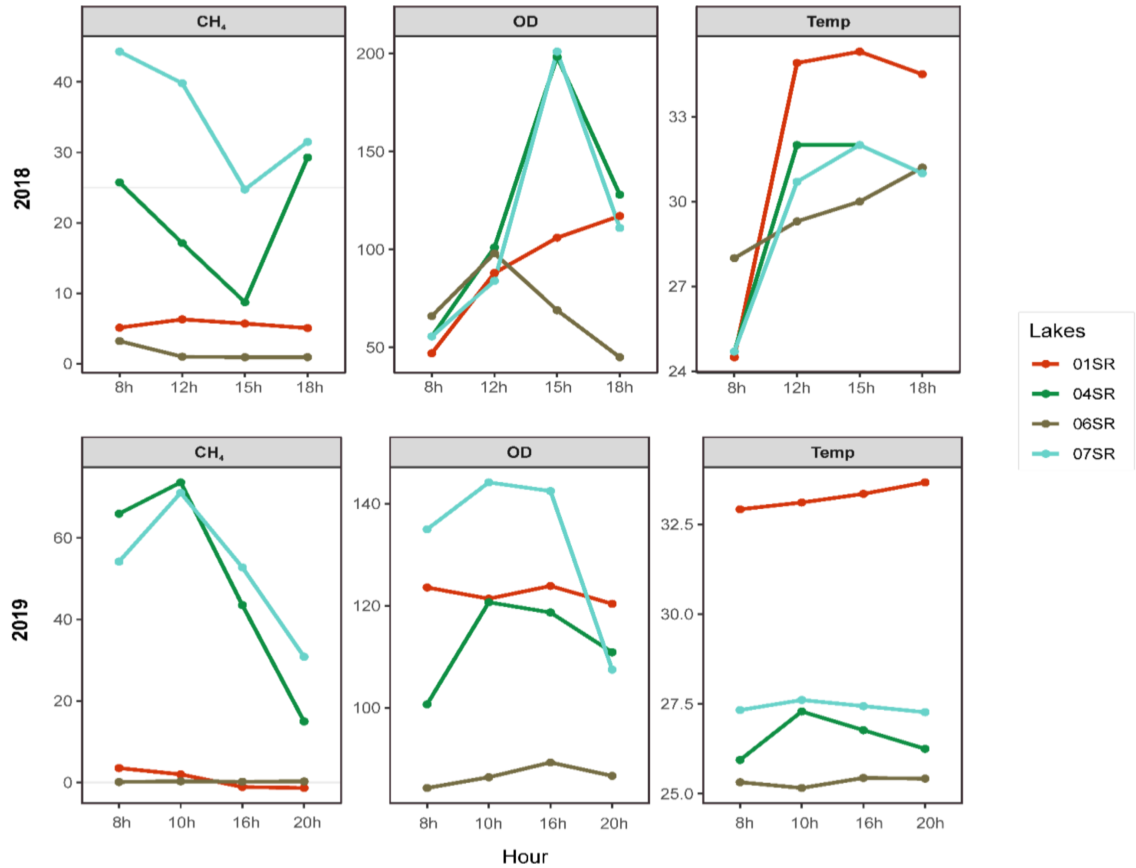

Figure 5. Changes in CH_4 concentration (headspace method), dissolved O_2 and water temperature at 5 cm below the lake surface

Even on different sampling days, differences in water temperature were minimal between lakes. In the first campaign, the greatest differences were observed at 9 a.m. with the lowest range, and in the second campaign, at all measurement points of 01SR lake. The saturation of dissolved oxygen fluctuated between 45 and 200% during the first campaign, and between 85 and 145% during the second. In most of the lake samples, it was possible to observe O_2 supersaturation at some point. However, not reaching the O_2 bubble level (above 500 %).

2.3.3 PCA Analyses

Principal Components Analysis (PCA) relies on linear models of the original variables to reduce data. Our initial campaign results reveal the first two major components of water chemistry data and an accumulated emission of gases. According to the PCA plot, two axes in this graph accounted for 50.4% and 27.6% of the variance (Figure 6A).

For this campaign, we were able to observe a distinct distinction between lakes and the primary factors that govern emissions. During the methanogenesis process, black lakes (01SR and 06SR) are harmed primarily by high concentrations of terminal electron acceptors (TEAs). On the other hand, CO_2 and CH_4 emissions from the crystalline lake were positively correlated with the lake's volume and depth, as well as the water temperature. The PCA also revealed a strong positive correlation between dissolved oxygen and total nitrogen (TN) with N_2O emission from the green lake (04SR). A weakly positive correlation with CH_4 emissions and a weakly negative correlation with CO_2 emissions.

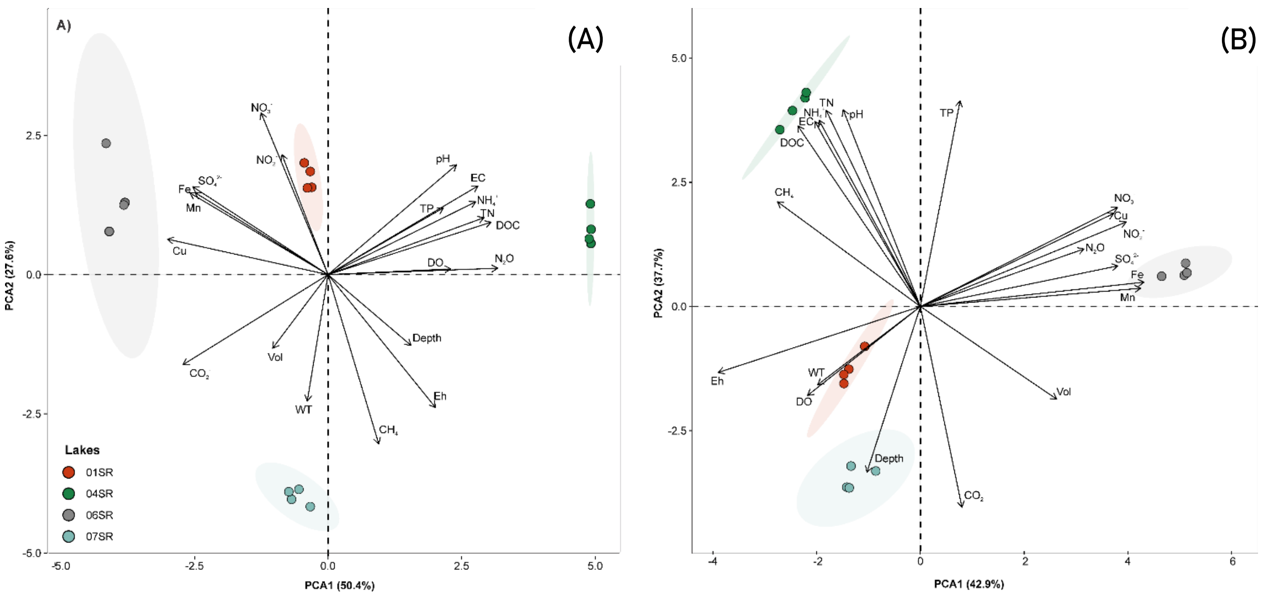

Figure 6. First and second extracted principal components (PCs) from chemical analysis of water and daily cumulative gas emission from saline-alkaline lakes in 2018 (A) and 2019 (B).

In contrast, the results of the PCA analysis for the year 2019 revealed distinct lake behaviors (Figure 6B). The first principal component explained 42.9% of the variance for this year, while the second component explained 37.7% of the variance.

As demonstrated by the PCA results for the second campaign, the TEAs demonstrated a negative correlation with CH_4 emission, particularly for 06SR lake, whereas 01SR lake did not exhibit a clear trend. In contrast to the results of the first campaign, there is no correlation between TN and N_2O in the green lake (04SR). For this lake, the dissolved organic carbon (DOC) was a crucial component of CH_4 emissions. In addition, green lake's methane emission had a negative correlation with volume, while 01SR lake's methane emission had a weakly positive correlation with water temperature. The lake's depth was a significant factor in its higher CO_2 emissions (07SR).

2.4 Discussion

The biogeochemical process through a variety of ecological interactions is the key to this challenge, which entails gaining a better understanding of the principal characteristics associated with water processes and gas formation. To investigate and explain how this complex ecosystem functions, we should examine these interactions in a variety of ways, depending on the lake or campaign of interest since the environment is dynamic.

Due to the phytoplankton and cyanobacterial biomass, Green Lake (04SR) is clearly a site for methane production. The presence of cyanobacterial blooms can increase sedimentary concentrations of CH_4 and atmospheric emissions (Bartosiewicz et al., 2021). These organisms are the primary precursors to biogenic methane formation in this ecosystem (Barbiero et al., 2018). Methane production can also be a byproduct of hydrogen produced by cyanobacterial nitrogen fixation, given the high nitrogen concentration in this lake (Yeung et al., 2017), and cyanobacteria are also potential CH_4 producers in oxic conditions (Berg et al., 2014). Some studies (Morana et al., 2020; Günthel et al., 2021) have demonstrated that oxic CH_4 production is closely related to phytoplankton metabolism. However, methane production in O_2 supersaturation in tropical lakes remains a paradox (Morana et al., 2020), despite being a common and well-understood condition in our ecosystem (Barbiero et al., 2018).

Since black water lakes have a lack on phytoplankton blooms, methane emissions are observed to be lower (Barbiero et al., 2018). However, the impact of TEA availability was the primary factor observed in both campaigns in relation to lower methane emissions from black lakes (01SR and 06SR). The presence of TEAs ($O_2 \rightarrow NO_3 \rightarrow Mn^{4+} \rightarrow Fe^{3+} \rightarrow SO_4^{2}$) is associated with low methane emissions (See Table S2). These are primarily consumed and do not promote methanogenesis, thereby inhibiting CH_4 production. In the absence of TEAs such as sulfate and nitrate, hydrocarbons are converted into their end products (CH_4 and CO_2) (Cruz; Marsaioli, 2012; Bansal; Tangen; Finocchiaro, 2016; Queiroz et al., 2019). In the second campaign, where nutrients were enriched, there was also a higher concentration of TEAs, resulting in decreased methane emissions.

Despite the low emission, the O_2 supersaturation and consequently higher oxidation had a positive correlation with the methane emission for the black lake 01SR in particular. Combined with the lower water volume, indicate that a significant portion of the CH_4 can be produced in this lake originated from the ebullition pathway. Similar what was observed during the first campaign, the same behavior was observed during the second campaign regarding methane emission from both black lakes with a high concentration of TEAs limiting CH_4 production, particularly for the 06SR lake. There are no significant differences in methane emissions between years for this lake. Due to high sulfate concentrations, the response of methane emission rates to changes in temperature and water depth is less sensitive in permanent wetlands (Bansal; Tangen; Finocchiaro, 2016).

Macrophytes are the dominant organisms in the crystalline lake (07SR) and a crucial aspect of gas behavior (Van der Valk, 2012; Ventura, 2014). Greater CH_4 emissions in the crystalline lake in both years are attributable to macrophyte detritus, which is potentially available for methane production from biological activity under anoxic sediment conditions (Fonseca et al., 2004; Grasset et al., 2019). The magnitude of organic sedimentation also affects methanogenesis in saline environments (Borges; Abril, 2011), where the high contribution of recent organic matter (OM) contributes to the rapid consumption of sulfate and increased CH_4 production rates.

The larger water column (> 100 cm) in this lake is a contributing factor to the increase in CH_4 transfers, as oxygen depletion at the lake bottom can prolong the anoxia period, thereby favoring the production of CH_4 (Bartosiewicz et al., 2019). According to DelSontro et al. (2016), the morphometry of a water column has a significant impact on methane transfer to the atmosphere. The contribution of ebullition to the CH_4 transport to the atmosphere decreases with depth. This is additional evidence of the CH_4 formation in sediments containing macrophyte detritus, suggesting that most of the methane transfer in a larger volume of water in the crystalline lake may occur via diffusion.

As demonstrated by the second campaign, the water temperature was also a significant factor in the crystalline lake's increased methane emission. The positive correlation between water temperature and CH_4 emissions in this system may be a result of higher temperatures causing a faster rate of decomposition of organic matter in sediments (Ba et al., 2020) and also a lower water column.

Despite their appearance as lakes with lower methane emissions, the black lakes are significant carbon dioxide sources. According to Barbiero et al. (2018), this lake emits more carbon dioxide at night, which was not observed in our study in either year (one point measured). Specifically, for these lakes, the organic carbon (OC) in the water is produced by the mineralization of OC from the surrounding terrestrial ecosystems, which can be transferred with the flood pulse. On the other hand, while our study did not find a correlation between CO_2 and DOC content, a few other studies did (Jonsson et al., 2003; Nydahl et al., 2018).

Regarding the CO_2 dynamics of the crystalline lake (07SR), our results demonstrated a consistent CO_2 flux into the atmosphere. Additionally, CH_4 oxidation rates to CO_2 are generally proportional to CH_4 production rates (Delsontro et al., 2016), and water column stratification can influence methane oxidation and the associated bacterial communities (Steinle et al., 2017). CH_4 that is available in the sediment and diffuses into the water column can be oxidized by methanotrophic bacteria into CO_2 before it diffuses into the atmosphere (Queiroz et al., 2019). Consequently, the greater water volume in the first campaign, the bioavailability of CH_4, and an O_2 supersaturated environment may be significant characteristics of this lake's CO_2 emissions. Although CO_2 emissions remained high during the second campaign, the lake's O_2 saturation decreased, and this may have contributed to a decrease in CH_4 oxidation (Figure 5). In addition, as methane oxidation is negatively correlated with nitrogen status (Figure 6), the low concentration of NO_2^- + NO_3^- + NH_4^+ in this lake (Supplementary Table 1) may promote higher CO_2 rates via CH_4 oxidation (Chan; Parkin, 2001).

For both campaigns, a greater abundance of emerged macrophytes in the crystalline lake (07SR) caused submersing macrophyte leaves to be less exposed to light, thereby limiting light penetration into the water and photosynthesis. Submerged macrophytes can use bicarbonate as a carbon source for photosynthesis, making them even less susceptible to carbon limitation from the atmosphere (Madsen; Jensen, 1991; Bowden; Glime; Riis, 2006; Wilzbach; Cummins, 2008). The presence of abundant floating leaves impedes the diffusion of gases into the atmosphere, and CO_2 and CH_4 supersaturation is anticipated in such environments (Fonseca; Marinho; Esteves, 2017).

Barbiero et al. (2018) also observed the accumulated consumption of CO_2 in green lakes. In saline-alkaline lakes in the Nhecolandia Pantanal, the authors found that despite the presence of significant CH_4 sources, green water lakes are also significant CO_2 sinks. The consumption of CO_2 from green lakes is associated with the photosynthesis of phytoplankton blooms, attributing the variation in the flows of emissions and/or consumption not only to the presence of these organisms, but also to their abundance. This behavior was attributed to organisms in the water that were actively undergoing photosynthesis and was observed during the daytime when the light intensity was the highest (Yang et al., 2015; Huang et al., 2019). Similarly, according to Bartosiewicz et al. (2019), CO_2 depletion in lakes with greater phytoplankton biomass can be associated with a warming of the water's surface. Therefore, green lakes have the potential to act as carbon sinks and provide an ideal environment for absorbing large amounts of CO_2 through photosynthesis.

During the second campaign, it was possible to observe that, instead of consuming CO_2, the green lake emitted CO_2 and had an 8-fold increase in methane emission. At times of higher ambient temperature, which are typically photosynthesis-dominant, it was not possible to observe CO_2 consumption in this setting (Supplementary Table S1). The increase in mean temperature in the months sampled in both campaigns (27.6 to 29.0) and the decrease in total precipitation (792.8 to 702.2) as well as the decrease in water volume between campaigns may have a significant relationship with these alterations. Drainage can transform lakes from a net sink to a net source of carbon dioxide (Yang et al., 2018). These observations indicate that green and black water lakes are more reactive and, with the impending rise in global temperature and the possible reduction of flooding periods in these regions as a result of climate change, will have an impact on essential functions and ecosystem services such as carbon sequestration and the increase in this gas's emission (Moomaw et al., 2018).

In our study, the crystalline lake exhibited high CO_2 and CH_4 emissions, with slight variations in both campaigns. In the second nutrient enrichment campaign, macrophytes play a significant role in absorbing excess nutrients and releasing them as gases through organic processes (Van der Valk, 2012). This result suggests that crystalline lakes are less reactive to changes in water's chemical properties than other studied lakes, and this can be a significant source of greenhouse gas emissions (GHG). According to Barbiero et al. (2018), crystalline lakes account for 5% of all Pantanal lakes, but the magnitude of emissions from this lake requires special attention and precise confirmation, highlighting the significance of studying your biogeochemical dynamics.

Compared to CO_2 and CH_4 emissions, the magnitude of N_2O emissions from lakes is relatively small, as demonstrated by our findings. Due to the anoxic conditions that prevail in wetland environments, large N_2O emissions are generally discouraged (Tangen et al., 2016; Lauerwald et al., 2019). Coastal wetland ecosystems, such as tropical mangroves, produce the most nitrous oxide gas (Ventura, 2014). Despite this, it is a significant greenhouse gas with a high global warming potential and a high level of persistence, which may increase their fluxes as a result of global warming (Cheng et al., 2020).

Due to the availability of nitrogen, especially ammonium and nitrate, lakes as sources of N_2O can have a variety of N_2O fluxes (Kortelainen et al., 2019). In our first campaign study, the N_2O emission for the green lake (04SR) was positively correlated with the total nitrogen

(TN) concentration in the water column. The positive correlation between N_2O emission and TN in the green lake can be explained by the fact that the substrate's high nitrogen content (higher NH_4–N and NO_3–N content) can promote nitrification and denitrification, thereby increasing N_2O emissions (Ba et al., 2020). Due to the positive correlation between DO, NH_4^+, and N_2O, this gas can be produced as a byproduct of nitrification in the green lake (04SR). In an aerobic process in which ammonium (NH_4^+) is oxidized to nitrate (NO_3^-) by nitrifying bacteria and archaea (Loscher et al., 2012), nitrous oxide is produced. As also discovered by Barbiero et al. (2018), green lakes with strong blooms consumed N_2O during the second campaign. The authors attributed the effect to alkaliphilic denitrifying microorganisms, which utilize organic substrates and convert nitrates and nitrous oxides into gaseous nitrogen. Denitrification can be an effective sink for N_2O (Conthe et al., 2019).

Consequently, NO_3^- limitation may be one of the factors responsible for N_2O consumption during denitrification and nitrification in the crystalline lake (07SR) (Audet et al., 2014; Mwagona et al., 2019). Plants can compete for the nitrogen source, so an abundance of macrophytes can promote changes in nitrogen-related processes and increase N_2O consumption (Mwagona et al., 2019; Mander et al., 2021).

Although our results did not adequately explain the behavior of N_2O fluxes to the 01SR lake, the availability of N sources in this lake was extremely low, and this was likely the limiting factor for N_2O fluxes. Sediments of these lakes have a high capacity to promote complete denitrification, removing nitrate from the environment and causing low N_2O emission (Mander et al., 2021). Between campaigns, there is no emission standard for the black lake (06SR), which was initially the lake with the highest consumption and is now the lake with the highest N_2O emission. The seasonality of N source concentration has a substantial impact on N_2O fluxes from wetland ecosystems (Cooke et al., 2008). Nitrate was the primary driver of N_2O emission during the second campaign, particularly in the black lake (06SR), which was not observed during the first campaign. Consequently, where N sources are abundant, a greater proportion of N_2O will not be reduced by denitrification and will be emitted (Cooke et al., 2008).

2.5 Conclusion

In fact, some lakes have a standard of emissions like green lakes are methane sources and carbon dioxide sinks, whereas black lakes are notable for their significant carbon dioxide emissions, and crystalline lake, reveal themselves as methane and carbon dioxide sources.

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3. EFFECTS OF SATURATION ZONES ON GREENHOUSE GAS EMISSIONS AND CARBON STOCK IN THE MARGINS OF SALINE-ALKALINE LAKES IN THE PANTANAL OF NHECOLÂNDIA/MS, BRAZIL

Abstract

Wetlands have a relatively high potential to sequester carbon in soil compared to other ecosystems and it can play an important component of the global carbon cycle to climate change adaptation. Pantanal is recognized as the world's largest tropical wetland with a mosaic of alluvial fans. This mosaic brings to us a heterogenicity of lakes with distinct chemical-physical parameters that can provide highly variable soil organic carbon (SOC) stocks and sequestration rates. These ecosystems are strongly influenced by flood pulses and rainfall that can alter the terrestrial to aquatic phase in lakes margins. In face of the climate change and hot extreme events, the wet phase in this environment is compromised. Over time, these changes in hydrologic conditions can lead to shifts in species communities as well as to biogeochemical changes in the soil which can affect the soil's greenhouse gas emission and soil carbon storage. Our objective is to estimate soil greenhouse gas emissions and soil carbon stock in two campaigns, following three different zones of saturation [Saturated Zone (SZ), Intermediate Zone (IZ) and Unsaturated Zone (UZ)] from the margins of four different lakes: one green lake, two black lakes, and one crystalline lake. In general, our results showed greater CH_4 emission was observed for the chambers located in the most saturated zone (SZ). As the sampling point moved away from the wetting front (IZ→UZ), it was observed the reduction of CH_4 emissions and an increase in CO_2 and N_2O emissions. Green lake showed a CH_4 emission amplitude that was much higher than other lakes in both campaigns. The margins of the black lake (06SR) were the only ones to present CO_2 consumption at SZ and IZ points in the first campaign. No clear trend toward emission or consumption of N_2O was observed. Higher C storage was observed in the black lake (06SR), especially in SZ in response to the abundant presence of grasses. Our results showed that saturated zones can emit higher methane rates than oxygenated zones. However, is in these zones that more carbon can be stored. Unsaturated zones can result in losses of C to the atmosphere.

Keywords: Carbon sequestration; Greenhouse gas emissions; Soil; Pantanal; Wetland.

3.1 Introduction

Globally, wetlands cover about 6 - 9% of the Earth's surface, with the potential to store 20–30% of the terrestrial soil organic carbon (SOC) which can play an important in component of the global carbon cycle to climate change adaptation (Nahlik and Fennessy, 2016; Limpert et al. 2020). However, wetlands can be vulnerable to the impacts of climate change and increasingly challenge their ecological function (AR6 WGI, IPCC, 2021). Impacts on wetlands may include loss of carbon stored in the soil, changes in soil structure, and more frequent drying or flooding wich can change the biogeochemistry and function of the wetland (Moomaw et al., 2018; Salimi; Almuktar; Scholz, 2021).

Pantanal is a sedimentary basin is recognized as the world's largest tropical wetland with a mosaic of alluvial fans and geographic subdivisions. The Pantanal of Nhecolândia (~ 26,000 km²) is the second largest subdivision, localized in the south portion of the fluvial Taquari megafan, in the state of Mato Grosso do Sul, Brazil with a unique and remarkably biodiversity. The main characteristic of this environment is the presence of around 15.000 small lakes, with saline or non-saline waters that can be accompanied by a high pH (alkaline properties) (Barbiero et al., 2018). Saline lakes are supplied by groundwater flow and rain (Becker et al., 2018), which can change the terrestrial to aquatic phase in lakes margins and can alter the biogeochemical functions of this ecosytem. As it is under a tropical climate with high and constant temperatures (~30°C), the conservation of these systems, therefore, has implications for the dynamics of greenhouse gases in the Pantanal (Guerreiro et al., 2019).

Soil is vital in climate regulation and has shown an important but complex role in the global carbon cycle of wetlands. Soils can behave as sources or sinks of GHG, and this exchange between soil and atmosphere is determined by environmental factors and natural conditions. Wetlands are strongly influenced by flood pulses which can alter dry to wet phase (or oxic to anoxic) soil conditions that can influence the activity of microorganisms (Johnson-Beebout et al., 2009; Rubol et al., 2012; Wang et al., 2018) and reflect in different sources of GHG emissions (Jacotot; Marchand; Allenbach, 2019). The availability of O_2 can modulate the biogeochemical processes involved in the production and emission of GHG (Liengaard et al., 2013). When periods of flooding are predominant, the soil presents the main pores saturated with water and the anaerobic conditions of the soil are precursors of CH_4 formation in the methanogenesis process. However, when the water table is lower and aerobic soil conditions are more prevalent, this favors aerobic respiration (Limpert et al., 2020).

The influence of flood pulses on soil GHG emissions can occur especially in the upper soil layer (0-10 cm) with the change of soil properties, such as moisture and salinity (Vicente, 2021). The oscillation between terrestrial and aquatic phases and changes in soil moisture can influence nitrogen availability and, consequently the production and transport of N_2O in wetlands (Feng et al., 2015; Stoliker et al., 2016). High salinity can affect physicochemical properties and especially biomass and microbial activity, causing changes in the gas formation such as uptake of CH_4 in the soil and N_2O emissions (Pathak; Rao, 1998; Yin et al., 2017; Yang et al., 2018). When soil salinity and alkalinity increase, N_2O reductase is affected, and N_2O produced by nitrification in the soil will increase (Resham; Amitava; Abbey, 2017). Likewise, some studies have shown a positive correlation between soil and temperature, with CO_2 and N_2O fluxes (Gudasz et al., 2010; Alhassan et al., 2018; Cheng et al., 2020) as well as for CH_4 (Cui et al., 2015).

Due to the accumulation of organic matter in the surface horizon and their migration along the profile (Westin, 1953), the alkaline soil systems of the Nhecolândia Pantanal lakes are frequently referred to as sodium black soil systems ("black alkali") such as: (1) - When they occur in environments with very specific physical and chemical conditions, such as high pH, sometimes accompanied by high electrical conductivity of the circulating soil solutions. (2) – These environments are dynamic, usually under the influence of strong evaporation: they favor concentration processes of soil solutions, both the formation and destruction of clay, with certain degree of reversibility, which can be quite rapid. (3) - The reversibility of these processes is, however, relative. In fact, water transfers, which are the main vectors formation, transformation, and destruction of these systems, can be limited by the loss of structure and decreased soil permeability, or even by the formation of horizons cemented by accumulations of amorphous silica (Silcretes), which become impermeable. (4) - Finally, these environments enable interactions between biotic and abiotic processes, due to the high production and solubility of organic matter resulting from high pH, which can, therefore, migrate in the system with soil solutions (Barbiero et al. 2018).

Hydrogeomorphology is also an important factor for C storage (Amendola et al., 2018; Perez-Rojas et al., 2019). The decomposition of soil organic matter (OM) represents the main loss pathway for SOC and plays an important role in the processes of formation/emission of greenhouse gases (Vega et al., 2014). Inundated wetlands can potentially sequester substantial amounts of soil carbon. The continuous cycle of flooding and draining can deliver sediment and OM to the lake's margins, creating potential for high C reservoirs (Sutfin; Wohl; Dwire, 2016). Some studies showed us an important change in the SOC stocks in Pantanal, primarily, attributed to the degradation of the grassland ecosystem (Johnson et al., 2013) and indicate a low carbon storage potential of its soils (Couto; Oliveira, 2011). The investigation of organic carbon (OC) reservoirs makes it possible to determine the balance between C losses and gains, generating knowledge about the flow of matter and energy in the soil system (Roscoe et al., 2006).

The role of wetlands in the global carbon cycle requires further research, especially in front of climate change, which may undermine the sequestration potential of wetlands. This work aimed to understand the behavior of greenhouse gas emissions from soil and soil organic carbon storage under different hydrological conditions.

3.2 Material and Methods

3.2.1 Site description

The Pantanal of Nhecolândia presents different landscape units. The first, a unit usually moist, represented by the lowest part of the relief that usually remains with moist soil and, as a result of flooding, with submerged soil. The second, a usually seasonal unit located in the most intermediate part of the relief with periods of wet or dry soil, depending on the time of year. The third and last unit of the landscape is called “Cordilheiras”, which is usually dry, located in the upper part of the relief with heights up to 3-4 meters above the level of lakes with the predominance of arboreal vegetation, which are common areas that are not affected by flooding (Bacani; Sakamoto; Quenol, 2006; Rodela et al., 2007).

Predominantly, the soils of the landscape units in the subregion of Nhecolândia, fall into the class of Entisols (USDA. Soil Survey Staff, 2014). Depending on the smaller or greater influence of hydromorphic conditions, they are differentiated as Orthic Entisols and Hydromorphic Entisols, the latter located in the lowest positions, where the water table is closer to the surface (Cardoso et al., 2016). “Cordilheiras” soils have very low clay content (2 to 4%), high base saturation, very low acidity, dominance of flocculating cations (Ca, Mg and Fe), low carbon/nitrogen ratio (C/N), and high content of soluble phosphorus (Cunha, 1980). Despite their very low levels of organic carbon, the soils of the “Cordilheiras” differ from the other units of the landscape due to the conditions of natural fertility, which is much higher especially in horizons below 2 m in depth, even with Na^+ concentration relatively high and higher available P contents (Cardoso et al., 2016).

3.2.2 Soil GHG emissions measurements

The sampling of greenhouse gas emissions was a performance in two campaigns (2018 and 2019). Four lakes were selected: one with green water (identified as 04SR); two black (01SR and 06SR), and one crystalline (07SR) in order to characterize the greenhouse gas flow and C storage variability between them (Figure 1). The denomination used "SR" refers to the collection site (São Roque farm) and the numbering to the corresponding number of each pond selected in the field.

In order to assess the influence of soil saturation at the lake's margins and simulate the natural flood pulse on the gases emissions, collections took place at three points from the edge. For each collection point, three static chambers with 10L volume were used, located in toposequence and spaced at a distance of around two meters from a more saturated zone (front of wetting next to the lake - SZ), an intermediate zone (IZ) and one unsaturated zone (UZ). Consider *saturated zone* where the soil is covered by a small layer of water (about 0.5 cm); *Intermediate zone* when the water table was between 30 cm deep; *Unsaturated zone* when a water table does not reach the sampled depth of 50 cm.

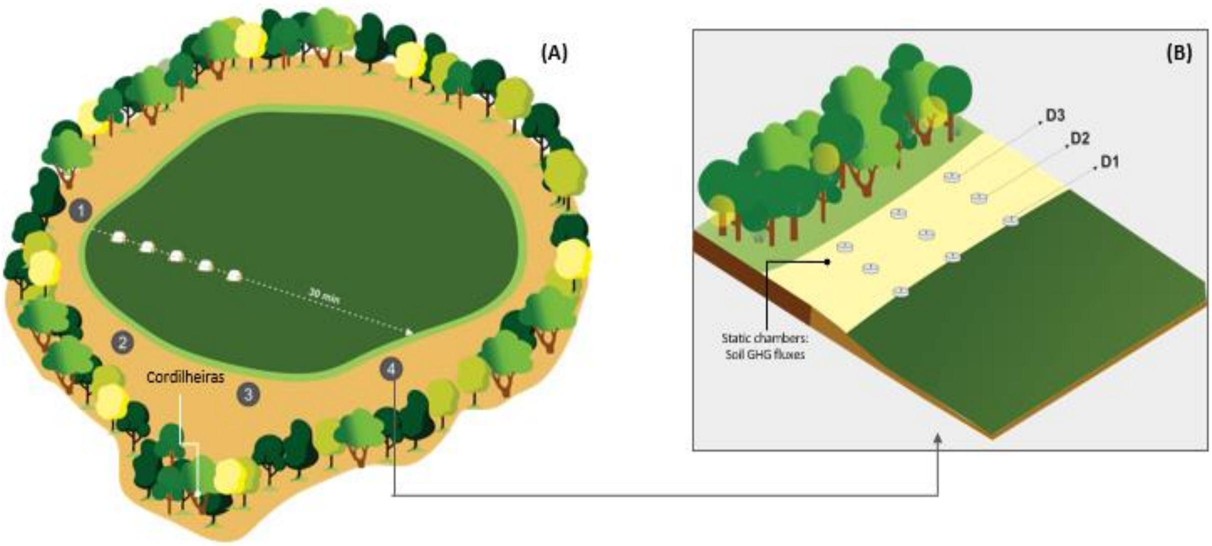

Figure 1. Sampling points (A) and arrangement of chambers for soil GHG fluxes measurements with three distances from the wetting front (B)

The sampling was carried out four times counted from the closing of the chambers being T_0: representing the atmospheric air; T_1: five minutes after closing the chambers; T_2: fifteen minutes after closing the chambers; and T_3: Thirty minutes after closing the chambers. The sampling was performed using 60 mL nylon syringes (Becton DickinsonInd. Surgical Inc.) with a check valve. The sampled gases were transferred into 30 mL glass bottles, previously capped with gas-tight, and evacuated with a hand vacuum pump at 0.75 kPa. All collections occurred in two periods: in the morning between 9:00 and 11:00 h, and in the afternoon, between 14:00 and 16:00 h. During sampling, ambient temperature and atmospheric pressure were monitored. Sampling was carried out in two campaigns: the first in 2018, and the second in 2019.

3.2.3 GHG samples analysis

GHG concentrations were measured by gas chromatography (SRIGC-110®, Torrance, USA) with a packaged HAYESP ™ column (80–100 mesh) maintained at 82 °C to separate the molecular gases. The concentration of N_2O was quantified using an electron capture detector (ECD), and the concentrations of CO_2 and CH_4 were estimated through a flame ionization detector (FID). GHG fluxes were calculated by linear variation in the amount of each gas in the chambers (obtained by the Clapeyron equation) as a function of the incubation time (30 minutes).

3.2.4 Soil sampling and physical-chemical analysis

Soil samplings were performed manually with the aid of an auger at the same point when gas samples were collected after the gas sampling (Figure 2B). The samples were carried out in order to contemplate the layers 0-10, 10-20, 20-30, 30-40, and 40-50 cm, loaded into a sealed bag, stored, and sent to the laboratory. In the laboratory, the samples were sieved for chemical analysis at LSO (ESALQ/USP), and ground for total C and N analysis at the Stable Isotope Laboratory (CENA/USP).

The particle size distribution was determined according to the method described in Embrapa (2017). The separation of fractions was determined by sieving and sedimentation and the measurement of separated fractions was by weighing them after drying in an oven. The soil chemical analysis was performed in 0-10 cm layer of SZ and UZ points to investigate that was possible differences between the points sampled. Soil water content was determined based on the difference between measurement weight (mass of wet soil minus ring weight) and the oven-dry soil mass of samples. Soil temperature was determined on site by inserting a temperature probe into the 5-cm soil layer. The soil pH and EC were measured in the supernatant of 1:5 (w/v) soil–water mixtures using a pH meter and a conductivity meter (Mettler Toledo, USA). The soil samples were used to determine micronutrient concentration: B by hot water; Cu, Fe, Mn, Zn determined by DTPA (diethylenetriaminepentaacetic acid) extraction solution; Ca, K, Mg, and P were extracted with Mehlich-1 and Mehlich-3 solutions, and membrane resin; OM: colorimetric determination; pH: $CaCl_2$. Total carbon (TC) and total nitrogen (TN) were determined by combustion (Shimadzu model TOC-5000A analyzer).

3.2.5 Soil Carbon Storage

Soil C stock per each sampled depth, per area, was obtained as shown by Eq. 1:

$$Eq. 1: CS = (C * BD * W)/10$$

where: CS is the carbon storage (Mg C ha^{-1}), C is the carbon content (g kg^{-1}), BD is the bulk density (kg dm^{-3}), and W is the width of the soil layer (cm).

The values of bulk density (BD) were obtained in peer-review papers which could represent the same environment of this study. For this, we selected the values presents in Schiavo et al. (2012) in a study that was carried out in the Pantanal of Nhecolândia as well, in soils with the same sandy texture.

3.2.6 Statistical analysis

R statistical software was used for all statistical analyses (R Core Team, 2017). One-way ANOVA was conducted to identify the differences in the greenhouse gas emission and soil carbon content between saturation zones in four margins lakes. Differences were considered to be significant if $p < 0.05$. Pearson correlation analysis was performed to reveal the relationships between GHG emissions and environmental parameters. For means comparisons tests Tukey was used with $p < 0.05$ (*Package 'rstatix'*).

3.3 Results

3.3.1 Physical-chemical properties

The particle size distribution of the samples collected up to 50 cm deep on the margins of the lakes highlighted the similarity between the sampled units, which have sand as the predominant textural class (above 90% sand) (Supplementary table 1). The high sand content in these samples is due to their source material, considering that the Pantanal is a lowered plain formed from the deposition of sandy sediments. Thus, in general, the margins have practically no silt + clay, with emphasis on 04SR with almost 100% sand and 06SR among the four margins lakes studied with lower contents. Likewise, it was not possible to observe significant variations in depth.

The highest concentrations of organic matter (OM) and Fe were found in the samples collected around lake 06SR (Table 1). It is observed that although the lakes constitute saline-alkaline environments, the pH of the soils in the points sampled at the lakes margins does not indicate this character. At the point of highest saturation (SZ), the pH ranged from 5.07 to 7.80, respectively, in lakes 07SR and 01SR. In the unsaturated zone, (UZ), the pH variation ranged from 4.60 to 7.88, with the lowest and highest values being found, respectively, in lakes 06SR and 01SR. The highest concentrations of P, Ca and highest CTC were observed in lake 04SR. Likewise, the highest salinity was observed in the saturated zone of lake 04SR. About this property, only 06SR showed us an increase in values following the wetting front. All other property values were very similar across all lakes and both saturation points analyzed.

Table 1. Soil chemical analysis for 2018 sampling in the 0-10cm layer

Lake ID	pH	ST	Umi	EC	OM	P	SO_4^{2-}	K	Ca	Mg	H+Al	SB	CEC	V	B	Cu	Fe	Mn	Zn
	-	°C	%		g.dm⁻³	mg.dm⁻³		mmolc.dm⁻³						%	mg.dm⁻³				
Saturated zone																			
01SR	7.80	25.47	2.36	55.06	2.87	5.81	9.55	3.11	5.27	0.66	6.67	9.10	15.77	57.67	0.25	0.24	9.43	2.16	0.11
04SR	6.73	24.00	0.96	106.52	3.06	63.67	8.40	7.25	55.56	1.87	7.67	64.60	72.27	89.67	0.25	0.22	1.62	4.15	0.14
06SR	5.73	26.50	11.08	39.37	6.13	2.94	15.84	3.01	0.66	0.18	13.33	4.03	17.37	31.00	0.15	0.27	51.83	3.13	0.07
07SR	5.07	23.10	5.28	48.77	3.66	2.75	8.30	2.61	3.18	1.99	9.33	7.75	16.25	50.67	0.17	0.21	10.60	4.68	0.06
Unsaturated zone																			
01SR	7.88	28.97	1.62	49.40	2.77	7.62	9.60	2.35	5.65	0.48	6.33	4.85	11.35	66.00	0.34	0.19	3.24	0.54	0.08
04SR	7.87	30.63	0.45	70.40	2.17	63.58	9.64	8.39	42.46	1.39	6.33	52.40	58.73	89.00	0.26	0.24	1.86	3.29	0.15
06SR	4.60	31.03	2.63	89.13	7.31	1.88	10.15	2.25	0.62	0.36	15.67	3.23	18.90	17.00	0.13	0.26	70.34	2.04	0.09
07SR	5.83	28.57	2.75	26.23	2.37	2.13	7.05	2.41	3.04	1.45	8.33	5.90	15.67	46.00	0.12	0.17	6.94	1.64	0.06

ST - Soil temperature; EC - Electrivity conductivity; Umi - Umidity; OM - Organic matter; SB - Sum of bases; CEC: Cation exchange capacity; H + Al – potential acidity; V – base saturation. (n = 3)

3.3.2 Soil GHG emission monitoring

The greenhouse gas emission from the soil in the margins of the lakes showed different behaviors between margins and the wetting front. Despite this, the trends presented by the emissions observed during the two campaigns were similar, even if for the second campaign (2019) the emissions, especially for CO_2 and CH_4, have lower magnitudes when compared to the first campaign (2018) (Figure 2).

Our results are consistent with what is known regarding methane production. In general, greater CH_4 emission was observed for the chambers located in the most saturated and anoxic environment (SZ; Figure 2). Despite the variation between the saturation zones, especially in IZ and UZ for some lakes, the proportion of methane emission reductions, for the first campaign in SZ compared to UZ was around 20, 80 and 100% for 01SR, 06SR and 04SR margins, respectively. For the second campaign, the reductions were around 92 and 100% for 01SR and 04SR margins, respectively.

Margins of lake 04SR (green), for the first campaign, showed a CH_4 emission amplitude was much higher than other lakes, especially when compared in position SZ at the lake margins (~ 98% greater than in lake 01SR) (Figure 2). For the second campaign, despite smaller magnitudes, from SZ, the same proportion of methane emission from the 04SR lake margins in relation to the black lake margins (01SR) was observed. In two years of evaluation, the margins of black (01SR and 06SR) and crystalline (07SR) lakes were not presented as important sources of CH_4 emissions but followed the emission reduction trends of this gas following the wetting front (SZ → IZ → UZ).

As the sampling point moved away from the wetting front, greater oxygenation of the soil (IZ→UZ) was observed, reflecting the reduction of CH_4 emissions and the increase in CO_2 and N_2O emissions (Figure 2). We can observe that the proportion of CO_2 emission increases, for the first campaign in SZ compared to UZ was around 23, 217, and 218% for 04SR, 01SR, and 07SR lakes margins, respectively. For the second campaign, the increases were around 66 and 68% for 07SR and 04SR, respectively.

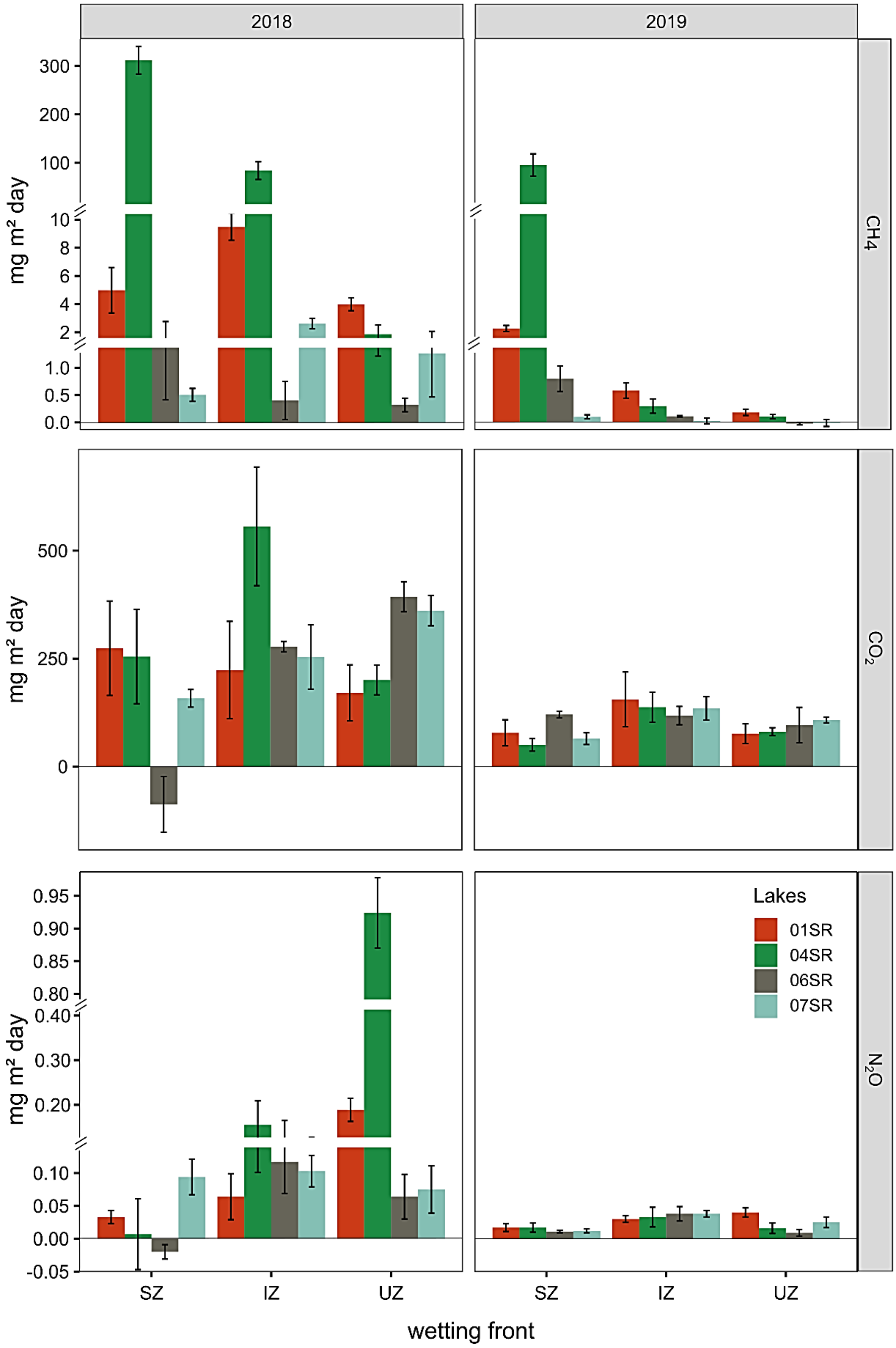

Figure 2. Greenhouse gas emissions in three saturation zones from soils at the margins of saline-alkaline lakes in the Pantanal of Nhecolândia, where (A) CH_4, (B) CO_2, (C) N_2O

The 04SR lakes margins were also responsible for the highest CO_2 emissions compared to the other lakes for the first campaign (Figure 2), while for the subsequent year the greatest CO_2 emission was observed by 01SR lakes margins (black). However, the margins of the 06SR lake were the only ones to present CO_2 consumption at SZ point in the first campaign. In the following year, none of the margins presented CO_2 consumption.

N_2O emissions agreed with the results obtained for CO_2 and CH_4, which for the first year of evaluation the magnitudes of emissions were higher than those of the following year. For the first campaign, the highest emissions were on the edges of the green lake (04SR), especially at point UZ. For the following campaign, the margins of the black lake (06SR) were the ones with the highest emissions, despite not having great differences between the margins.

3.3.3 Soil carbon stock

Mean soil carbon stocks at four different lakes margins at the five consecutive depth intervals (0-10; 10-20; 20-30; 30-40 and 40-50 cm) and different zones of saturation are presented below (Figure 3). The carbon storage in the two campaigns showed us a standard: surface soil layers most contributed to the total soil carbon stock in the upper 50 cm and most of the time decrease into the wetting front (SZ → UZ).

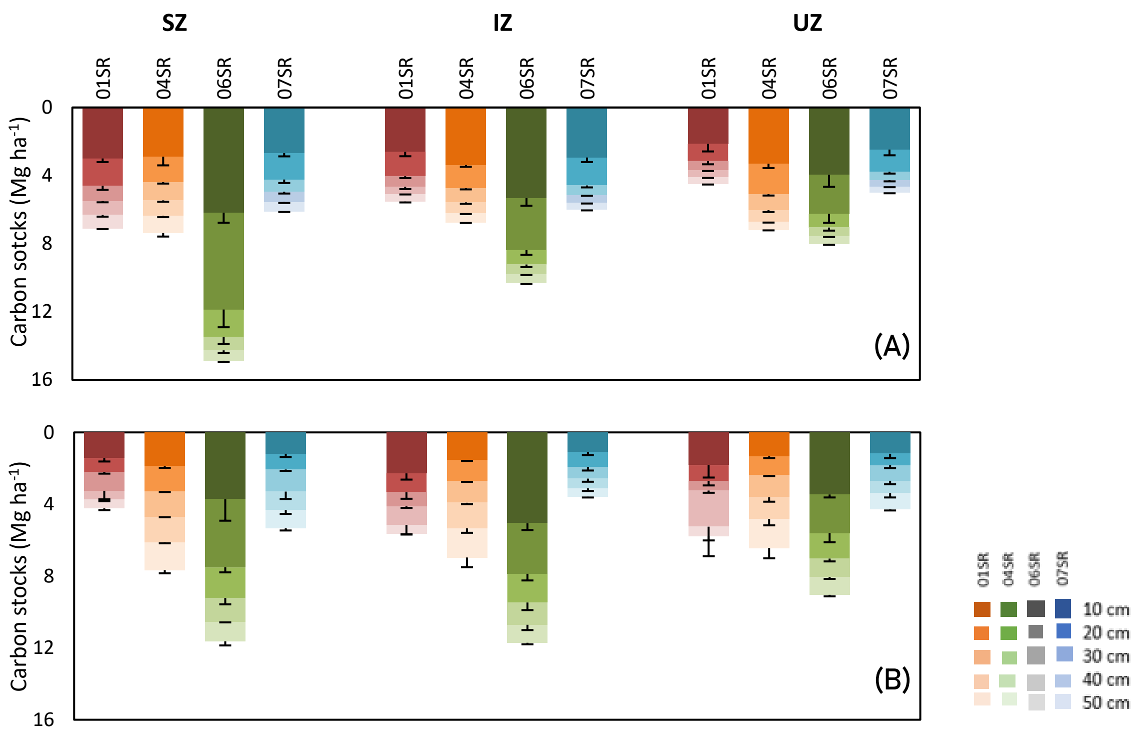

Figure 3. Estimated carbon stocks to a depth of 50 cm in margins of saline-alkaline lakes of Pantanal of Nhecolândia/Brazil in 2018 (A) and 2019 (B)

Although it is possible to observe significant differences for the first campaign with values that statistically demonstrate greater carbon stock in the SZ, with the exception of the 07SR (ns) lake (Supplementary Table S3), the margins of the lakes do not present statistical differences between the saturation zones for the second campaign. In the top 50 cm soils, the margins of black lake 06SR showed us the greatest amount of soil carbon in both campaigns in SZ and IZ. The SOC in 06SR lakes margins was significantly higher than others in 2018 with values above 50 ~ 60% and also in 2019 with values above 30 ~ 60% in comparison to the other margins.

3.4 Discussion

3.4.1 Soil GHG

The impact between flooding and subsequent drying can be the major driver of substantial biogeochemical changes on soil under the influence of processes such as sedimentation, nutrient uptake by the biota and changes in redox conditions that can consequently alter the production and emission processes of GHG's (Liengaard et al., 2013; Ponting et al., 2021). It is known that the formation of methane occurs predominantly in anoxic environments (in the absence of O_2) and its production can be quite variable with respect to soil oxygen availability. In our case, methane is produced in anaerobic zones after flooding and before drainage, especially in the SZ (Conrad, 2020). In this line, the SZ is an area that has great water influence, so the physical-chemical properties of the water can influence the dynamic of GHG's in this zone. The presence of cyanobacteria and archaea in the green lake water, which are the main promoters of methane formation (Tian et al., 2012), is known (Barbiero et al., 2018). So, greater methane emission of green lake margins in SZ may have been due to the greater biomass of methanogenic microorganisms in the zone where oxygen restriction persists.

In the same line, despite no statistical correlation with soil chemical properties, for the same saturation zone, the high content of terminal electron acceptors (TEAs) like Mn, SO_4^{2-} and Fe^{+} in the water (Pellegrinetti et al., 2022) can be responsible to lower methane formation in black lake margins (01SR and 06SR) (Bansal; Tangen; Finocchiaro, 2016; Queiroz et al., 2019). When the lakes show low concentrations of these inorganic electron acceptors methanogenesis is the predominant terminal electron-accepting process (Kolton et al., 2019).

In the same way, the salt concentration and the P increasement can affect microbial cell activity and change the soil microbial community which can alter transport of CH_4 like in 07SR lake's margins for the saturated zone, as 04SR and 06SR for the unsaturated zone (Song et al., 2012; Yang et al., 2018).

Low methane emissions in zones with less oxygen restriction, after drainage, limits the formation of an anaerobic environment and can result in low rates of methanogenesis (Nyamadzawo et al., 2015). Likewise, when the terrestrial phase is predominant in the wetland, it can affect the response of microbial communities involved in CH_4 production/consumption resulting in a reduction in the size and structure of the Archaea community, even that, methane production has already been observed in aerobic soils (Angle et al., 2017). Wagner (2017) demonstrated the existence of methanogenic organisms in aerobic horizons since, in his study, 25% of CH_4 was produced in the oxic horizon of the studied environment.

Most previous studies in soils have observed a continuous increase in CH_4 production over the temperature in anaerobic conditions. However, similar to our results for 06SR and 07SR lakes, Inglett et al. (2012) observed methane emission with a positive linear correlation between temperatures in aerobic environments. The increase in methane emission in aerobic zones indicate that the temperature sensitivity of methanogenesis was probably resulting of the increased availability of C to higher temperatures.

The soil under water-saturated conditions can decrease the gaseous diffusivity of surface soils and the oxygen limitation affects microbial activity and reduces CO_2 fluxes (Liu et al., 2017). The diffusion of gases is about 10.000 times less in water than in air (Agostinetto, 2002). CO_2 emissions are lower when the soil is saturated (SZ) because the anaerobic conditions reduced soil respiration (Saurich et al., 2019; Philben et al., 2020). However, in comparison with methane emissions, some lakes like 01SR and 07SR show an increase of CO_2 emissions in the same zone, as a result of the water's chemical influence. On the other hand, the CO_2 consumption on the margins of lake 06SR for the first campaign in ZN and IZ could be a photosynthesis process in response to the abundant presence of grasses, which could not be excluded from our cameras. However, this trend was not possible to observe in the following campaign due to the lower water levels that did not allow covering the areas of these plants.

Zones without oxygen restriction should inhibit the activity of methanogenic organisms, resulting in the CH_4 oxidation to CO_2 as it diffuses to the soil surface (Wagner et al., 2017). At the point of greatest oxygenation (UZ) the CO_2 emission levels in all lakes margins were similar due, characteristically, that this point has lower water table influence, and is also a place of passage for animals, which also may be responsible for higher N_2O emissions on the margins of lake 04SR for the first campaign, either by trampling or by the presence of waste such as faeces and urine (Figure 2C) (Alves, 2016).

The consumption of N_2O in the soil from the saturated zone (SZ) of the 06SR lakes margins for the first campaign can be justified by processes such as soil adsorption, as an electron acceptor in C mineralization processes in an anaerobic environment and in the production of N_2 (Dalal; Allen, 2008). Less gaseous diffusion resulting from the soil water saturation can promote the consumption of N_2O and with this N_2 becomes the dominantly released gas. Under moderately humid conditions, some fraction of N_2O may diffuse into the atmosphere before consumption. Furthermore, it can remain in the soil and be released if the soil dries out (Ussiri; Lal, 2013). Gas migration in the unsaturated zone is influenced by soil depth above the water table (Forde et al. 2019). According to Toczydlowski et al. (2020), maintaining a water table below about 15 cm depth in black ash wetlands may avoid large N_2O fluxes.

3.4.2 SOC Stocks

The magnitude of wetlands to carbon sequestration varies on the type and size of the wetland, vegetation, depth of wetland soils, hydrology, and other factors (Tangen; Bansal, 2020). Our results showed lower carbon storage in all margins lakes sampled when compared with other studies. Drainage can promote large net losses of organic carbon to the lake bottom sediments, mainly due to the alkalinity of the lake waters and the large amount of dissolved organic matter that can be transported, thus causing low storage of C in the margin profiles (Ward et al., 2017). A sampling contemplating the deeper layers could have shown us the improvement in these values. This indicative is based on previous deeper soil samplings (above 150 cm) in the margins of these lakes that showed black patches of soil, indicating higher organic matter content in depth. In this line, Nahlik and Fenessy (2016) found in US wetlands 65% of the total wetland soil carbon stored between 30 and 120 cm. Besides that, our study does not cover forest areas (Cordilheiras) that surround the lakes which probably have a greater potential for increased soil C amount.

Despite the low carbon stock in all studied lakes margins, it is worth noting that the capacity to store carbon in Entisols, which has a predominance of the sand fraction due to the low expression of pedogenetic processes (Santos et al., 2012), is lower than that found in Alfisols, Ultisols or Spodosols, which is also common in the region. Fine-textured materials (clays, sediments, loams) show a tendency to storage more C than coarse-textured materials because of the greater surface area for C adsorption (Tangen; Bansal, 2020).

The anoxic wet conditions in wetlands can hinder the decomposition of soil organic matter and benefit carbon sequestration (Zhao et al., 2020). The increase can be above 41% of total SOC stock from dry sites to slightly moist conditions (Olsson et al. ,2009). Along these lines, AminiTabrizi et al. (2020) suggest supplementary pathways when SOM decomposition in saturated locations is slow, such as thermodynamic and abiotic processes. Salinity, despite not having directly affected the gas emissions, can positively contribute to a greater permanence of OM in the soil due to the limitation of organisms responsible for its composition (Zhao et al., 2020).

In particular, the higher C storage in the black lake (06SR), especially in SZ, can be because of the higher organic matter content, lower decomposition, and lead to the accumulation of organic matter. The presence of “capim rabo-de-burro” (*Schizachyrium microstachyum*) in these margins can promote a higher amount of organic matter. The lability of organic matter components can be an important indicator of both the storage capacity of C in the soil (Kuruppuarachchi; Seneviratne; Madurapperuma, 2016) and the emission of greenhouse gases (Heintze et al., 2017; Philben et al., 2020). Depending on the material's lability or recalcitrance about 20-95% of the C in organic material can be transformed into gaseous compounds during anaerobic digestion (Möller, 2015). Our knowledge of substrate quality (e.g. compounds, lability) limits an assertive prediction about its influence on carbon stock and transformation into GHG's. However, some ongoing studies in our study area have shown a greater humification degree of organic matter found on the 06SR margins lake, which can also ensure a longer stay in the soil.

The water chemistry for SZ can change the OM decomposition pathway and also the GHG emissions. This may be indicative of the influence of dissolved organic matter in pond water “trapped” in soils after sedimentation. The presence of SO_4^{2-}, in 06SR margin’s lake, for example, can favor other organic mineralization pathways among which the sulfate reduction stands out, pathways where the decomposition of organic matter is slower (Zhao et al., 2020). This is also indicative of the reduction in the methane emission rate due to the higher S content for 06SR lake, despite being in an unsaturated zone (Inubushi et al., 1997).

3.5 Conclusions

The current study provides evidence for the soil greenhouse gas emission and carbon storage potential in different saturation zones of the margins at lakes in Pantanal of Nhecolândia. Our results confirm the trend of higher methane emission in saturated soil zones, while in aerobic zones the highest emissions occur for carbon dioxide and nitrous oxide.

Despite the soil's saturated zones can emit most methane, it is in that zone that the carbon has the most capacity to be stored because of the lower decomposition of organic matter. When drainage is predominantly (intermediate and unsaturated zones), lower is the soil storage capacity, which can result in massive losses of C to the atmosphere. Therefore, our results suggest that, given the imminent higher temperature as a result of global warming, fewer saturated zones can be found and the biogeochemical functions in carbon storage will be impaired.

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4. FINAL REMARKS

This doctoral research investigated greenhouse gas emissions on CO_2, CH_4 and N_2O, and the process behind the formation of these gases in saline-alkaline systems of the Pantanal of Nhecolândia in two campaigns. With our results, we can understand the behavior behind distinct lakes and how these lakes, based on their microbial and water chemical composition, might be affected by the impending rise in global temperature.

Our results also demonstrated the different behavior of GHG emitted from the soil. Evidence that the local hydrology can promote different behaviors of emission of gases, especially in the more accentuated emission of CH_4 in saturated zones, and emission of CO_2 and N_2O in unsaturated zones.

Our findings also demonstrate the need for further research into the dynamics of greenhouse gas emissions in this ecosystem. The seasonality can change the dynamics of these lakes and thus promote a change in the formation of these gases. Most lakes are reactive to this type of change, that is, a small change can alter the biogeochemical cycle of these lakes and the way as organisms respond to environmental changes will give us different emission behaviors.

In addition to our study, global warming is expected to have a significant impact on local and regional climate regimes, which in turn would impact hydrological and water resource systems. As concentrations of greenhouse gases increase, their effects become more pronounced.

APPENDICES

Appendix A: Supplementary material of chapter 2

Supplementary Materials includes: Supplementary Table: Table S1~S2

Supplementary Table S1. Synthesis physical and chemical variables, major ions and trace elements dissolved in water of sampled lakes in Nhecolândia, during two campaigns.

	Propertie	unit	2018				2019			
			01SR	04SR	06SR	07SR	01SR	04SR	06SR	07SR
Landscape properties	Volume		101115	171915	230300	212430	58750	73438	147000	148800
	Depth	cm	95	110	82	110	63	59	60	78
Physical-chemical	WT	°C	32.3	29.93	29.63	29.60	33.26	26.56	25.34	27.41
	EC	mS cm^{-1}	1.12	1.73	0.68	0.56	2.01	3.20	1.28	0.69
	Sal	g L^{-1}	0.95	1.63	0.83	0.53	1.58	2.43	0.90	0.41
	Alk	mmol L^{-1}	5.34	8.94	3.72	3.60	9.78	16.46	5.70	3.45
	TDS	g L^{-1}	0.99	1.72	0.84	0.55	1.68	2.70	0.95	0.46
	pH	-	9.26	10.03	9.09	8.62	9.68	10.26	9.45	9.05
	Eh	mV	73.35	190.70	74.23	207.10	235.68	267.22	81.98	330.00
	DO	%	89.53	120.75	69.50	112.90	122.33	112.75	86.66	132.3
Nutrients	NH_4^+	(mg L^{-1})	0.35	0.69	0.04	0.04	0.04	1.14	0.04	0.02
	NO_2		0.20	0.03	0.09	0.00	0.04	0.06	0.20	0.00
	NO_3		0.24	0.12	0.25	0.01	0.12	0.32	0.90	0.01
	DOC		31.23	79.02	12.08	15.95	74.37	251.90	35.99	33.96
	DIC		107.27	171.01	54.87	48.23	164.74	406.63	96.03	83.41
	TP		0,18	3,35	1,28	0,07	0,48	22,81	15,03	0,03
	TN		6.01	17.49	1.99	2.23	25.40	90.43	18.24	10.56
Major ions	Na	(mg L^{-1})	347.83	563.95	222.95	84.17	762.36	1085.63	350.98	173.81
	K		38.98	150.56	49.13	46.71	84.83	335.09	77.34	95.33
	Ca		57.97	66.92	78.51	41.46	43.07	58.14	50.17	67.95
	Mg		11.13	24.07	14.81	20.65	8.59	22.67	9.01	53.10
	Cl-		55.59	40.00	20.23	7.00	115.40	79.30	26.54	11.83
	SO_4^{2-}		6.33	0.01	22.73	0.48	16.23	5.92	35.34	0.00
Trace elements	B	(mg L^{-1})	0.27	0.51	0.10	0.09	0.38	0.90	0.15	0.12
	Cu		0.001	0.000	0.003	0.001	0.004	0.005	0.011	0.001
	Fe		8.11	0.14	41.64	0.07	12.39	0.17	77.72	0.03
	Mn		0.41	0.01	1.60	0.07	0.73	0.02	2.74	0.02
	Zn		0.010	0.006	0.060	0.012	0.018	0.012	0.038	0.001

WT: Water temperature; DO = Dissolved oxygen; EC = electric conductivity; TSS: Total suspended solids; Alkalinity: as (HCO_3^- + CO_3^-); DOC: Dissolved organic carbon; DIC: Dissolved inorganic carbon; TN: Total nitrogen; TDN: Total dissolved nitrogen; N.A.: Not available data. Source: Pellegrineti et al. (2022)

Supplementary Table S2. Greenhouse gas emissions from saline-alkaline lakes between hours in two campaigns of Nhecolândia Pantanal.

Campaign	Time	Gas	Unit	01SR	04SR	06SR	07SR
2018	8h	CO_2	mmol m² h⁻¹	1.80 ± 0.27	-4.16 ± 0.24	2.08 ± 0.08	5.42 ± 0.47
	10h			1.88 ± 0.55	0.62 ± 0.80	3.87 ± 0.54	4.70 ± 0.59
	12h			1.75 ± 0.28	-1.29 ± 0.36	5.07 ± 1.10	3.16 ± 0.57
	16h			1.92 ± 0.31	-0.77 ± 0.19	3.21 ± 0.54	4.14 ± 0.29
	8h	CH_4		0.56 ± 0.22	1.42 ± 0.43	0.03 ± 0.01	1.15 ± 0.10
	10h			0.09 ± 0.02	0.40 ± 0.04	0.03 ± 0.001	0.83 ± 0.06
	12h			0.13 ± 0.05	0.18 ± 0.01	0.02 ± 0.001	1.58 ± 0.18
	16h			0.02 ± 0.001	0.45 ± 0.06	0.01 ± 0.001	0.88 ± 0.07
	8h	N_2O	µmol m² h⁻¹	-0.40 ± 0.05	2.11 ± 0.14	-0.33 ± 0.05	0.31 ± 0.15
	10h			-0.13 ± 0.13	0.43 ± 0.15	-0.87 ± 0.24	-0.09 ± 0.09
	12h			0.25 ± 0.03	-0.10 ± 0.05	-0.32 ± 0.08	-0.09 ± 0.20
	16h			-0.07 ± 0.09	0.13 ± 0.07	0.001 ± 0.08	-0.13 ± 0.11
2019	8h	CO_2	mmol m² h⁻¹	0.68 ± 0.15	2.31 ± 0.84	4.25 ± 1.18	1.54 ± 0.01
	10h			1.05 ± 0.34	1.22 ± 0.28	1.99 ± 0.33	1.67 ± 0.14
	12h			2.00 ± 0.28	-1.29 ± 0.09	1.72 ± 0.70	4.11 ± 0.30
	16h			2.60 ± 0.08	2.52 ± 0.62	1.15 ± 0.22	2.08 ± 0.17
	8h	CH_4		0.06 ± 0.01	1.83 ± 0.17	0.01 ± 0.001	1.09 ± 0.19
	10h			0.03 ± 0.001	3.22 ± 0.07	0.01 ± 0.001	1.63 ± 0.18
	16h			0.02 ± 0.001	2.19 ± 0.39	0.001 ± 0.001	1.35 ± 0.18
	20h			0.02 ± 0.001	1.22 ± 0.18	0.001 ± 0.001	1.08 ± 0.03
	8h	N_2O	µmol m² h⁻¹	-0.19 ± 0.23	0.01 ± 0.06	-0.27 ± 0.13	-0.37 ± 0.07
	10h			-0.66 ± 0.14	-0.07 ± 0.03	0.05 ± 0.13	0.01 ± 0.10
	16h			0.10 ± 0.12	0.001 ± 0.05	0.68 ± 0.13	0.18 ± 0.09
	20h			-0.08 ± 0.15	-0.01 ± 0.04	-0.14 ± 0.12	-0.11 ± 0.08

Appendix B: Supplementary material of chapter 3

Supplementary Materials includes: Supplementary Table: Table S1~S3

Supplementary Table S1. Geographic coordinates, physical and granulometric analyzes in the study area before experiment installation.

ID	Geographic Coordinates	Area** (m^2)	Soil layer (cm)	Bulk density * (g cm³)	Sandy (%)	Clay + Silt (%)
01SR	19°23'08,4"S 56°19'46,0"W	102450	0-10	1.37	97.49	2.51
			10-20	1.37	98.49	1.51
			20-30	1.71	98.14	1.86
			30-40	1.79	97.58	2.42
			40-50	1.79	97.40	2.60
04SR	19°22'52,0"S 56°19'33,2"W	148000	0-10	1.37	99.05	0.95
			10-20	1.37	99.39	0.61
			20-30	1.71	99.71	0.29
			30-40	1.79	99.60	0.40
			40-50	1.79	96.90	3.10
06SR	19°23'25,2"S 56°19'20,8"W	263000	0-10	1.37	91.53	8.47
			10-20	1.37	89.01	10.99
			20-30	1.71	94.55	5.45
			30-40	1.79	97.67	2.33
			40-50	1.79	97.34	2.66
07SR	19°23'50,3"S 56°19'57,2"W	190000	0-10	1.37	96.73	3.27
			10-20	1.37	93.86	6.14
			20-30	1.71	96.53	3.47
			30-40	1.79	97.23	2.77
			40-50	1.79	97.86	2.14

* Source: Schiavo et al. (2012)

Supplementary Table S2. Pearson's correlation between chemical variables and greenhouse gases from two point of saturation zones in saline-alkaline systems of Pantanal of Nhecolândia.

Lake	GAS	pH	EC	Temp	Umidity	OM	P	S	K	Ca	Mg	B	Cu	Fe	Mn	Zn
								Saturated zone								
01SR	CO_2	0.50	0.88	0.99*	-0.60	-0.72	0.24	0.98	-0.21	0.14	0.33	-0.68	0.87	0.98	0.36	0.98
	CH_4	-0.98	0.14	-0.45	-0.55	0.90	-0.99*	-0.54	-0.85	-0.98	0.78	-0.46	0.17	-0.16	-1.00*	-0.16
	N_2O	0.50	-0.85	-0.40	0.99*	-0.24	0.72	-0.30	0.95	0.79	-0.98	0.98	-0.87	-0.66	0.63	-0.65
04SR	CO_2	0.37	-0.75	-0.57	0.07	-0.24	0.50	-0.06	0.50	-0.96	0.93	-0.92	-0.50	0.41	-0.85	-1.00*
	CH_4	0.95	0.62	0.79	-0.99*	-0.98**	0.89	-1.00*	0.90	0.22	0.41	0.34	0.84	-0.89	-0.57	-0.06
	N_2O	0.99**	0.20	0.43	-0.83	-0.96	1.00*	-0.89	1.00*	-0.24	0.78	-0.12	0.50	-0.59	-0.88	-0.50
06SR	CO_2	0.99**	-0.50	-0.53	-1.00*	-0.20	-0.73	0.11	0.99*	0.91	0.00	1.00*	-0.59	-0.81	-0.91	-0.59
	CH_4	-0.90	0.75	0.24	0.97	0.50	0.91	-0.41	-0.91	-1.00*	0.00	-0.95	0.81	0.58	1.00*	0.81
	N_2O	-0.61	-0.50	1.00*	0.44	-0.75	-0.23	0.81	-0.59	-0.10	0.00	-0.49	-0.41	0.91	0.10	-0.41
07SR	CO_2	-0.37	0.99*	0.33	-0.87	-0.12	0.98	-0.79	-0.65	0.40	-0.60	0.50	0.92	0.98*	-0.40	0.00
	CH_4	0.48	-1.00*	-0.21	0.80	0.23	-1.00*	0.85	0.73	-0.29	0.69	-0.60	-0.87	-0.95	0.29	0.00
	N_2O	-0.88	0.85	-0.35	-0.35	-0.72	0.87	-1.00*	-0.98	-0.28	-0.97	0.94	0.46	0.62	0.28	0.00
								Unsaturated zone								
01SR	CO_2	0.87	0.78	-0.29	-0.89	-0.99*	-0.50	-0.66	-0.50	-0.50	-0.96	-0.50	-0.87	-0.50	-0.50	-1.00*
	CH_4	-0.46	-0.59	0.94	0.41	-0.16	0.84	-0.78	-0.89	0.84	0.23	0.84	-0.54	-0.89	-0.89	-0.04
	N_2O	0.44	0.58	-0.94	-0.39	0.18	-0.83	0.79	0.90	-0.83	-0.21	-0.83	0.56	0.90	0.90	0.07
04SR	CO_2	0.33	-0.70	0.74	-0.10	0.87	0.50	-0.82	0.86	-0.53	0.00	0.94	-0.19	-0.84	-0.97	-0.87
	CH_4	-1.00	0.94	0.30	0.95	0.09	-1.00*	-0.17	-0.83	-0.55	-0.91	-0.70	-0.81	-0.14	0.19	-0.09
	N_2O	-0.42	-0.02	1.00*	0.62	0.97	-0.24	-0.99	0.26	-0.97	-0.69	0.44	-0.82	-0.98	-0.86	-0.97
06SR	CO_2	0.00	-0.64	1.00	0.75	0.00	-0.98	-1.00	-0.79	-0.24	0.50	-0.33	0.00	0.21	0.50	0.33
	CH_4	-0.18	-0.77	0.99*	0.86	0.18	-1.00*	-0.98**	-0.67	-0.06	0.33	-0.15	0.18	0.38	0.65	0.49
	N_2O	0.00	0.64	-1.00*	-0.75	0.00	0.98	1.00*	0.79	0.24	-0.50	0.33	0.00	-0.21	-0.50	-0.33
07SR	CO_2	-0.63	0.28	0.34	-0.98**	-0.60	0.69	0.00	0.60	0.98**	0.41	0.80	1.00*	-0.60	0.60	0.00
	CH_4	-0.86	-0.90	0.98**	-0.35	0.70	-0.61	0.00	-0.70	0.35	0.96	0.71	0.08	0.70	-0.70	0.00
	N_2O	-1.00*	-0.48	0.91	-0.83	0.15	-0.04	0.00	-0.15	0.83	0.94	0.99**	0.65	0.15	-0.15	0.00

when significant ($\alpha = 0.01$) p values are * and when significant ($\alpha = 0.05$) p values are **.

Supplementary Table S3. Carbon stock in 0-50cm layer in a wet front in four lakes margins of two campaigns in the Pantanal of Nheolândia, Brazil.

Lake	SZ	IZ	UZ	SZ	IZ	UZ
		2018			2019	
01SR	7.11 aa	5.53 ba	4.50 ca	4.22 ab	5.65 aa	5.78 aa
04SR	7.34 aa	6.76 aa	7.20 aa	7.67 aa	6.96 aa	6.43 aa
06SR	14.88 aa	10.32 ba	8.02 ba	11.63 aa	11.71 aa	9.04 aa
07SR	6.10 aa	6.00 aa	5.00 aa	5.33 aa	3.58 aa	4.28 aa

when the first letter represents means of carbon stocks in the same lake and campaign, between zone; second letter same lake and the zone between campaigns; when $p < 0.05$.