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Biogeochemical diversity, O₂-supersaturation and hot moments of GHG emissions from shallow alkaline lakes in the Pantanal of Nhecolândia, Brazil

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Abstract. Nhecolândia is a vast sub-region of the Pantanal wetland in Brazil with great diversity in surface water chemistry evolving in a sodic alkaline pathway under the influence of evaporation. In this region, more than 15,000 shallow lakes are likely to contribute an enormous quantity of greenhouse gas to the atmosphere, but the diversity of the biogeochemical scenarios and their variability in time and space is a major challenge to estimate the regional contribution. From 4 selected alkaline lakes, we compiled measurements of the physico-chemical characteristics of water and sediments, gas fluxes in floating chambers, and sedimentation rates to illustrate this diversity. Although these lakes have a similar chemical composition, the results confirm a difference between the black-water and green-water alkaline lakes, corresponding to distinct biogeochemical functioning. This difference does not appear to affect lake sedimentation rates, but is reflected in gas emissions. Black-water lakes are CO₂ and CH₄ sources, with fairly constant emissions throughout the seasons. Annual carbon dioxide and methane emissions approach 0.86 mol m⁻² y⁻¹ and 0.07 mol m⁻² y⁻¹, respectively, and no clear trend towards N₂O capture or emission was observed. By contrast, green-water lakes are CO₂ and N₂O sinks but important CH₄ sources with fluxes varying significantly throughout the seasons, depending on the magnitude of the phytoplankton bloom. The results highlight important daily and seasonal variations in gas fluxes, and in particular a hot moments for methane emissions, when the O₂-supersaturation is reached during the afternoon under extreme bloom and sunny weather conditions, provoking an abrupt O₂ purging of the lakes. Taking into account the seasonal variability, annual methane emissions are around 10.2 mol m⁻² y⁻¹, i.e., much higher than reported in previous studies for alkaline lakes in Nhecolândia. Carbon dioxide and nitrous oxide consumption is estimated about 1.9 mol m⁻² y⁻¹ and 0.73 mmol m⁻² y⁻¹, respectively. However, these balances must be better constrained with systematic and targeted measurements throughout the seasons.

1 Introduction

Wetlands contribute to the creation of large reservoirs of biodiversity, improve the quality of surface water, reduce flood risk associated with extreme rainfall, and supply streams during low water periods (Brinson et al., 1981; Fustec and Lefeuvre, 2000; Mitsch and Gosselink, 2015; Reddy and DeLaune, 2008; Turner, 1991; Whiting and Chanton, 2001). They are also critically important to global warming because of their role in modulating atmospheric CO₂, CH₄, and N₂O concentrations (Bastviken et al., 2004, 2011; Lienggaard et al., 2012; Wang et al., 1993). Among the wetlands, tropical wetlands are known to be highly reactive, as permanent high temperatures increase the velocity of the biogeochemical reactions (Fustec and Lefeuvre, 2000; Reddy and DeLaune, 2008). As an additional restriction, continental alkaline wetlands are characterized by an increase in water pH during evaporation, favoring the solubilization, transfer and accumulation of organic matter in the landscape. Collectively, these conditions can lead to highly reactive portions of landscape; i.e. emission variability in time and space where the greenhouse gas fluxes are poorly constrained (Peixoto et al., 2015).

A data compilation from 196 saline lakes around the world highlighted their role in the global CO₂ emission. Lakes with pH below 9 were identified rather as CO₂ sources, while the most alkaline ones, with higher primary production, were generally weak CO₂ sinks (Duarte et al., 2008). CH₄ released from wetlands accounts for more than 75% of natural CH₄ source, and more than 20% of the global CH₄ source (Schlesinger, 1997), although an important uncertainty on the CH₄ global budget is today attributable to emissions from wetland and other inland waters (Saunio et al., 2016). Regarding N₂O, global emission remains largely uncertain, ranging from 6.7 to 36.6 Tg N/yr (IPCC, 2007). About 25% of the global N₂O emission is attributed to uncultivated tropical soils, but exact locations and controlling mechanisms are not clear. Wetland ecosystems contribute considerably to N₂O budgets (XU et al., 2008) and Lienggaard et al. (2012) suggest that the Pantanal wetland, which covers an area of about 140 000 km² in Brazil, potentially contributes about 1.7%, a significant single source of N₂O. Face to these considerations, our research team has been conducting parallel pedological, hydrological, geochemical, geophysical and biogeochemical investigations on three experimental areas in the Pantanal of Nhecolândia, in order to better understand the hydro-bio-geochemical functioning of this huge alkaline wetland. One of the objectives is to establish a regional budget on greenhouse gas emissions. Here, we present the first steps towards this assessment.

Nhecolândia is a sub-region of the Pantanal wetland, where a myriad of shallow saline-alkaline, oligosaline and freshwater lakes coexist in the landscape, sometimes at short distances from each other (~200 m). The number of lakes was estimated from 12,000 to 17,500 (Costa et al., 2015; Evans and Costa, 2013). Under the influence of cumulative evaporation over the years, the pH of some saline lakes has reached high values, close to or above 10, resulting in an increasing solubility of the organic matter, with dissolved organic carbon (DOC) values up to 750 mg L⁻¹ (Barbiero et al., 2016; Mariot et al., 2007). Among the lakes, 500 to 600 show saline-alkaline waters (soda lakes).

There are many studies of GHG emissions from the Amazon floodplain (Melack et al., 2004) but the Pantanal have received much less attention. Collectively, the size of the region, the number of lakes and diversity of biogeochemical conditions in space and time (day-night and seasonal change) make it difficult to estimate the regional greenhouse gas emissions from Nhecolândia. A prerequisite for such a regional balance and its contribution to the global budget is a better understanding of the diversity of scenarios and of their variability in time and space (Peixoto et al., 2015). The aim of this study is precisely to present this diversity in the specific context of Nhecolândia, and to provide preliminary results of the range of greenhouse gas fluxes (CH₄, CO₂ and N₂O) from the most alkaline lakes.

2 Materials and Methods

2.1. Studied area

The Pantanal wetland, considered the largest wetland of the world (Por, 1995), is an immense tropical floodplain located between 15° and 22°S and 55° and 60°W (Fig. 1). This depression is supplied and drained by the Paraguay River and its tributaries, most of them joining on the eastern bank, from the surrounding mountains and plateaus. Characterized by low altitudes (100-200 m) and extremely low topographical gradients (0.02 to 0.03°), the alluvial plain is partially covered by seasonal flooding mainly in summer (from November to March) exerting a marked modulating effect on the Paraguay River hydrology (Junk and Nunes de Cunha, 2005). At the regional scale, this wetland consists of a mosaic of sub-wetlands that usually differ in

various aspects, i.e. hydrological, geomorphological, pedological and geochemical (Rezende-Filho et al., 2012; 2015). Nhecolândia is one of the largest (24,000 km²) sub-regions delimited by the Taquari River in the north and northwest, a portion of the Paraguay River in the west, the Negro River in the south, and by a highland plateau in the east, called Serra de Maracajú (Fig. 1). The region is characterized by an abundance of small, shallow (0.5 to 1.5m deep), non-stratified, round or irregular-shaped lakes and ponds (Pott and Pott, 2011). Nhecolândia has relatively closed drainage with little connection to major fluvial systems. Semihumid climate patterns, classified as tropical humid with short dry season (“Aw” type in the Köppen classification), are controlled by the seasonal migration of the Intertropical Convergence Zone (ITCZ). The mean annual air temperature is ~25 °C ranging from 21 °C during dry winters to 32 °C during rainy summers. The Mean annual precipitation is ~1100 mm, and the annual evapotranspiration (ETP) is approximately 1400 mm, providing a hydrological deficit of about 300 mm. At the local level, the strong thermal contrast between saline lakes and surrounding forested area causes low day–night alternating winds that enhance evaporation (Quénol et al., 2006).

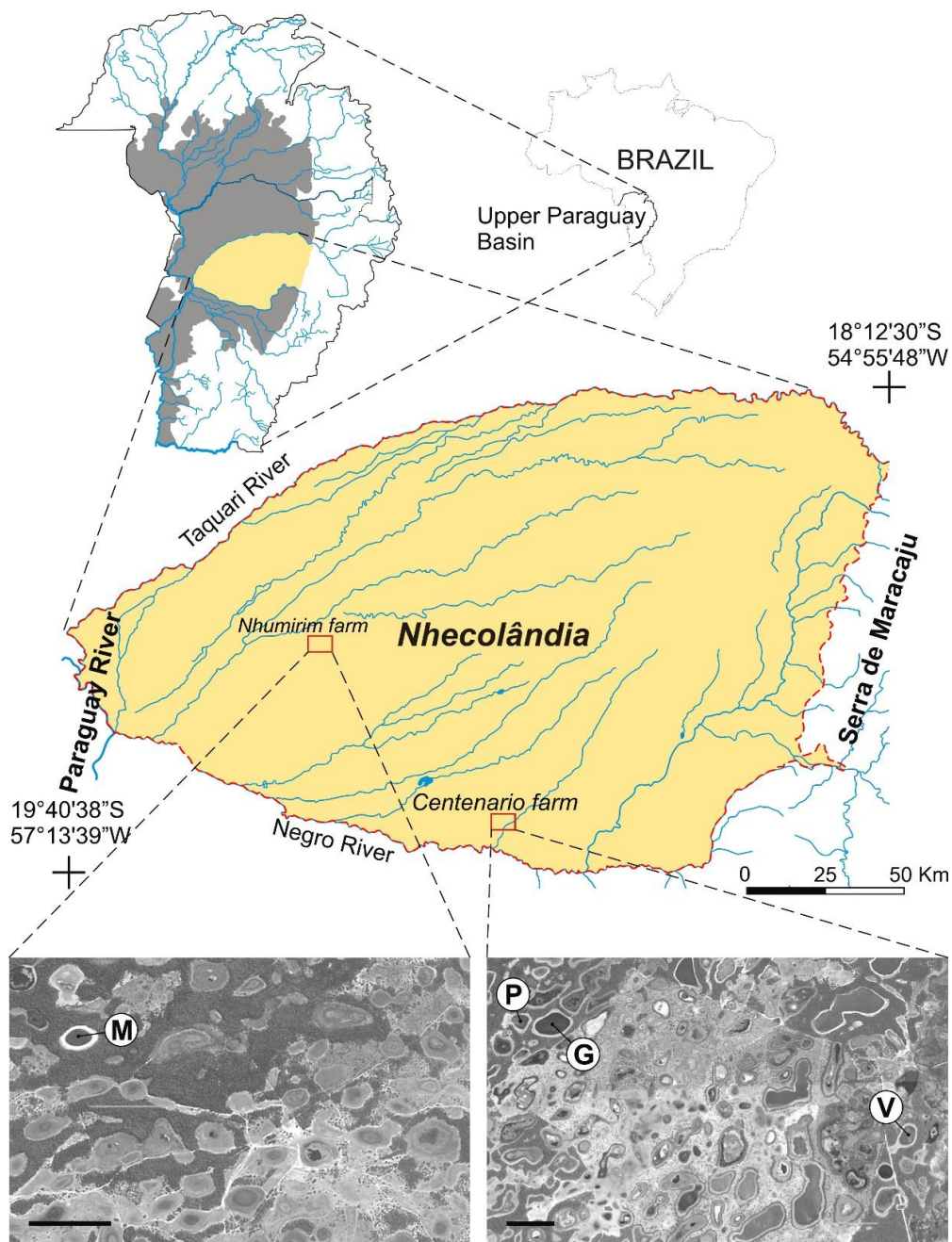


Figure 1: Location of the Pantanal wetland, Nhecolândia region, Nhumirim and Centenario farms and studied lakes, bar = 1 km (Spot5 satellite images, CNES/Airbus©2017).

The co-existence of freshwater and saline lakes occurs mainly in the southern and south western, lowland portions of Nhecolândia. Furian et al. (2013) have shown that the presence of salinity in the lakes results from an ongoing process of evapo-concentration under relatively humid climate but poor drainage conditions. These authors have determined that the evaporation process and associated mineral precipitations that control dissolved Ca, Mg and K account for at least 86% of the chemical variability in surface waters (n = 147 lakes) based on major ion chemistry. The geochemical processes occurring in the lakes are known. With increasing salinity, K⁺ is withdrawn from the solution to form Fe-mica (Furquim et al., 2010a; Barbiero et al., 2016), whereas alkalinity is involved in the formation of other clay minerals and calcite. The cations Ca²⁺ and Mg²⁺ are controlled by the formation of Mg-calcite with about 5 % Mg (Barbiero et al., 2008) and Mg-smectites of stevensite and saponite types (Furquim et al., 2008; 2010b). Since the waters evolve in a sodic-alkaline pathway, the salinity range is associated with a wide range in pH values, which affects both surface water (5.5 < pH < 10.5) and lake sediments (5.7 < pH < 9.9) (Barbiero et al., 2002; 2004). According to Rezende Filho et al. (2012), the gradual and continuous chemical changes from the most diluted to the most concentrated waters allowed to link their origin to the chemistry of the Taquari River freshwater that supply the region. Alkaline lakes are isolated from the regional freshwater flow throughout the Pantanal. Consequently they maintain saline alkaline waters and show high organic matter contents that depends more on the local cycles than on terrestrial inputs by the annual inundation pulse (Mariot et al., 2007). Martins (2012) noticed that waters of neighboring alkaline lakes with almost similar major ions composition can have permanent black or green color (Photo 1 Supplement S1). Such opposition in water color results from distinct biogeochemical functioning, but the parameters that control such differences are still poorly understood. No clear difference in nutrient status was observed between the two types of alkaline lake. P, nitrate and ammonia contents range usually from 2-4, 1.5-3 and 0.2-0.4 mg.l⁻¹, respectively, while NO₂⁻ levels are very low (Martins, 2012). The lakes with green or black waters represent the great majority of the alkaline lakes of the region (> 95%). Only a few alkaline lakes have crystalline waters and were not considered in this study. The high pH conditions are adverse to many phytoplankton organisms, but may support growth of the dense alkaliphilic cyanobacteria blooms observed in green water lakes. Two major bloom-forming cyanobacterium have been identified (Andreote et al., 2014; Costa et al., 2016; Genuário et al., 2017; Vaz et al., 2015), *Anabaenopsis elenikinii* and *Arthrospira platensis*, primary producer (halo)alkaliphilic oxygenic cyanobacteria that fix inorganic carbon and produce oxygen (Sorokin et al., 2015). *Anabaenopsis* spp. are *heterocytous* cyanobacteria that fix molecular nitrogen from the atmosphere during photosynthesis, whereas *Arthrospira* appears to be not active in this respect (Grant, 2006). The high pH conditions favour the loss by volatilization of ammonia, a N-containing product from dead cells degradation. Therefore, the blooms are crucial for the internal nitrogen cycle of green water lakes. Usually, the most extreme phytoplankton blooms are found during the driest period (August to November), with the highest alkalinity, EC and temperature values (Santos et al., 2011) and disappear after the first heavy rains of the beginning of the wet season.

Previous studies have confirmed a high CH₄ flux from the Pantanal wetland, but have focused on spatial variability within lakes or have been limited through the use of short measurement periods throughout the year (Bastviken et al., 2010; Marani and Alvalá, 2007). Other recent studies have been performed out of Nhecolândia, i.e. out of the specific chemical context with a wide range of alkaline salinity (Peixoto et al., 2015).

The study was carried out in two different forested regions of Nhecolândia, in 3 lakes (V, P, G) at the Centenário farm (private land), and 1 lake (M) at the Nhumirim farm that belong to the Brazilian Agricultural Research Corporation (Fig. 1). The main activity of these farms is cattle breeding. The selected lakes, with a surface area between 0.05 and 0.29 km² (Table 1), are shallow with water columns hardly exceeding 1 m during the rainy season, with the exception of lake P, which can reach 2 m in its deepest point. These 4 lakes are alkaline with pH ranging from 8.8 to 10.5 throughout the year. We have previously verified that the annual changes in their water chemical composition are consistent with the results obtained by Furian et al. (2013) from a regional study. The alkaline lakes were selected so as to cover a wide range of water electrical conductivity, and according to the absence or presence and magnitude of phytoplankton blooms. Lakes M, V and G are green water lakes, while P is a black water lake. Because of flooding that makes it impossible to access the studied site, no data were collected in the height of the wet season, and fieldwork was concentrated in the early (May-June), medium (July-September), and in the late dry season (October-December) from 2012 to 2015. The gas emission data were acquired during 24-hour cycle monitoring (usually every 2 or 3 hours) and are supplemented by data acquired occasionally but systematically in each field campaign.

2.2. Study Design and Analytical Methods

2.2.1. Gas emission

Gas fluxes from the lake to the atmosphere were measured using 32-L polyethylene floating chambers, having a base area of 0.195 m². The main conditions during the field campaigns are summarized in table 1. Two procedures were used for these measurements with fixed or slowly moving chambers. The procedure using slowly moving chambers (Photo 2 Supplement S1) was favored when the water level was sufficient and the lake diameter not too large to allow to cross from one bank to another. In this case, depending on the lake diameter, a train of 3 to 6 floating chambers was attached, leaving a gap of 10 meters between two successive floating chambers. Floating chambers were placed in the water every minute at a distance of about 30 m from the lake shore, and then slowly pulled toward the opposite bank at a maximum rate of 5 m min⁻¹. This experimental design allows for scanning the various water column heights, with the least turbulence disruption to the lake surface. To minimize artificial turbulence effects, foam elements were adjusted so that a maximum of 2 cm of the chamber penetrated below the water surface. The collects were carried out once each chamber reached a distance of about 30 m from the opposite bank. The collection times were variable since the first chamber reached the other margin in approximately 20 to 25 minutes, whereas the last chamber took about 35 to 40 minutes. When the water level was too low, or the lake too wide, we opted for a procedure with fixed floating chambers (Photo 3 Supplement S1). In order not to disturb the sediment just below the chamber, they were anchored with a 10-m line to avoid drifting. The line was equipped with a float to the vertical of the anchor. The chambers were located from the center to the border of the lake, and the collects were carried out after 20 min from an inflatable boat with shallow draft. Due to the low water column, it was not possible to place a bubble shield to prevent bubbles from reaching the chamber. Therefore, the results represent the sum of both fluxes by diffusion and ebullition. A thermometer was inserted in the floating chambers to monitor the temperature. For each chamber, gas samples were collected in duplicate (about 2 minutes apart) through a 60-mL syringe. Then they were transferred into 30-mL glass bottles, previously capped with gas-tight, 10-mm thick butyl rubber septa and aluminum caps, and evacuated with a hand vacuum pump at 0.75 kPa. Air samples were also collected at the departure of the chamber train for the ambient gas levels. Gas fluxes were calculated by the linear change in the amount of gas in the chambers as a function of sampled time. Thus, for example for a 6-chambers protocol, the mean and standard deviation on 12 measurements are presented as single gas emission value and error bars, respectively, for a given hour that corresponds to the launching of the first chambers. This operation was repeated every two or three hours in order to present a complete 24-hour cycle.

Table 1: Date, location, lake characteristics and general conditions during greenhouse gas emission monitoring.

Date	Type of lake (name) Surface km ²	Weather conditions	Phyt. Bloom conditions	EC range µS.cm ⁻¹	pH range	DOC mg.L ⁻¹	Procedure Num of chambers	Water column range meter	Time of gas coll. Minute
Sept. 13, 2012	Black (P) 0.087	Sunny	-	1400-1599	8.81-8.99	51	Fixed 3	0.3 – 0.8	20
Sept. 14, 2012	Green (V) 0.109	Sunny	Moderate	2420-2888	9.48-9.73	236	Fixed 3	0.1 – 0.4	20
Aug. 30, 2013	Black (P) 0.091	Sunny	-	1715-1855	9.21-9.33	37	Fixed 3	0.3 – 1.1	20
Sept. 1, 2013	Green (V) 0.109	Partially cloudy	Strong	2302-2410	9.67-9.78	265	Fixed 3	0.1 – 0.5	20
Dec. 2, 2014	Green (M) 0.053	sunny	No	2014-2204	9.37-9.51	102	Sl. moving 6	0.1 – 0.4	23 to 43
Jul. 7, 2015	Green (M) 0.055	sunny	No	1940-2030	9.28-9.37	82	Sl. moving 3	0.1 – 0.4	21 to 37
Sept. 10, 2015	Green (G) 0.285	Sunny (evening storm)	Strong	34000-35100	10.3-10.44	326	Fixed 3	0.1 – 0.2	20
Sept. 12, 2015	Black (P) 0.093	Strongly rainy	-	1382-1450	9.3-9.4	36	Fixed 3	0.4 – 0.7	20

Gas concentrations in the liquid phase were estimated indirectly using a headspace displacement method (Hope et al., 1995) with a 120-mL syringe and an air:water volume proportion of 1:3 (30:90 mL). For this, water samples were collected 5 cm below the surface, about 30 m from the edge of the lake. To equilibrate the headspace with the liquid phase, the syringe was shaken for 2 min by hand before injecting the headspace gas into the 30-mL glass bottle. For CH₄, the coefficient of gas transfer velocity (K_{600} , m d⁻¹) was calculated from the flux, the dissolved CH₄ concentration in water and the CH₄ partial pressure in the floating chamber as described by Bastviken et al. (2004).

Gas concentrations (CH_4 , CO_2 and N_2O) were measured by gas chromatography model Shimadzu GC-2014 (Shimadzu Co., Columbia, MD, 5 USA). The chromatographer was equipped with a packed column, an electron capture detector (ECD) to analyze N_2O , and a flame ionization detector (FID) to quantify CO_2 and CH_4 . Prior to detection, CO_2 was reduced to CH_4 using a methanizer. The gas analyzer was calibrated with NOAA CMDL certified standards CO_2 (357.5 and 1531 ppm), CH_4 (1.016 and 9.639 ppm) and N_2O (313 and 11,240 ppb) gas standards (minimum and maximum, respectively). Analytical accuracy was better than 0.02 ppm CH_4 and precision was better than 0.005 ppm expressed as the standard error of the mean for multiple measurements of standards. The analyses were performed in the Environmental Science Laboratory (UFSCar, Sorocaba, Brazil).

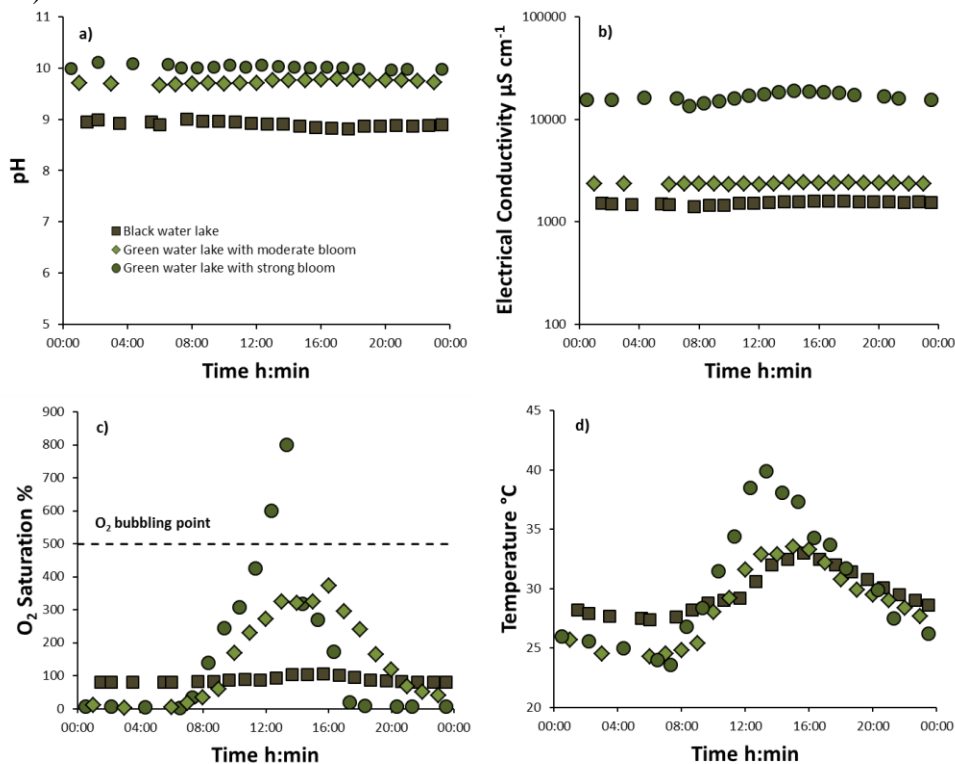


Figure 2: Changes in (a) pH, (b) E.C., (c) dissolved O_2 and (d) temperature at 5 cm below the lake surface, over 24-hours monitoring. The measurement were carried out with similar climate conditions on September 13th, 2012 for black water lake P and green water lake G with strong bloom, and on September 14th, 2012 for lake V with moderate bloom. The dashed line in Fig. 2c represents the O_2 bubbling point for a solution at the equilibrium with atmospheric O_2 .

2.2.2. Field physico-chemical measurements

A set of basic physico-chemical data was collected in water (pH, electrical conductivity ($\mu\text{S cm}^{-1}$), temperature ($^{\circ}\text{C}$), dissolved O_2 saturation (%), turbidity (NTU)), and sediments (pH and oxidation-reduction potential (mV)) as well as air temperature inside and outside the floating chambers. To obtain the oxidation-reduction potential, a value of +203 mV was added to the Pt-probe measured potential, assuming that the temperature was almost constant close to 30 $^{\circ}\text{C}$.

2.2.3. Dissolved organic matter and sedimentation rate

Water samples were taken from the lakes about 30 m from the shore and centrifuged in the field (15 min at 6000 rpm: Relative Centrifuge Force = 3200 g) to remove phytoplankton and other suspended particles. The supernatant was then filtered on glass fiber filter and stored in previously combusted glass vials. Dissolved organic carbon (DOC) concentrations were determined by combustion with a Shimadzu TOC-5000A.

Vertical sediment cores were collected from lakes V, G and P using a one-inch polyethylene tube in order to determine the age of the sediments and to identify any drastic change in the rate of sediment deposition in the lakes over the last 100 years. The age and the sedimentation rate determination were achieved by the unsupported ^{210}Pb method (half-life 22.3 years). Each core was sliced into 2-cm sub samples, sifted in 0.09-

mm sieves (170 mesh) with Milli-Q water, oven dried at 60°C and homogenized in a glass mortar. A 1-g aliquot of each slice was dissolved in acid (HNO₃ (65%), HF (40%)) and H₂O₂ 30% in a microwave digester and submitted to a sequential procedure for radiochemical determination of ²²⁶Ra and ²¹⁰Pb. The procedure consists of an initial precipitation of Ra and Pb with 3M-H₂SO₄, dissolution in nitrile tri-acetic acid at basic pH, precipitation of Ba (²²⁶Ra)SO₄ with ammonium sulfate, and ²¹⁰PbCrO₄ by sodium chromate. The ²²⁶Ra concentration was assessed measuring the alpha counting on the precipitate Ba(²²⁶Ra)SO₄, whereas the ²¹⁰Pb concentration was assessed through its disintegration product ²¹⁰Bi, measured by beta counting on the precipitate ²¹⁰PbCrO₄ (Moreira et al., 2003). Unsupported ²¹⁰Pb (denoted ²¹⁰Pb_{Exc}) were obtained from the ²²⁶Ra and total ²¹⁰Pb activities. Radionuclides were measured in a low background gas-flow proportional counter at IPEN (São Paulo). Ages and sedimentation rates were calculated using the CRS (Constant Rate of Supply) model (Appleby and Oldfield, 1978).

3 Results

3.1. Alkaline salinity range and indicators of biogeochemical functioning

The lakes chemistry covered a wide range of alkaline salinity throughout the seasons. The ionic proportions were substantially similar for lakes with green or black water. It should be noted, however, that during these 3 years of monitoring, the salinity range observed in green-water lakes ($700 \mu\text{S cm}^{-1} < \text{EC} < 35,000 \mu\text{S cm}^{-1}$) was larger than that observed in black-water lakes ($500 \mu\text{S cm}^{-1} < \text{EC} < 9,800 \mu\text{S cm}^{-1}$), but the two EC ranges overlapped significantly over a factor of 12. Field parameters measured during 24-h monitoring are presented in Fig. 2. To illustrate the variations of these parameters, we selected the results obtained on two successive days with similar weather conditions (September 13 and 14, 2012). The fluctuations are roughly similar to those observed during the other campaigns. The results clearly highlight two distinct biogeochemical functions in saline alkaline lakes, associated with black or green waters. Such difference is permanent, since the black water lakes never presented phytoplankton blooms, whereas green water lakes showed regular blooms throughout the dry seasons that disappeared quite abruptly (within a few hours) after each significant rain. For black water lakes, the changes in the biogeochemical indicators over 24 hours were moderate. Electrical conductivity, pH and turbidity were stable, showing only slight variations. The turbidity values were within the range of 100 to 350 NTU depending on the season. The daily temperature oscillations were about 5 to 6°C amplitude. Dissolved oxygen saturation evolved in a range of 80 % to 120 % during night and day time, respectively. Similarly, changes in EC, pH and turbidity in green water lakes were fairly moderate between day and night. However, deep differences were observed depending on the stage of development of the phytoplankton bloom, which made it possible to distinguish 3 cases: (i) in the absence of bloom, the water turbidity remained moderate (<20 NTU), the temperature fluctuated in a range of about 10 degrees on sunny days (24-34 °C), with a minimum at about 6 a.m., and a maximum at 2 p.m. Dissolved oxygen saturation varied from a minimal value of about 3 % at the end of the night, and reached about 120 % at 2 p.m.; (ii) with a moderate bloom, the turbidity and the daily temperature oscillation were usually in the range of 500-800 NTU and 23-36 °C, respectively. The dissolved O₂ saturation values dropped below 1 % during the night, and increased to 300 or 350% (20 to 25 ppm) from 2 to 4 p.m. Then, the values decreased regularly to fall below 100 % around 9 p.m., then below 1 % around midnight; (iii) when the bloom was strong, the turbidity values exceeded 1000 NTU (up to 3500 NTU) and the daily temperature fluctuations on sunny days were about 20 °C (23 to 42 °C). During the day and in the absence of clouds (lake G on September 15, 2015), dissolved O₂ saturation values increased very rapidly, exceeding 500 % around noon. These values then exceeded the technical range of the equipment, but they continued to increase progressively and values up to 800% (~ 55 ppm) have been noted at about 1:20 p.m. over the whole water column. Then, within a few minutes the values dropped down to 300% (~ 20 ppm), accompanied by a generalized ebullition of the lake (Photo 4, Supplement S1). The bubbles were generally less than 0.1 mm in diameter and formed within the whole water column. When the bloom was strong but the weather cloudy (lake V on September 1, 2013), fluctuations similar to a case with moderate bloom were observed, with dissolved O₂ reaching a maximum of about 450 %.

3.2. Sediment pH and oxidation-reduction conditions

The pH and oxidation-reduction conditions in the lake sediments varied respectively from 7.4 to 8.9 and -200 mV to +250 mV in the black water lake and 9.2 to 10.2 and -360 mv to -50 mv in the green water lakes. In September 10, 2015, a 150-mm rainstorm within 3 hours caused a significant dilution in green water lake G.

The water electrical conductivity dropped from 35,000 $\mu\text{S cm}^{-1}$ to 3600 $\mu\text{S cm}^{-1}$, while the pH ranged from 10.4 to 10.3. We noted that the bloom disappeared, the turbidity values dropped from about 3500 NTU to 37 NTU and massive amounts of phytoplanktonic organic matter were deposited, causing low oxidation-reduction potentials at -400 mV, whereas the pH dropped from 9.8 to 7.8 in the upper part of the sediment (arrow on Fig. 3). These conditions were maintained for several days.

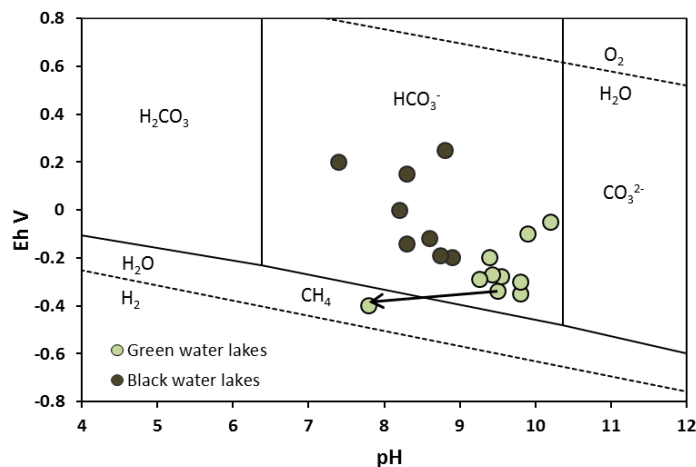


Figure 3: Oxidation – reduction potential and pH conditions in lake sediments. Note the drop in the pH value (arrow) occurring from September 10 to 11, 2015, in lake G after rainfall and disappearance of the cyanobacterial bloom.

3.3. Sedimentation rates

The mean sedimentation rates for the cores obtained through ^{210}Pb dating method were 0.41 cm Y^{-1} for the black water lake P, and 0.77 cm Y^{-1} and 0.24 cm Y^{-1} for green water lakes G and V respectively. Although the sedimentation rate for lake P was rather constant, that of lake G was much more scattered around the mean value (Fig. 4). For Lake V, the results seem to indicate the presence of two periods with a sedimentation rate of 0.1 cm y^{-1} for the period 1945-2010 and 0.56 cm y^{-1} for the period 1920-1945.

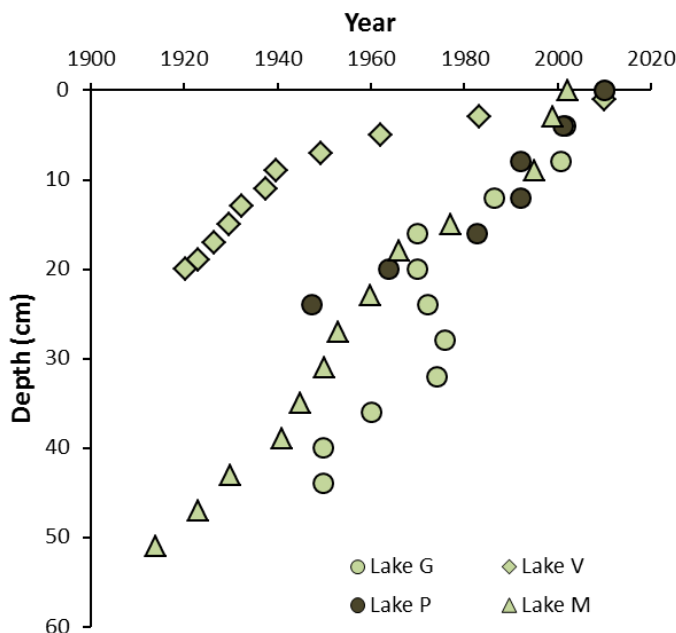


Figure 4: Sedimentation rates obtained by unsupported ^{210}Pb method. Results for lake M are from Fávoro et al. (2006).

3.4. Gas emission

Gas emissions vary significantly throughout 24-hour cycles and depending on the type of lake. In green water lakes, CO₂ measurements (Fig. 5) indicated a consumption that increased with increasing development of the phytoplankton. Without bloom, it was of 1.8 mmol m⁻² d⁻¹, higher during the day (3 to 4 mmol m⁻² d⁻¹) than during the night (0.5 to 1 mmol m⁻² d⁻¹) and showing small variations between chambers. With moderate bloom, CO₂ consumption increased significantly up to 15 to 20 mmol m⁻² d⁻¹ during the day and 2 to 5 mmol m⁻² d⁻¹ at night. The maximum values were obtained in a strong bloom condition, with a consumption of about 25 mmol m⁻² d⁻¹ in the beginning of the afternoon, decreasing to 8 mmol m⁻² d⁻¹ at the beginning of the night, and large variations observed between the chambers. Finally, black water lakes emitted CO₂ mainly during the night (~5 mmol m⁻² d⁻¹), and to a lesser extent during the day (~1 mmol m⁻² d⁻¹), giving a mean value of 2.36 mmol m⁻² d⁻¹. No marked difference was detected between the 3 campaigns on lake P, whether the weather was sunny or rainy.

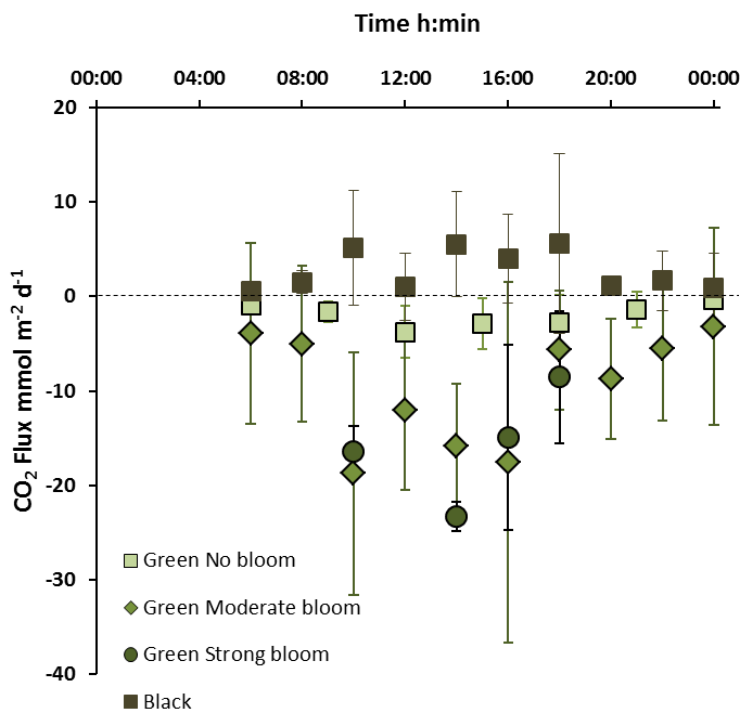


Figure 5: Daily cycle of carbon dioxide fluxes showing emission from black water lake (P), and increasing consumption with increasing magnitude of the cyanobacterial bloom in green water lakes for no- (lake M), moderate- (lake V) and strong (lake G) bloom conditions.

Figure 6a shows the CH₄ concentration in the lakes water calculated from the headspace measurements. For green water lakes, the mean values were of 0.64 μmol L⁻¹ without bloom (lake M), 4 μmol L⁻¹ for a moderate bloom (V) and 35-56 μmol L⁻¹ for a strong bloom (V and G, respectively). All the lakes showed a supersaturation with respect to the atmosphere. For black water lakes, CH₄ concentrations were much lower with a mean value of 0.12 μmol L⁻¹. Figure 6b shows the CH₄ emissions obtained on black- and green-water lakes. Two campaigns were conducted on green water lake M in the absence of bloom, giving similar results and therefore, only one is presented (December 2014, 6 chambers). An average CH₄ emission of 0.8 mmol m⁻² d⁻¹ was calculated, being slightly higher during the night (1.2 mmol m⁻² d⁻¹). The differences in the emission values between the floating chambers, represented by error bars, were moderate. At the beginning of the phytoplankton bloom (1 campaign on lake V with 3 chambers), similar trends were observed with higher CH₄ emissions of about 6 mmol m⁻² d⁻¹ overnight and 2 mmol m⁻² d⁻¹ at the peak of the day. Again, the short error bars emphasize that the variations between the chambers are small. With a stronger phytoplankton bloom established for several weeks (1 campaign on lake G and 1 on lake V, both with 3 chambers), methane emissions increased, reaching values close to 56 (V) and 74 (G) mmol m⁻² d⁻¹ in the middle of the morning. For lake V on September 1, 2013, the weather was partially cloudy and despite the magnitude of the bloom, dissolved O₂ reached a maximal value of 450% saturation. No generalized ebullition was noted during the afternoon and CH₄ emissions maintained from 17 to 44 mmol m⁻² d⁻¹. By contrast on lake G with sunny weather

on September 15, 2015, ebullition started at 1:20 p.m. and CH_4 emissions shifted abruptly up to about $600 \text{ mmol m}^{-2} \text{ d}^{-1}$. The shift is reflected in the calculated $\text{CH}_4\text{-}K_{600}$ values, which were ranging from 0.5 to 2 m d^{-1} for lake V and 1.3 for Lake G in the morning, but shifted from 4 to 10 m d^{-1} during the afternoon (Fig. 7). Such values were maintained at least until 6 p.m. Unfortunately, because of a 150-mm storm, the monitoring was interrupted as it was not possible to continue the measurements overnight. The methane fluxes measured from the black water lake P (3 campaigns with 3 chambers) were significantly lower with a mean value of $0.19 \text{ mmol m}^{-2} \text{ d}^{-1}$ and a standard deviation of $0.05 \text{ mmol m}^{-2} \text{ d}^{-1}$.

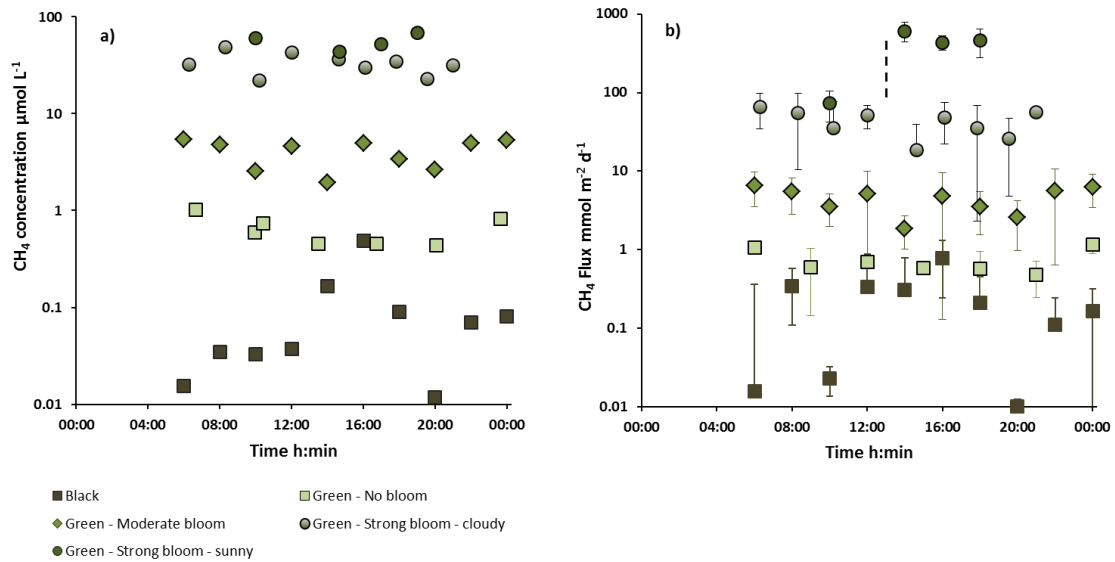


Figure 6: (a) Dissolved methane concentrations at the top of the water column, (b) and methane fluxes over 24 hours monitoring in black water lake (lake P) and green water lakes for no- (lake M), moderate- (lake V) and strong-bloom, with cloudy (lake V) and sunny (lake G) weather condition. Due to the logarithmic scale used, some negative values of the error bars (denoting standard deviations) are not drawn. The dashed line represents the beginning of the ebullition in lake G (13:20).

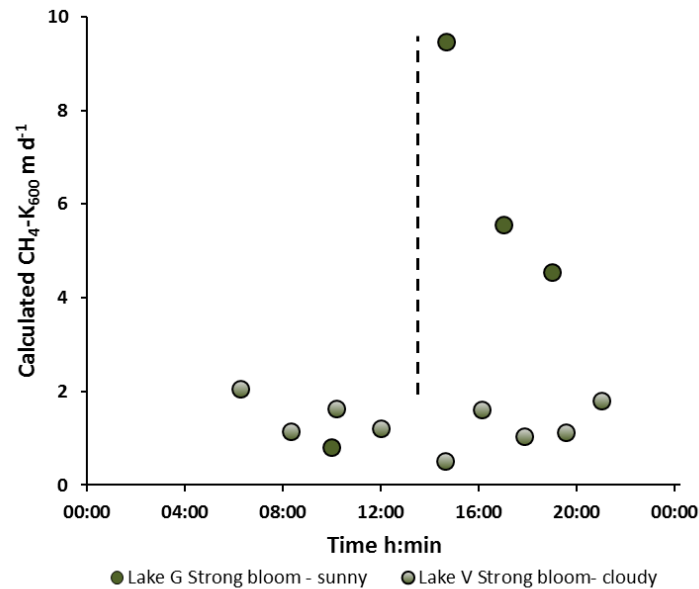


Figure 7: Calculated exchange gas coefficient for methane in lakes V and G in strong bloom but cloudy and sunny weather condition, respectively. The dashed line represents the beginning of the ebullition in lake G (13:20).

N_2O measurements indicated consumption from 0 to $2 \mu\text{mol m}^{-2} \text{ d}^{-1}$ for the no-bloom and moderate-bloom conditions, respectively, with an increase up to a mean value of $7 \mu\text{mol m}^{-2} \text{ d}^{-1}$, although with large error bars, when the bloom was strong (Fig. 8). For the black water lake, no clear trend towards emission or consumption of N_2O was observed during the 3 campaigns. Only large variations between the chambers can be noted.

Based on 4 years of green water lake observation (2012-2015), a year can be divided into approximately 200 days without bloom throughout the rainy season, 100 days with moderate phytoplankton bloom during the dry season, and 65 days with strong bloom, and with lake ebullition during 3 hours a day. Taking into consideration these seasonal variations, the methane flux estimate may reach $10.2 \text{ mol m}^{-2} \text{ y}^{-1}$ (Fig. 9). In the latter case, no-bloom, moderate-bloom and extreme-bloom conditions represent about 2 %, 4 %, and 94 % of the yearly CH_4 emissions, respectively. An estimate of the CO_2 consumption from green water lakes is about $1,9 \text{ mol m}^{-2} \text{ y}^{-1}$, distributed in 19 %, 46 %, and 35 % during no-, moderate- and extreme-bloom conditions, respectively. Similarly, it is of about $0.73 \text{ mmol m}^{-2} \text{ y}^{-1}$ for N_2O , distributed in 44%, 13% and 43%. For black water alkaline lakes, annual emission estimates for CO_2 and CH_4 were about 0.86 and $0.07 \text{ mol m}^{-2} \text{ y}^{-1}$, respectively.

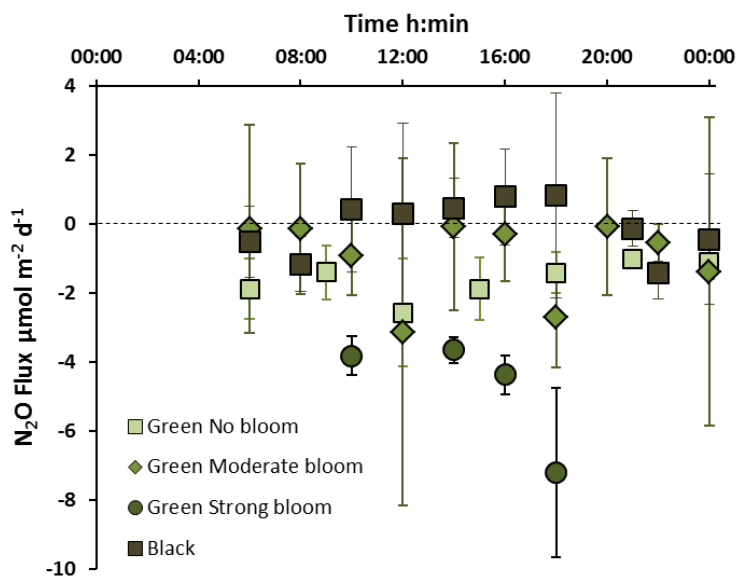


Figure 8: Nitrous oxide fluxes from black water lake and green water lakes for no-, moderate- and strong bloom conditions.

4 Discussion

Our results confirmed previous evidences on the different functioning of black and green water alkaline lakes (Martins, 2012), despite a very similar mineral major ions chemistry throughout the seasons. Although we can expect a higher accretion rate for the sediments that are seasonally supplied by the organic matter from the phytoplankton blooms, the sedimentation rates do not seem to reflect this difference in biogeochemical functioning (Fig. 4). The rates are relatively similar for black or green water lakes and also very similar to those presented by Fávares et al. (2006) from a core collected on Lake M (0.61 cm Y^{-1}) using the same methodology. The low sedimentation rates observed for the recent sediments in Lake V are difficult to interpret. By contrast, the oscillations observed for Lake G may be due to its shallow depth that causes this lake to dry out during the most severe droughts and cause large cracks to appear in the sediment. The fall of more recent material from the top down to the depth between the prisms may explain the results obtained for lake G.

The difference in biogeochemical functioning has implications for GHG emissions. During our campaigns, black water lake P was low CO_2 and CH_4 sources ($2.36 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $0.19 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively). No radical changes were observed in the water electrical conductivity, pH, daily dissolved O_2 fluctuations, sediment oxidation-reduction conditions and water turbidity throughout the year. In addition, measurements made in sunny and rainy weather conditions gave similar results. Therefore, we assume that gas fluxes are almost constant throughout the year. It seems that black water lakes are much less reactive than those with green water, which were clearly CH_4 sources and CO_2 and N_2O sinks. However for the green water lakes, methane emissions varied largely depending on a combination of factors, i.e. the magnitude of the phytoplankton bloom, solar radiation and important rainfall. In the absence of phytoplankton bloom, dissolved methane concentrations were of the order of 0.7 µM , i.e. slightly higher than reported by Bastviken et al. (2010) for lake M during a field campaign in 2009 (0.17 µM) and in moderate bloom conditions (lake M is referred

to by these authors as lake N7a). The CH₄ fluxes measured by these authors were of about 1.42 mmol m⁻² d⁻¹, with 54 and 46 % of ebullitive and diffusive fluxes, respectively. We obtained roughly similar fluxes with an average value of 0.78 mmol m⁻² d⁻¹. However, our data show that the water methane concentration increases with the magnitude of the bloom. With a moderate bloom, the water CH₄ concentrations increased up to 4.26 μM but these values remained within the typical range of 0.01 to 10 μM observed in many surface freshwaters including previous measurements in the Pantanal (Bastviken et al., 2010; Marani and Alvalá, 2007). This is no longer the case, however, in the presence of a strong bloom in lakes V and G with dissolved CH₄ contents reaching about 50 μM. Methane fluxes increase considerably up to 27-81 and 74 mmol m⁻² d⁻¹ (for V and G respectively) in the morning. These values are maintained during the afternoon. However, while the fluxes remain in the same order of magnitude for Lake V, they are practically multiplied by 10 for Lake G, reaching exceptional values of about 600 mmol m⁻² d⁻¹. The consistent change in the calculated K₆₀₀ values (Fig. 7), which coincided with the occurrence of the abrupt generalized ebullition of lake G, emphasize that CH₄ behave quite differently in these 2 lakes.

A dissolved O₂ probe was conventionally calibrated before each measurement considering probe-atmosphere equilibrium as 100 % value. Since the atmosphere is approximately composed of one-fifth O₂ and four-fifths N₂, the value of 500 % corresponds to O₂-supersaturation, i.e. the limit value of O₂ bubble formation in a water column in equilibrium with the atmosphere. This bubble point of O₂ was reached and exceeded at the beginning of the afternoon under the effect of the photosynthetic O₂ production in condition of strong bloom and high incidence of solar radiation. Once this point was exceeded, the data showed a rapid purge of O₂ from the lake. It should be noted, however, that the start of the lake ebullition was not immediate when the bubble point is exceeded. The reaction seems to take a few minutes to start. On the other hand, once it has started, ebullition is maintained for about 3 hours, even if the dissolved O₂ dropped quickly below the bubble point. Ebullition was maintained as O₂ production was supplied by ongoing photosynthesis under the strong solar radiation during the afternoon. A rough estimate makes it possible to evaluate that about 90% of the annual emissions occur during O₂ supersaturation periods. This estimate highlights the importance of O₂ microbubbles on the annual methane emission, a process not considered in conventional Fickian diffusion calculations (McGinnis et al., 2015). The most widely recognized form of non-diffusive gas exchange is the ebullition of macrobubbles from sediments, quickly rising through the water column and releasing their content to the atmosphere. Recently, the effect of surface micro bubbling on gas exchange, consequence of the interplay between water current and wind speed, rain or wave, was revealed for large rivers (Beaulieu et al., 2012) and lakes (McGinnis et al., 2015). The conditions of gas-supersaturation under the influence of primary production are very rare, although they are relatively standard in the green water lakes of Nhecolândia during the dry season. In any case, to our knowledge the consequences of natural O₂ purging on GHG emissions have never been reported for inland waters. Such O₂ micro bubbling has two effects. On the one hand, it significantly increases the surface of contact between the liquid and gaseous phase, favouring the diffusion from the liquid phase to the gaseous one inside the bubbles. The effect on methane diffusion can be significant because of its low solubility in water (mole fraction solubility of 2.34×10^{-5} at 30°C). On the other hand, compared to a simple diffusion process, it also increases the transfer rates of methane to the lake surface, as the ascension of the bubbles is faster than the diffusion through the water column, enhancing gas transfer velocities. Here, O₂ micro bubbling results in a CH₄ emission that is two orders of magnitude greater than previously reported for these environments. Surprisingly, it shows that these extreme oxic conditions that are favorable to rapid oxidation of CH₄ to CO₂ by methanotrophs correspond, on the contrary, to a hot moment of methane emission. The peak emission of CH₄ was maintained for 2 to 3 hours per day, during approximately 2 months at the height of the dry season, and abruptly disappeared at the first important rainfall.

From the data summarized on Fig. 9, the balance points to a carbon deficit of the order of 8 mol m⁻² y⁻¹ in green-water lakes. This imbalance is significant, and several hypotheses must be put forward. The first point is that CO₂ capture was measured when the phytoplankton bloom was already very advanced. Maximum CO₂ capture should occur during the growth of the bloom but no data are available for this period, and the annual CO₂ capture budget may be underestimated. Another hypothesis is that the C budget of the lake is not balanced every year, but over the long term. A surplus year may succeed to a deficit year in terms of emission of C. This can be conceived for example in the case of a single consequent rain (> 20 mm) rather early in the dry season. This rain is likely to make the bloom disappear. It will then resume its growth but reach a sufficient density to induce O₂-supersaturation only close to the beginning of the rainy season when it will disappear again. Periods with O₂-supersaturation will be restricted, thus considerably limiting methane emissions during this year. At the same time, bloom successions are likely to significantly increase the amount of carbon captured for the same year. Finally, it is possible to imagine an influx of C from the surrounding forest. However, it would be in disagreement with our observations on alkaline lakes hydrology (Furian et al., 2013; Barbiero et al., 2016).

These are supplied by subsurface flows of low C-charge waters during the rainy season. On the other hand, during the dry season, transfers are made from the lake towards the beach via a soil solution with high organic matter content (up to $750 \text{ mg}_C \text{ l}^{-1}$). This functioning would therefore tend to increase the carbon deficit in the lake.

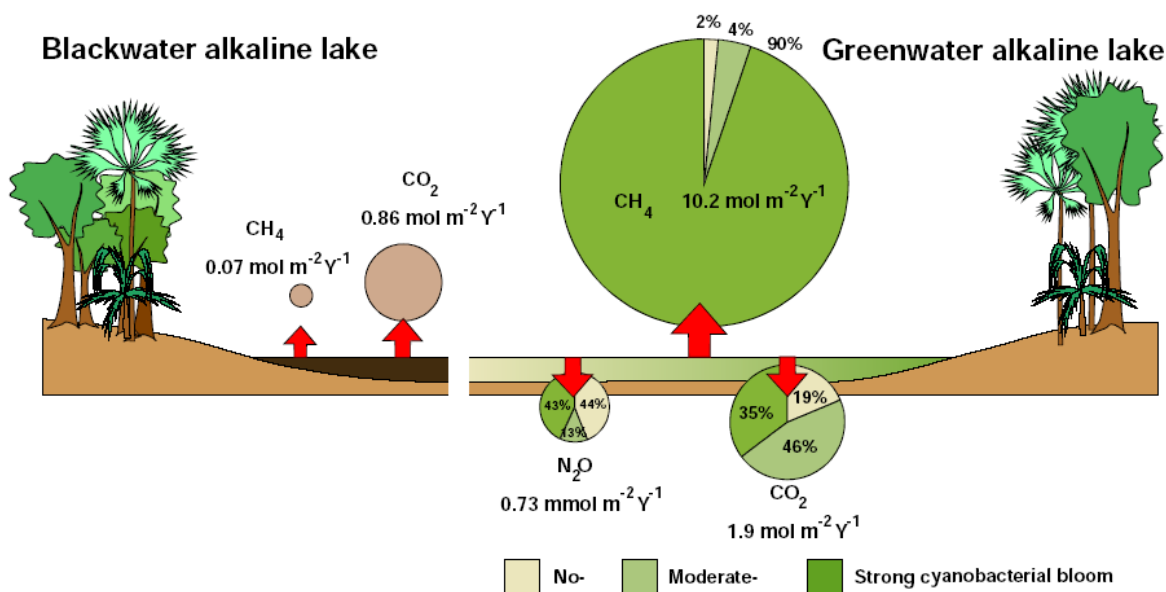


Figure 9: Annual estimates of methane, carbon dioxide and nitrous oxide fluxes from black and green water lakes for no-, moderate- and strong bloom conditions. Note that no clear trend towards N_2O capture or emission from black water lake was observed.

A consumption of N_2O in green water lakes is observed that is possibly the effect of alkaliphilic denitrifier microorganisms, identified in other soda lakes in Africa and Asia, able to use a large range of organic substrates and reduce nitrates and nitrous oxide to gaseous nitrogen (Boltynskaya et al., 2007; Sorokin et al., 2015). This aspect of the N cycle is currently under study.

Both, seasonal and daily monitoring reveals the influence of the type of biogeochemical functioning and more particularly of the bloom and its magnitude on methane, carbon dioxide and nitrous oxide emissions. Daily variations, such as the contrasts between day and night emissions (Fig. 5), or more dramatically the peak of CH_4 emissions for green-water lakes during strong bloom periods (Fig. 6b) can only be apprehended by systematic measurements over 24-hour cycles. In agreement with the observations of Duarte et al. (2008) from global review for saline lakes, black-water alkaline lakes of Nhecolândia are closer to a group of saline lakes with pH below 9, which are generally stronger sources of CO_2 to the atmosphere. However, in our case their contribution appears much lower than the mean value calculated by these authors (2.16 against $81\text{-}105 \text{ mmol m}^{-2} \text{ d}^{-1}$). By contrast, green-water lakes behave similarly to saline alkaline lakes with pH greater than 9, which are more productive and consequently have lower CO_2 partial pressure, and are commonly weak CO_2 sinks. For these green-water saline lakes, it appears necessary to consider several situations throughout the year, particularly for the methane budget (Fig. 9). Indeed, on the basis of the fluxes measured outside the bloom period, the annual CH_4 flux estimate revolves around $0.3 \text{ mol m}^{-2} \text{ y}^{-1}$. This value is slightly lower, but of the same order of magnitude (about $0.5 \text{ mol m}^{-2} \text{ y}^{-1}$) as that calculated by Bastviken et al. (2010). Taking into account the diversity of situations throughout the year, our estimate of CH_4 emissions is much higher and reaches $10 \text{ mol m}^{-2} \text{ y}^{-1}$. This finding suggests the need to better define during which periods of the year, under what weather conditions, with what bloom magnitude, the O_2 bubble point is exceeded.

Immediately after the first rain of the season, the bloom disappeared in a few hours, and substrates to methanogens, in the form of very labile organic carbon, deposited massively at the bottom of the lake. It resulted in a drastic decrease in pH in the upper part of the sediments probably due to the release of organic acids that accompany the onset of mineralization. For a few days, the drop in the sediment pH (about 2 units) created conditions more favorable to the synthesis of CH_4 , although specific methanogens inherent to alkaline grow and produce methane at pH above 9. The proximity between the sediments and the water-atmosphere exchange surface due to a thin water column (generally $<0.5 \text{ m}$) is likely to favor methane diffusion and emissions. Unfortunately, due to the beginning of the flooding of the Pantanal, it was not possible to continue the measures. No value of GHG flux is associated with this period, which will have to be monitored in the future.

5 Future Studies and Conclusion

Nhecolândia is a vast sub-region of the Pantanal wetland characterized by a high range of salinity and pH of surface waters. It results in a diversity of environmental conditions, a major obstacle to estimating the regional contribution in terms of GHG emissions. Both, green- and black water alkaline lakes (soda lakes) have a similar major ions composition, however, our results emphasize that green-water lakes, characterized by a seasonal phytoplankton bloom, behave as CO₂ and N₂O sink and CH₄ source, whereas black-water lake are CO₂ and CH₄ sources, probably with steady fluxes throughout the year.

Our study also provides helpful information in several aspects. First, the substantial daily variation of gas fluxes confirms the necessity to conducted 24-h monitoring for a relevant assessment of daily emissions. Second, the seasonal variations also suggest long term observations across the seasons, based on key indicators, here, the magnitude of the bloom, dissolved O₂ variation, and, possibly as just mentioned, sediment pH. Previous studies have revealed that methane emission variability within a lake may be equal to or more important than between lakes, mainly because of the diversity of habitats within lakes. Our work complements these studies, assessing the variability over time, within lakes, over the daily cycle and year seasons. The high daily and seasonal variability has to be taken into account to estimate annual GHG emissions from these lakes. However, the large emission variability requires special attention and accurate confirmation. Third, the difference in gas fluxes among the type of lake implies that it will be necessary to resort to remote sensing tools capable of discriminating them, but also to monitor the development of the phytoplankton bloom throughout the season for any perspective of a regional GHG contribution estimate from surface water to the atmosphere. Lakes with green and black waters are the most common among Nhecolândia's alkaline lakes, but there are also some crystalline-water alkaline lakes, not to mention a wide range of freshwater lakes for which few data are available. In any case, all these lakes cannot be treated as one or two functional types.

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