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Research Articles

Greenhouse gas emission from a eutrophic coastal lagoon in Rio de Janeiro, Brazil

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ABSTRACT. Greenhouse gases increased in concentrations over pre-industrial values by 257% for methane and 145% for carbon dioxide in 2016. Such increased levels are the main climate change drivers and may affect aquatic systems that accumulate and carry carbon to the ocean and the atmosphere. Additionally, these systems are sensitive to environmental changes since their physical, chemical and biological properties respond rapidly to changes. Therefore, this study focus on the greenhouse gases dynamic over an urban eutrophic tropical lagoon. Samplings were performed in the Rodrigo de Freitas Lagoon by covering four periods in 2016 (April, June, October and December). Mean diffusive flux was -1,466.8 mg m^{-2} d^{-1} of carbon dioxide and 113.7 mg m^{-2} d^{-1} of methane. Regarding the bubbling, fluxes were 58.28 mg m^{-2} d^{-1} for methane and negligible for carbon dioxide (mean value of 5.01 mg m^{-2} d^{-1}). Environmental parameters such as depth, water temperature and sediment particle size were strongly related to the fluxes. In conclusion, the region is a sink of carbon dioxide and a source of methane to the atmosphere. Additionally, the rivers discharge impacts the lagoon by generating a methane hotspot emission region.

Keywords: carbon dioxide; methane; diffusive flux; ebullitive flux; sink; source; southern Brazil

INTRODUCTION

Greenhouse gas concentrations reached alarming levels and are higher than that found in the ice cores of the last 800,000 years (IPCC, 2013). According to the latest World Meteorological Organization Bulletin, WMO Greenhouse Gas, the increase of these gases concentrations over pre-industrial values has already reached 145% for carbon dioxide and 257% for methane (WMO, 2018). In 2016, the values recorded were 403.3 ± 0.1 ppm of CO_2 and 1,853 ± 2 ppb of CH_4 in the atmosphere. The increase in CO_2 concentration over the years 2015-2016 was higher than the 2014-2015 increase, but these concentrations were slightly lower for methane (WMO, 2018). Such increased levels of greenhouse gases are the main cause of climate change by increasing atmospheric temperature, which was 0.46°C ± 0.1°C in 1981-2010 (WMO, 2018).

At the beginning of the decade, atmospheric CO_2 concentration had already risen by 23% over the 1960s, with fossil fuel burning being the main source into the atmosphere (Le Quére *et al*., 2015). From the anthropogenic emissions of CO_2, 240 Gt C accumulated in the atmosphere and 155 Gt C in the oceans. These levels of carbon in the ocean surface can account for a pH decrease of 0.1 since the pre-industrial era (IPCC, 2013). Aquatic systems such as ponds, lakes, wetlands, rivers and reservoirs, generally accumulate about 0.6 Pg C yr^{-1} and carry carbon to the oceans and the atmosphere, resulting in approximately 2.7 Pg C yr^{-1} in these environments (Battin *et al*., 2009). Regarding emissions to the air, some studies have estimated 0.65 Pg C (CO_2eq) yr^{-1} as CH_4 and 1.4 Pg C yr^{-1} as CO_2 (Tranvik *et al*., 2009; Bastviken *et al*., 2011). Also, emissions to the atmosphere from tropical aquatic bodies account for about 50% of total emissions (Bastiviken *et al*., 2011).

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Inland aquatic ecosystems cover about 3% of the planet's surface and are considered important sentinels for climate change by being sensitive and rapidly responding to environmental changes (Downing *et al*., 2006). One of the main direct effects of climate change on tropical lagoons is the increase in surface water temperature, which affect the preservation of habitats in these ecosystems (Adrian *et al*., 2009).

Coastal lagoons are fragile marine environments and have suffered from urban expansion. High population densities in their environment expose them to eutrophication processes due to increases in nutrient concentrations in water and pollution (Marques-Junior *et al*., 2009; Van Weerelt *et al*., 2012; Fonseca *et al*., 2013). The eutrophication can be natural due to the excessive input of nutrients into the ecosystem, but anthropogenic activities can also accelerate it. Organic pollution carried by rivers is one of the main causes (Marques-Junior *et al*., 2009). This process may cause impacts, such as algae blooms, consuming high amounts of inorganic nutrients (Marques-Junior *et al*., 2009). Lakes and lagoons have long water retention time (Kjerfve, 1986), generating regions of fate and accumulation of organic and inorganic matter (Sobek *et al*., 2003; Tranvik *et al*., 2009). Thus, the carbon coming to this environment can be degraded and then emitted into the atmosphere (Utsumi *et al*., 1998; Cole *et al*., 2007; Bastviken *et al*., 2008).

Methane emissions, whose warming potential is 28 times higher than carbon dioxide (IPCC, 2013), corresponding to 6-16% of non-anthropogenic emissions in aquatic ecosystems (Wuebbles & Hayhoe, 2002; Tranvik *et al*., 2009). Methane is the main product of carbon mineralization in lagoons, and the methanogenesis is accounted for almost 70% of the anaerobic carbon mineralization, which corresponds to 10-50% of all mineralized carbon (Bédard & Knowles, 1991; Bastviken *et al*., 2008). Methanogenesis is the process in which the organic matter is reduced to CH_4 by methanotrophic bacterial under an anoxic environment. In the case of CO_2, the balance between respiration and primary production is considered the main component of its metabolism (Cole *et al*., 2007), although also occurring in the carbon mineralization.

Among the methods for evaluating gas transport into the atmosphere, there is the diffusive flux and bubbling (ebullitive) flux analyses. Diffusive flux occurs at the water-air interface due to the difference of the partial gas concentration between water and atmosphere. Gas disperses in the water column by molecular diffusion, and one part undergoes oxidation, decreasing its concentrations in surface waters (Bastiviken *et al*., 2008). When the partial pressure of the gas is higher in one of the sections, the gas flows from the part of higher pressure to the one of lower pressure. Flows are considered positive from water to the atmosphere and negative from the atmosphere to water (Esteves & Marinho, 2011). Bubbling flux occurs through the emanation of bubbles direct from the sediment, especially in shallow environments. In this case, oxidation is reduced compared to the diffusive flux. Generally, this flux is the main route of methane emission and may exceed 90% of the gas emission into the atmosphere (Bastviken *et al*., 2004; Abe *et al*., 2012). Eutrophication is enough to increase from 51 to 75% the ebullitive flux and mean annual bubbling flux may increase at least 1900 mg CH_4-C m^{-2} yr^{-1} with a combination of haeting (treatments of +2-3 and +4-5°C) (Davidson *et al*., 2018) and eutrophication. However, a discrete increase was observed in diffusive flux (63 mg CH_4-C m^{-2} yr^{-1}) (Davidson *et al*., 2018)

The gas concentration measurement in the water column is also meaningful to evaluate the distribution mechanism of such gases, as analyzed in other studies such as those of Casper *et al*. (2000) and Cotovicz Jr. *et al*. (2015, 2016). This analysis helps in understanding its formation, higher regions of concentration, and how they are related to the fluxes. Considering that the atmosphere and ocean temperatures have been increasing and urban environments have been suffering from eutrophication, the study on carbon processes and greenhouse gases pattern at coastal environments is essential to understand how climate changes may affect them.

Therefore, this study describes how a eutrophic coastal lagoon behaves with greenhouse fluxes, whether as a source or a sink, and how environmental parameters may interfere with the behavior of these gases. The study area is a chocked lagoon that receives discharges of organic matter and irregular domestic sewage but a very relevant tourist landscape to the city of Rio de Janeiro. Additionally, this work contributes to the generation of fluxes data of these gases in tropical urban environments.

MATERIALS AND METHODS

Study area

Rodrigo de Freitas Lagoon is situated in the city of Rio de Janeiro, Brazil, between 22°57’22” to 22°58’09”S and 43°11’09” to 43°13'03"W (Fig. 1). The area is the main sightseeing of the city and has great landscape relevance. According to the Contingency and Monitoring Plan of the Rodrigo de Freitas Lagoon, its surface is 2.2 km², average depth of 2.8 m, and 7.8 km of the perimeter, with a volume of approximately 6,200,000 m³ (SMAC, 2012). Near the lagoon, five

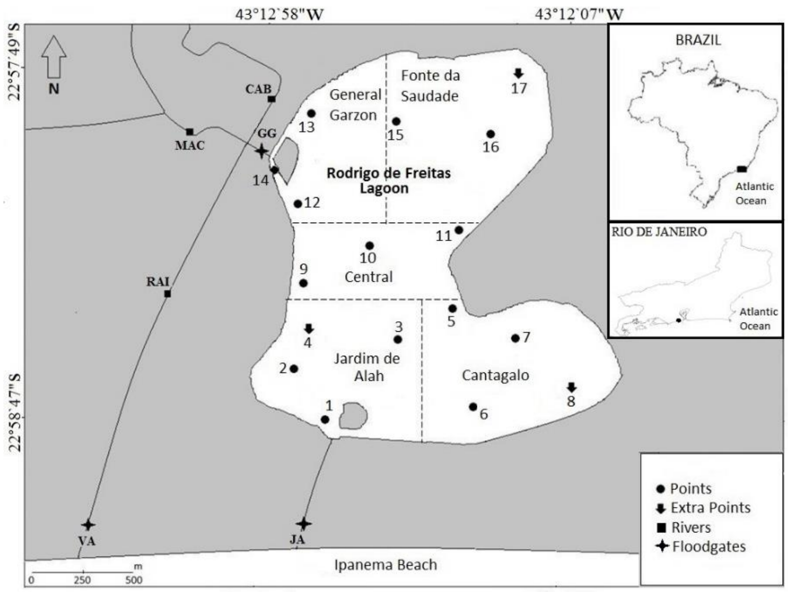

Figure 1. Rodrigo de Freitas Lagoon map showing collection sites (1, 2, 3, 5, 6, 7, 9, 10, 11, 12, 13, 14, 15, 16 and 17), extra collection sites (4, 8, 17), rivers that flow into the Lagoon (CAB: Cabeças River, MAC: Macacos River, RAI: Rainha River), dams comprising the hydric system (GG: General Garzon, VA: Visconde de Albuquerque, JA: Jardim de Alah) and the name of the regions as defined in the present study: Fonte da Saudade, Central, Cantagalo, Jardim de Alah and General Garzon. It is adapted from Oliveira (*unpubl. data*).

residential districts are totaling a population of 157,282 inhabitants (IBGE, 2010) being recognized as an urban lagoon in the city of Rio de Janeiro (Braz *et al*., 2012). The choice of the site was due to its high relevance for the city of Rio de Janeiro since it has scenic beauty and an important leisure area. However, the lagoon is eutrophic, and its water quality is affected by the low renovation and the input of domestic sewage (Van Weerelt *et al*., 2012), mainly during rainy periods (Rosman, 2012).

The water basin area of Rodrigo de Freitas Lagoon is about 32 km^2. It includes Cabeça and Macacos rivers, which rises in the Tijuca National Park, a forested conservation unit entirely located in the city of Rio de Janeiro, and Rainha River, which rises from the ridge Serra da Carioca.

However, these rivers pass through urbanized areas during their courses and receive enormous loads of irregular domestic effluents. The water system also includes three floodgates located at the General Garzon Street, at the Visconde de Albuquerque Avenue and the Jardim de Alah Channel (Fig. 1). They remain mostly closed, avoiding the constant depletion of the rivers, which are great sources of organic matter and sediment to the lagoon (SMAC, 2012). Jardim de Alah floodgate is opened in almost all the days because of the tide flux, but General Garzon and Visconde de Albuquerque floodgates are opened mainly in case of rains.

Rodrigo de Freitas Lagoon is considered a chocked lagoon (Kjerfve & Magil, 1989) because it has only one connection with the sea, the Jardim de Alah Channel, 800 m long and 10-18 m wide, which is mostly silted. Thus, water exchange is very inefficient, resulting in accumulation of suspended particles and organic matter inside the lagoon arising from the rivers (Araújo, 2008).

Rodrigo de Freitas Lagoon was divided into five regions in this study. Jardim de Alah Region, in the southwest, where sites 1, 2, 3 and 4 are located. The Jardim de Alah Channel (with 12 pluvial drain discharges), and the gate controls the water balance of the area. Cantagalo Region, in the southeast, where sites 5, 6, 7 and 8 are situated, plus eight pluvial drainage sites. Central Region, located in the middle of the Lagoon, where sites 9, 10 and 11 are situated, with four sites of pluvial drainage. General Garzon Region, in the northwest, where sites 12, 13 and 14 are situated. Plus, eight sites of pluvial discharge, the discharge of Cabeça and Macacos Rivers and the General Garzon floodgate, which controls the influence of these rivers on the waters of Rodrigo de Freitas Lagoon and Fonte da Saudade Region, located to the northeast, where sites 15, 16 and 17 are situated, and with seven pluvial drainage sites (Fig. 1). This division was based in hydrodynamics. General Garzon Region influences the discharge of rivers, and Jardim de Alah Channel is influenced by seawater directly. Central and Cantagalo regions are not directly influenced by any discharge of rivers or connection with seawater. Fonte da Saudade also is not directly influenced, but this region receives irregular sewage inputs.

Samples

Samplings were carried out using a boat provided by the local Fishermen's Colony. They consisted of four campaigns from April to December 2016 (collection 1: April 18 and 19, 2016; collection 2: June 14 and 15, 2016; collection 3: October 16 and 17, 2016; collection 4: December 13 and 14, 2016) to sample at different temperatures of the year. June presents the lower temperature, April and December present the higher and October presents an intermediate temperature no se entiende. April represents the dry season, December represents the wet season, and June and October represent a midseason. The samplings occurred at 14 sites of Rodrigo de Freitas Lagoon (Table 1, Fig. 1) in the same order from 08:00 to 16:00 h.

Six sites coincided with the monitoring of the Municipal Secretariat of Environment (SMAC) and the others were chosen to represent the whole lagoon and to analyze strategic sites, such as near the discharge of Cabeça and Macacos rivers, Jardim de Alah channel and where there was the recent presence of sewage according to the SMAC reports.

In addition, another three sampling sites were included from June 2016 (sites 4, 8 and 17) because dredging was performed on the location between June and July due to the Olympic and Paralympic Games, during which Rodrigo de Freitas Lagoon was the venue for rowing and canoeing. Sites 8 and 17, places for starting and finishing the rowing events, had dredged sediment from the site and this material was deposited at site 4.

Physical and chemical parameters such as depth, temperature, pH, salinity and dissolved oxygen of surface (around 20 cm in the water) and bottom water were measured at all sites using a YSI multiparameter probe. Parameters such as wind were also measured with a portable anemometer at the time of collections.

By using a Van-Veen dredge, sediment samples were collected in the superficial sediment for analysis of granulometry and organic matter. It occurred only in one site in each region (sites 1, 7, 10, 14 and 16). Granulometry analysis was performed using the Malvern Mastersizer 2000, a laser diffraction equipment used to evaluate particle size distribution, mostly for fine sediments. Data were analyzed by the software Gradistat 6.0 using the screening methodology for thicker sediments. The particle size fractions were determined according to the Wentworth scale (1922). The limits of these classes were slab (>256 mm), pebble (256-64 mm), gravel (64-4 mm), granule (4-2 mm), sand (2-0.062 mm), silt (0.062-0.004 mm) and clay (<0.004 mm). Granulometry analysis was performed only in for the first collection (April).

Total organic matter was determined by the gravimetric method, available in the ABNT (Associação Brasileira de Normas Técnicas) - NBR 10664. In this method, 25 to 50 g of sample was transferred to an empty capsule (previously placed in the muffle at 550 ± 50°C for 1 h and weighed to the nearest 10 mg) and placed in an oven between 103 to 105°C for at least 12 h, and later weighed with accuracy of 10 mg. The total residue was according to the formula: % total residue = (m_{10} × 100) mg^{-1}, where m_{10} = mass of the total residue in grams, and mg = mass of the sample in grams.

Samples of surface and bottom water were collected using a Van Dorn bottle to verify gas concentration. These samples were stored in a refrigerated bag with ice (<5°C) during the collection period, and the headspace technique was performed immediately after collections. This technique consists of applying 30 mL of helium gas in a syringe containing 60 mL of volume water and then analyzed in the Gas Chromatography equipment. Ometto *et al.* (2013), De Mello (2015) and De Mello *et al.* (2017) also refrigerated samples before analysis. Additionally, the methanogenic population was metabolically active at 4 to 45°C (Zeikus & Winfrey, 1976), and its optimal growth is at 20-35°C (Semrau *et al.*, 2010), thus keeping samples refrigerated for short periods reduces bacterial activity.

The calculation of dissolved gases concentration was determined by the following formula:

$$C = Q \times P$$

where:

Q = headspace volume (L) / (sample volume × 0.082 L atm K^{-1} mol^{-1} × temperature in the laboratory in K) + 54.85exp $(A + B/T + C \ln T + DT + E T^2)$,

P = gas partial pressure in ppm × 10^{-9} × pressure in the laboratory in mmHg / 760 atm.

The following Sandler empirical constants for methane were used: A = -416.159289; B = 15557.5631; C = 65.2552591; D = -0.061697573; E = 0; and for carbon dioxide were used: A = -4957.82; B = 105288.4; C = 933.17; D = -2.85489; E = $1.480857E^{-3}$, both as determined in Abe *et al.* (2012).

Gas emission analysis was conducted using two methodologies: diffusive flux analysis and bubbling flux analysis. Diffusive flux used a flotation chamber with a volume of 0.001 m^3 and area of 0.045 m^2, and the samples were run at times zero, 2, 4 and 8 min

Table 1. Coordinates and depth (m) of Rodrigo de Freitas Lagoon sampling sites.

Site	Coordinates		Depth	Site	Coordinates		Depth
	Lat (S)	Long (W)			Lat (S)	Long (W)	
1	22°58'40"	43°12'36"	2.3	10	22°58'20"	43°12'41"	4.0
2	22°58'46"	43°12'49"	3.1	11	22°58'31"	43°12'33"	4.3
3	22°58'28"	43°12'52"	2.6	12	22°58'9"	43°12'26"	2.1
4	22º58'31"	43º12'55"	3.4	13	22°58'18"	43°12'49"	2.5
5	22°58'28"	43°12'43"	4.3	14	22°58'7"	43°12'48"	0.9
6	22°58'46"	43°12'24"	3.5	15	22°57'59"	43°12'43"	3.7
7	22°58'37"	43°12'18"	3.7	16	22°57'57"	43°12'23"	4.0
8	22º58'38"	43º12'07"	3.2	17	22º57'49"	43º12'20"	3.0
9	22°58'36"	43°12'56"	3.5				

(Marcelino *et al*., 2015; Rosa *et al*., 2016; Santos *et al*., 2016; De Mello *et al*., 2017). This time is related to the flotation chamber volume (1,000 mL) in order to obtain measurements before saturation. Moreover, in this study, the diffusive fluxes were calculated in 17 sites. Thus, the period of the measures in each site was up to eight minutes but in a way to represent all the lagoon area. More information about the method is available in IEA (2012). A 60 mL plastic syringe was inserted for removal of an aliquot of gas at the specified times, transferred to gasometric ampoules for transport, and then analyzed by gas chromatography in the laboratory. Flux was calculated using the following formula, according to Ometto *et al.* (2013):

$$\text{Flux} = (\text{Rate} \times P \times F1 \times F2 \times V) / (SP \times R \times T \times A)$$

Where, Rate: increase rate in gas concentration in time (ppm s^{-1}) given by the slope of the line; P: atmospheric pressure in the laboratory at the time of analysis (atm); F1: gas molecular weight (44 for CO_2, 16 for CH_4); F2: conversion factor from seconds to days (86,400 s); V: volume of air inside the chamber (m^3); SP: standard pressure at sea level (101.33 kPa); R: universal gas constant (0.08207 L atm Mol^{-1} K^{-1}); A: area of the chamber in contact with water (m^2); T: air temperature in the laboratory at the time of analysis (K). The result is represented as mg (gas) m^{-2} d^{-1}.

For bubbling flux, "inverted" hopper funnels were used by covering 0.69 m^2. One or two funnels were installed at each site and bubbles released from the bottom were captured in the collection bottles for 24 h.

After this period, an aliquot of gas was withdrawn and taken for analysis using gas chromatography. Methane flux was calculated by the following procedure, according to Abe *et al.* (2012) and adapted from UNESCO (2010):

Bubbling emission (mg m^{-2} d^{-1}) = (factor for CH_4 × P[mmHg] × % CH_4 × vol. col. [mL]) / (T [K] × Δt [h] × number of funnels)

For carbon dioxide, flux was calculated as follows:

Bubbling emission (mg m^{-2} d^{-1}) = (factor for CO_2 × P[mmHg] × % CO_2 × vol. col. [mL]) / (T [K] × Δt [h] × number of funnels), where: factor for CH_4 = 0.164541; factor for CO_2 = 0.452488; P [mmHg]: atmospheric pressure obtained in the laboratory at the time of the chromatographic analysis; %CH_4: result of the chromatographic analysis of methane in the sample; %CO_2: result of the chromatographic analysis of carbon dioxide in the sample; vol. col. [mL]: volume of gas collected by the funnel, or by the unification of funnel collections; T [K]: temperature in the laboratory, at the time of the gas sample chromatographic analysis (assuming that sample and laboratory temperature are in equilibrium); Δt [h]: time that the funnels were in the water; Number of funnels: number of funnels used in the collection.

The analyses of gas samples were performed using a Shimadzu gas chromatography equipment, model GC 2014, equipped with thermal conductivity detector (TCD) for CO_2 analyses, coupled with a Porapack Q column 3 m long, 1/8" inches diameter. Helium was the carrier gas, and the flow rate was 25 mL min^{-1}. For CH_4 analyses, GC 2014 was equipped with a flame ionization detector (FID), molecular column 5A, 2.5 m long, 1/8" inches diameter, detector temperature was 250°C, nitrogen was the carrier gas, and the gas flow rate was 20 mL min^{-1}. The calibration was performed in each campaign, using Linde standards; one at 5.04 ppm CH_4 and 515 ppm CO_2 and another with 50.64 ppm CH_4 and 915.7 ppm CO_2. The linear determination coefficient using these calibration standards was 0.9998 for CH_4, and 0.9839 for CO_2 analysis, and the adjustment factor calculated was 0.0060 for CH_4 and 0.055 for CO_2. The detection limit was 2 ppm for CH_4, and 200 ppm for CO_2 and the quantification limit follow the limit of detection. The variation in sample components detection reproducibility is less than 10%. Considering the standardization process, the absolute uncertainty level for methane was ± 0.05, and for carbon dioxide was ± 6. According to the Linde Standard test certificate, the measurement uncertainty is based on a combined standard uncertainty multiplied by a coverage factor K = 2.0. The result is a 95% confidence level.

Statistical analyses were performed using the Statistica 7.0 and Prisma software. Shapiro-Wilk test was used for data normality, and when non-normal data were detected, samples of diffusive and bubbling fluxes were compared using the Kruskal-Wallis test. Pearson correlation analysis was performed to check for relations among fluxes and the environmental parameters evaluated, and the Principal Component Analysis was run to verify the spatial and seasonal relations of variables in the regions, generating an appropriate data view.

RESULTS

Environmental parameters

During 2016, the period of the four collection campaigns, rainfall values were higher from January to March and from November to December, and lower from April to October (Fig. 2).

April presented the lowest rainfall; the values were smaller than those expected for the season and June presented an average level of rainfall, mainly at the beginning of the month. In October, even though it was the beginning of the period of greatest rainfall, rainfall was low, and December presented the highest rainfall level of the collection period, as expected, including during the collection days.

According to INMET data, the highest temperatures occurred in April, when the maximums on the days of the collection were higher than the climatological normal for the season, reaching 35°C. In December, the expected period of high temperatures, it was around 30°C on collection days. As expected, the lowest temperatures occurred in June, with a maximum of 25°C on the collection days. The parameters measured in field corroborate these data: maximum of 33°C of air temperature and 31°C of water temperature in April, and maximum of 24°C of air temperature and 22°C of water temperature in June.

The pH values were between 7.1 and 10.6, with most values between 8 and 9 (Table 2). The surface presented values of dissolved oxygen between 5.8 and 11.1 mg L^{-1}, and the lowest values were found in April. In the bottom, however, we observed values around 0.4 mg L^{-1} in October, and 11.3 mg L^{-1} in June and the lowest values occurred mainly in December. Salinity ranged from 9.9 in April to 31.6 in December (Table 2).

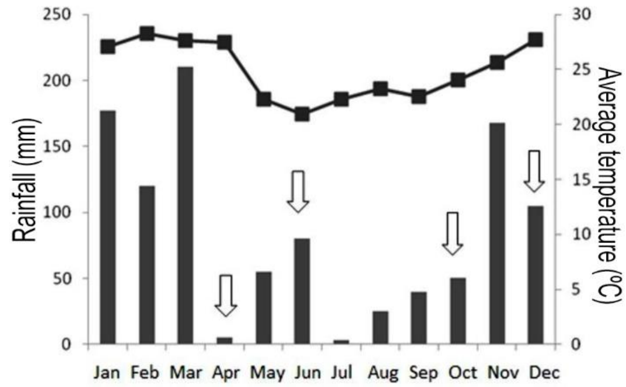

Figure 2. Rainfall data (mm) in bars and average temperature (°C) in lines of the city of Rio de Janeiro in 2016. The arrows indicate the collection period. Source: INMET (2017).

Sediment was predominantly silt/clay, except at General Garzon Region, where it was considered sand. Granulometry found 14.9% sand and 85% silt/clay, at site 16 (Fonte da Saudade Region); 9.9% sand and 90.1% silt/clay at site 10 (Central Region); 16.9% sand and 83.1% silt/clay at site 7 (Cantagalo Region); 22% sand and 78% clay at site 1 (Jardim de Alah Region); and 97.6% sand and 2.3% clay at site 14 (General Garzon Region).

Diffusive flux

The fluxes considered valid were those with a coefficient of determination $R^2 \geq 0.8$. Fluxes showed a great variation between the sites and campaigns. Concerning CH_4, values ranged from -83.39 mg m^{-2} d^{-1} at site 7 (Cantagalo Region) in December to 776.15 mg m^{-2} d^{-1} at site 14 (General Garzon Region) in April. Methane fluxes were predominantly positive (Table 3), and negative values occurred only in December. The highest average occurred in October, while the lowest average occurred in June. Results oscillation was not very high, compared to CO_2 results (Fig. 3a).

Regarding CO_2, values ranged from -7,199.8 mg m^{-2} d^{-1} at site 4 in December to 6,915.56 mg m^{-2} d^{-1} at site 17, also in December. Fluxes were predominantly negative in all campaigns (Table 3). The highest average occurred in October, as observed for methane, and the lowest average occurred in April. Data amplitude was very high in April and December (Fig. 3b).

According to Kruskal-Wallis test, CH_4 fluxes were considered significantly different in the four collections (April, June, October and December) ($P < 0.05$, $P = 0.0009$ (CH_4)). However, fluxes were not different for CO_2 ($P > 0.05$, $P = 0.164$).

Among the five regions analyzed in the Rodrigo de Freitas Lagoon (Rebouças Region, General Garzon

Table 2. Ammoniacal nitrogen (mg L^{-1}), m s^{-1}, air temperature (ºC), water temperature (ºC), pH, Salinity (ppt) and dissolved oxygen (mg L^{-1}) in four collections at the surface (S) and bottom (B) of Rodrigo de Freitas Lagoon. Data provided from Municipal Environment Secretariat/City Hall of the city of Rio de Janeiro (SMAC): Ammoniacal nitrogen in all collections, pH and salinity in the bottom in April, dissolved oxygen in April and October.

Month	NH_4	Wind	Air T	Water T	pH	Sal	DO
Apr (S)	0.13-0.15	0-4.6	29.5-33	29.9-31.8	8.0-9.2	9.9-11.0	5.8-7.8
Apr (B)	0.14-0.26			29.7-30.2	8.1-8.4	11.1-11.2	1.9-4.5
Jun (S)	0.07-0.23	0-4.1	19-24.5	20-22.5	8.3-9.5	14.2-14.9	5.9-11.1
Jun (B)	0.09-0.22			20.3-22.6	7.5-9.5	14.6-20.7	0.8-11.3
Oct (S)	0.13-0.25	0-3.4	28-31	27-30	8.6-10.6	16.4-17.3	8.5-8.8
Oct (B)	0.13-0.21			25.5-29.4	8.5-10.1	16-9-18.5	0.4-7.4
Dec (S)	0.06-0.39	1.3-3.3	28-31	28-31	7.6-8.9	20.1-24.3	6.5-8.9
Dec (B)	0.07-0.12			27.0-31.5	7.1-8.9	14-31.6	0.2-9.2

Region, Central Region, Cantagalo Region and Jardim de Alah Region), diffusive fluxes were not significantly different for all gases ($P > 0.05$, $P = 0.2344$ (CH_4); $P = 0.9706$ (CO_2)) (Figs. 3c-d).

Ebullitive flux

CH_4 bubbling flux ranged from 0.007 mg m^{-2} d^{-1} at site 6 in June 2016 to 888.4 mg m^{-2} d^{-1} at site 14 in April 2016. The highest fluxes were found in October 2016 (average of 130.4 mg m^{-2} d^{-1}), and the lowest values occurred in December 2016 (average of 4.0 mg m^{-2} d^{-1}) (Table 3, Fig. 4a).

CO_2 and CH_4 concentrations in bottom water and surface water

Methane concentrations in surface water ranged from 1.14 and 1.43 µmol L^{-1} in June and October 2016, respectively, to 3.3 µmol L^{-1} in December 2016. For CO_2, concentrations ranged from 3.19 µmol L^{-1} in October 2016 to 140.45 µmol L^{-1} in December 2016 (Table 3).

In the bottom water, the lowest methane values occurred in December 2016 (1.86 µmol L^{-1}), and the highest concentrations were found in April and June 2016 (3.0 µmol L^{-1}). For CO_2, the inverse was observed, with lower concentrations in October (7.05 µmol L^{-1}) and the highest value in December (840.2 µmol L^{-1}).

In general, methane gas concentrations showed higher values in the bottom water, except in December, when the highest values occurred in surface water. Carbon dioxide concentrations, in all seasons, also occurred at higher concentration in bottom water.

Statistical analysis

The correlations (Table 4) indicate the existence of a positive influence between surface water temperature and bubbling fluxes (Fig. 5), with values of 0.27 and 0.35 for the relationship between temperature and methane and carbon dioxide, respectively.

For diffusive fluxes, this influence was lower and did not have a significant correlation. Another parameter related to the bubbling flux was depth (Fig. 5). There were negative and significant correlations with fluxes and values of -0.53 and -0.54 for methane and carbon dioxide, respectively.

Diffusive fluxes presented a negative correlation with the wind, and the dissolved oxygen and salinity, in general, presented negative correlations with fluxes mainly at the bottom. The percentage of sand was significant for the bubbling flux with positive correlations. In the case of silt/clay, correlations were negative (Fig. 6).

By analyzing the regions delimited in the Rodrigo de Freitas Lagoon, the Principal Components Analysis (Fig. 7) indicated the formation of three groups. One only with the General Garzon Region, far from the others; another with the Fonte da Saudade Region; and the third group with the Jardim de Alah, Cantagalo and Central regions, indicating that the regions have different characteristics and may be influencing the production and gas elimination patterns.

Higher values of parameters, such as bubbling CO_2 and CH_4, CO_2 and CH_4 of bottom waters justify the differentiated character of the General Garzon Region about the other regions. For the Fonte da Saudade Region, a higher average of surface CH_4 is the main component separating it from the others, and the third group is grouped mainly by surface CO_2.

DISCUSSION

Results of diffusive flux of CO_2 showed Rodrigo de Freitas Lagoon behaved as a sink of CO_2 during the studied period with mean values of -1,466.8 ± 415.5. Although many lakes are considered sources of CO_2

Table 3. The mean and standard error of diffusive and ebullitive fluxes values for methane (CH_4) and carbon dioxide (CO_2) gases and mean values of methane (CH_4) and carbon dioxide (CO_2) concentration in surface and bottom water, in four collections at Rodrigo de Freitas Lagoon.

Month	Diffusive (mg m^{-2} d^{-1})		Ebullitive (mg m^{-2} d^{-1})		CH_4 in the water (µmol L^{-1})		CO_2 in the water (µmol L^{-1})	
	CH_4	CO_2	CH_4	CO_2	Surface	Bottom	Surface	Bottom
Apr	117.9 ± 73.3 (n=10)	-342.7 ± 899.3 (n=5)	87.3 ± 242.6	7.1 ± 25.2	2.77	3.00	21.31	26.50
Jun	55.1 ± 18.3 (n=15)	-1326.8 ± 218.5 (n=6)	15.5 ± 48.6	0.7 ± 1.3	1.14	3.06	23.43	68.40
Oct	158.4 ± 28.8 (n=17)	-1882.9 ± 101.4 (n=11)	130.4 ± 284.7	9.4 ± 26.8	1.43	2.57	3.19	7.05
Dec	119.1 ± 27.2 (n=14)	-1592.3 ± 982.5 (n=15)	4.0 ± 10.5	2.6 ± 9.2	3.30	1.86	140.45	840.20
Mean	113.7 ± 18	-1466.8 ± 415.5	58.3 ± 188.7	5.0 ± 18.8	2.16	2.62	47.09	235.53

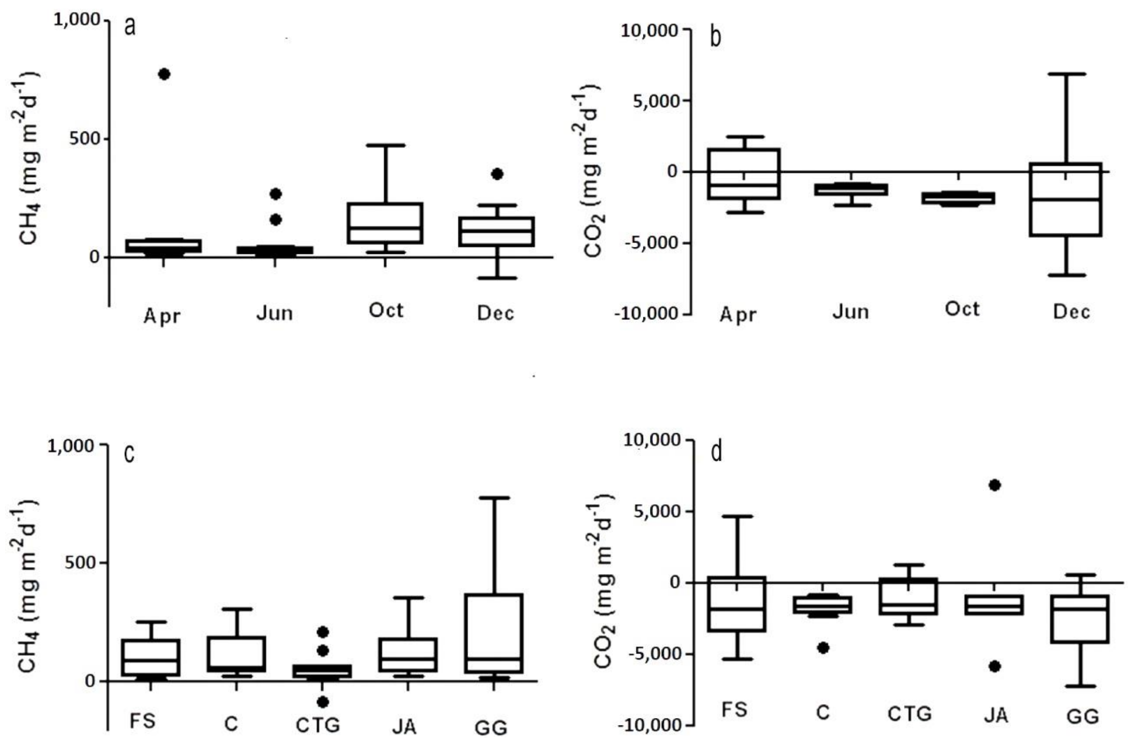

Figure 3. a) Box plot of CH_4 and b) CO_2 diffusive flux results in the four collections (April, June, October and December); c) CH_4, d) CO_2 according to the regions of Rodrigo de Freitas Lagoon, in 2016 (mg m^{-2} d^{-1}). JA (Jardim de Alah Region, sites 1, 2, 3 and 4), CTG (Cantagalo Region, sites 5, 6, 7 and 8), C (Central Region, sites 9, 10 and 11), GG (General Garzon Region, sites 12, 13 and 14) and FS (Fonte da Saudade Region, sites 15,16 and 17) as showed in Figure 1.

(Cole *et al.*, 1994; Abril *et al.*, 2005; Guérin *et al.*, 2006; Marotta *et al.*, 2009), this sink behavior have also been reported by other studies (Gu *et al.*, 2011; Mojica *et al.*, 2013; Cotovicz *et al.*, 2015). It is characteristic of eutrophic environments and suggests that the trophic state is one of the main factors controlling pCO_2 in aquatic environments (Duarte & Agustí, 1998; Gu *et al.*, 2011).

Cotovicz *et al.* (2015) studied Guanabara Bay, a tropical estuary considered eutrophic to hypereutrophic in the city of Rio de Janeiro, and also found a carbon dioxide sink, due to the high availability of nutrients, massive discharge of untreated domestic sewage and tropical conditions, such as high availability of light and stratification of the water column. In the cited study, the flux of CO_2 ranged from -115.2 to -219.6 g C m^{-2} yr^{-1}, values lower than those found for the Rodrigo de Freitas Lagoon. Mojica *et al.* (2013) found Três Palos Lagoon in Mexico, a coastal hypereutrophic lagoon that connects seasonally with the sea, as a carbon dioxide sink to the atmosphere with the flux of CO_2 around -1,300 mg m^{-2} d^{-1}, like the mean flux at

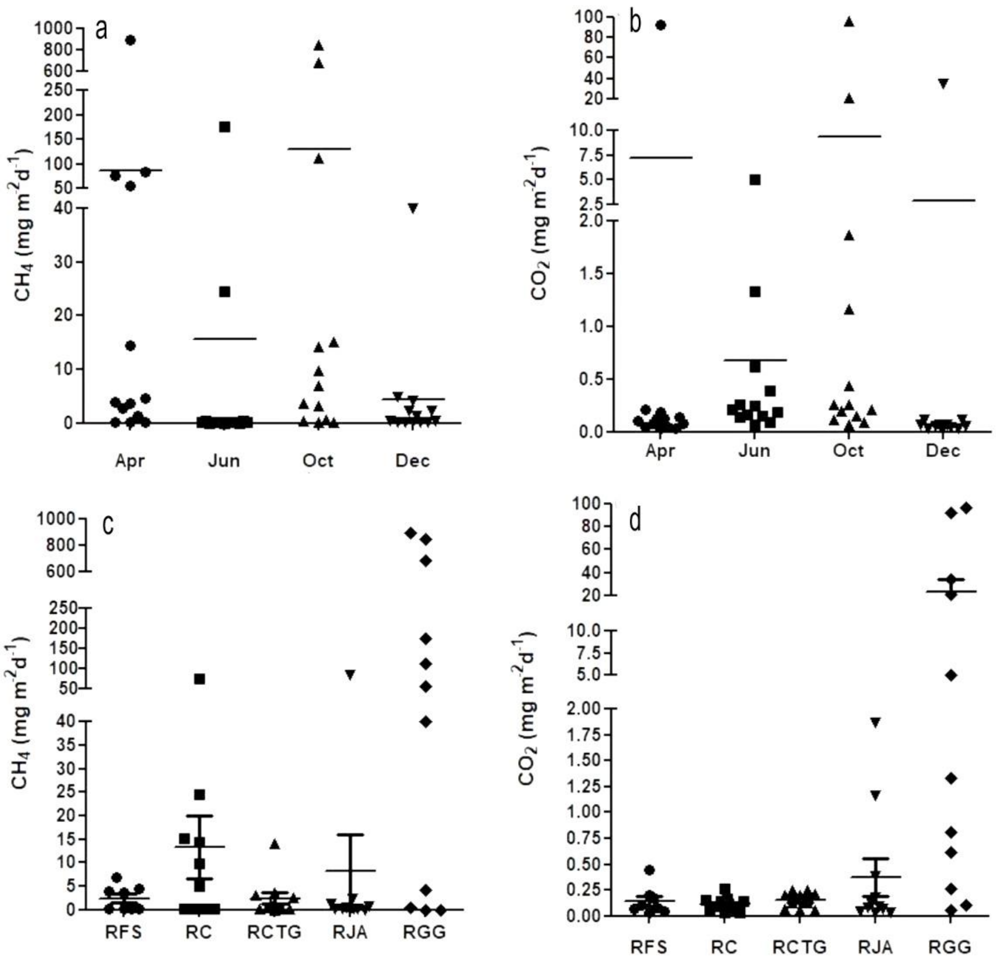

Figure 4. CH_4 (a) and CO_2 (b) ebullitive flux in the four collections (April, June, October and December); CH_4 (c) and CO_2 (d) according to the regions performed at Rodrigo de Freitas Lagoon in 2016. JA (Jardim de Alah Region - sites 1, 2, 3 and 4), CTG (Cantagalo Region - sites 5, 6, 7 and 8), C (Central Region - sites 9, 10 and 11), GG (General Garzon Region - sites 12, 13 and 14) and FS (Fonte da Saudade Region- sites 15,16 and 17) as showed in Figure 1. The symbols (circles, squares, triangles and rhombus) are the values of the flow in the sites, in each month or region. The horizontal lines are the median.

Table 4. Correlations of CH_4e and CO_2e ebullitive flux and CH_4d, CO_2d diffusive flux with the following environmental parameters: depth (D), wind (W), surface water temperature (WTs), surface pH (pHs), surface salinity (Sals), surface dissolved oxygen (O_2s), bottom water temperature (Wtb), bottom pH (pHb), bottom salinity (Salb), bottom dissolved oxygen (O_2b), sand percentage (sand), si/cl percentage (silt/clay) and organic matter (OM). *Indicate significant values (*P* < 0.05).

	D	W	WTs	pHs	Sals	O_2s	WTb	pHb	Salb	O_2b	Sand	Si/Clay	OM
CH_4e	-0.53*	0.01	0.27*	-0.15	-0.12	0.22	0.19	0.11	-0.15	-0.15	0.74*	-0.54*	-0.29
CO_2e	-0.54*	0.02	0.35*	-0.21	-0.11	0.18	0.20	0.07	-0.10	-0.07	0.79*	-0.56*	-0.26
CH_4d	0.06	-0.08	0.24	-0.05	0.13	-0.18	0.26	0.19	-0.01	-0.18	0.40*	-0.27	0.09
CO_2d	0.00	-0.16	0.05	-0.11	-0.10	-0.01	0.02	-0.09	0.02	-0.07	0.07	0.04	-0.20

Rodrigo de Freitas Lagoon. Guanabara Bay is an estuary with intense water circulation, differently from the Rodrigo de Freitas and Três Palos Lagoon that are chocked lagoons.

Although Cole *et al.* (2000) and Gu *et al.* (2011) indicated that many productive lakes have a period in the year with CO_2 input, when the primary production is high, and another period when the production is low,

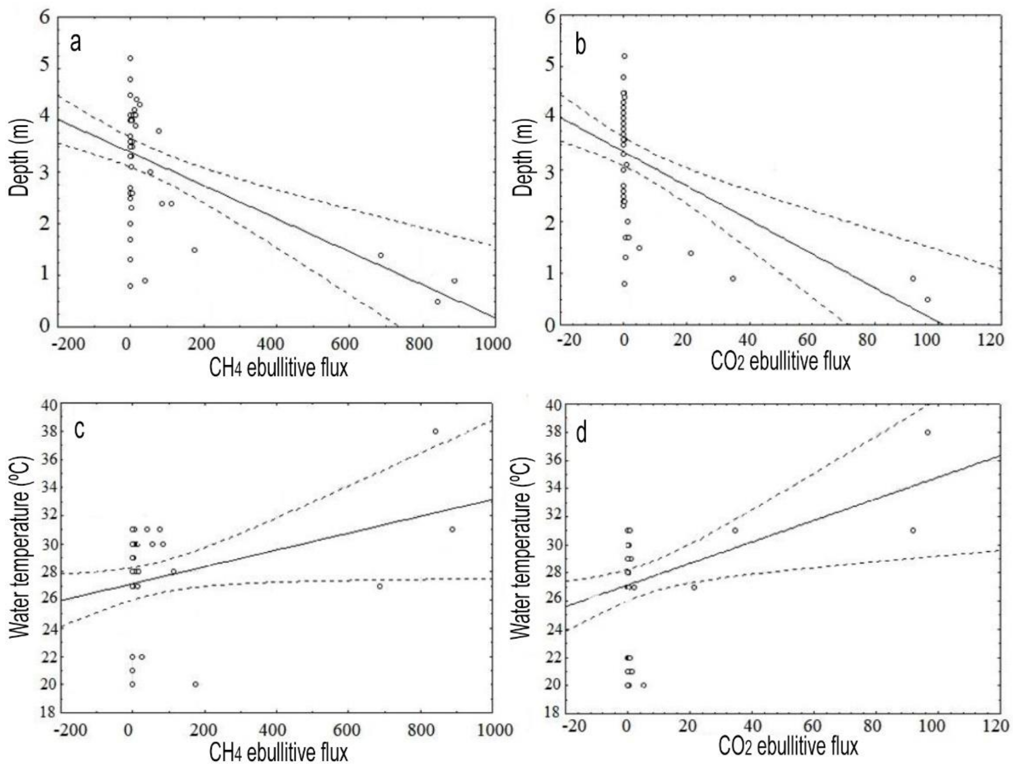

Figure 5. Linear regressions between a) CH_4 ebullitive flux and depth ($R^2 = 0.27$) and b) CO_2 ebullitive flux and depth ($R^2 = 0.28$); and between c) CH_4 ebullitive flux and water temperatures ($R^2 = 0.07$) and d) CO_2 ebullitive flux and water temperature ($R^2 = 0.12$). R^2 = determination coefficient.

this pattern was not found at Rodrigo de Freitas Lagoon. This region was a CO_2 sink in all periods of the year studied.

Rodrigo de Freitas Lagoon is a source of CH_4 to the atmosphere, with mean values of 113.7 ± 18 mg m^{-2} d^{-1} of diffusive flux. These values were lower than that at Três Palos Lagoon (mean of 1,350 mg m^{-2} d^{-1}) in Mexico (Mojica *et al*., 2013) but higher than that at Chautengo Lagoon (6.7 mg m^{-2} d^{-1}) in Mexico (Mojica *et al*., 2013). The differences in the flux from the two Lagoons in Mexico reflects the low circulation of seawater at Três Palos Lagoon, where the organic matter from the rivers accumulates and the better circulation in Chautengo Lagoon. Rodrigo de Freitas Lagoon has a very inefficient water exchange, but it is not like Três Palos Lagoon that did not connect with the sea most of the year.

Braz *et al*. (2012), in their study also in Rodrigo de Freitas Lagoon, found an average of 33 mg m^{-2} d^{-1} in two collections performed in the summer. These values were lower than those presented in this study. However, Braz *et al*. (2012) have analyzed only five sites in the Lagoon that did not have the highest values for methane emission, such as the General Garzon Region, which may explain this difference.

Cotovicz *et al*. (2016) also found positive methane fluxes from the Guanabara Bay, a eutrophic estuary in the city of Rio de Janeiro. Values ranged from 3.8 and 76.76 mg m^{-2} d^{-1}, also lower than the results presented in the Rodrigo de Freitas Lagoon. Despite the input of organic matter and the potential methane generation in the Guanabara Bay, this estuary is open, while the Rodrigo de Freitas Lagoon is semiclosed.

Koné *et al*. (2010) studied three Lagoon systems at Ivory Coast, West Africa, and found values between 0.3 and 38.5 mg m^{-2} d^{-1}, lower than the results from Rodrigo de Freitas Lagoon. The Grand-Lahou Lagoon and the Ebrié Lagoon system are restricted lagoons, and the Aby Lagoon is a chocked lagoon, but only the Ebrié Lagoon is considered polluted, while other lagoons are pristine.

Due to the lack of ebullitive flux studies in an urban coastal lagoon at the tropical region, the results were compared to similar environments. In the study of Kelley *et al*. (1990) at White Oak River estuary, the annual mean CH_4 flux was similar to that found at Rodrigo de Freitas Lagoon, approximately 50 mg CH_4 m^{-2} d^{-1}. A small coastal river estuary characterizes the White Oak River estuary in North Carolina with a narrow channel that opens to form the estuary, salinity ranges from 5 to 20, like that at Rodrigo de Freitas

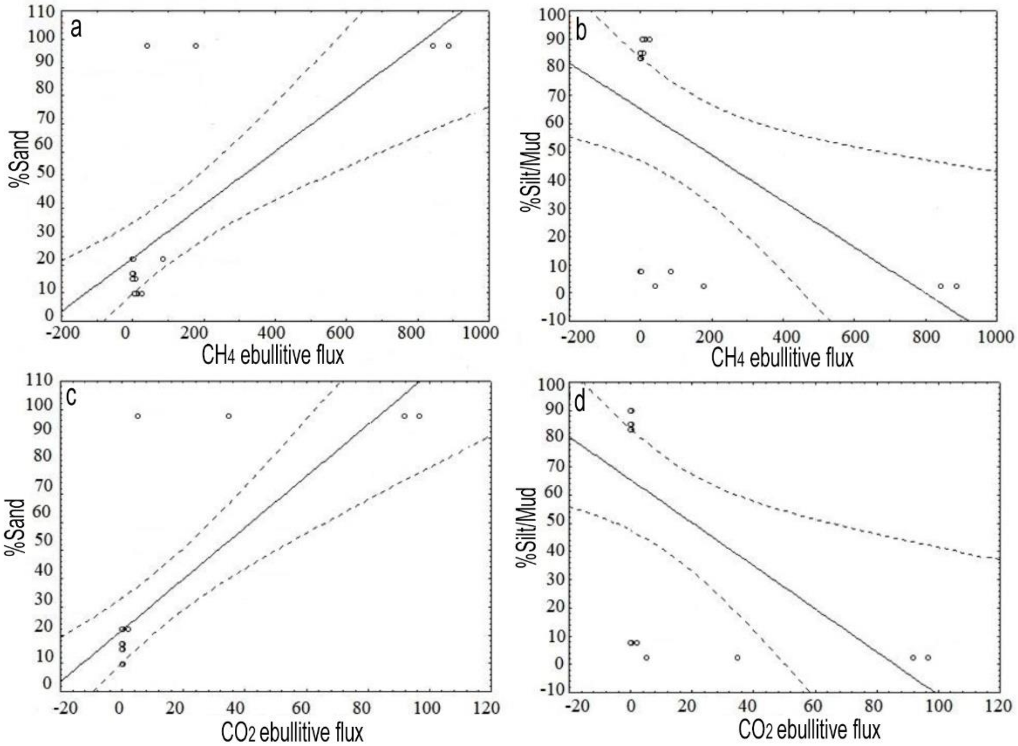

Figure 6. Linear regressions between a) CH_4 ebullitive flux and %sand ($R^2 = 0.54$), b) CH_4 ebullitive flux and %mud ($R^2 = 0.29$); and between c) CO_2 ebullitive flux and %sand ($R^2 = 0.62$), d) CO_2 ebullitive flux and %mud ($R^2 = 0.31$). R^2 = determination coefficient.

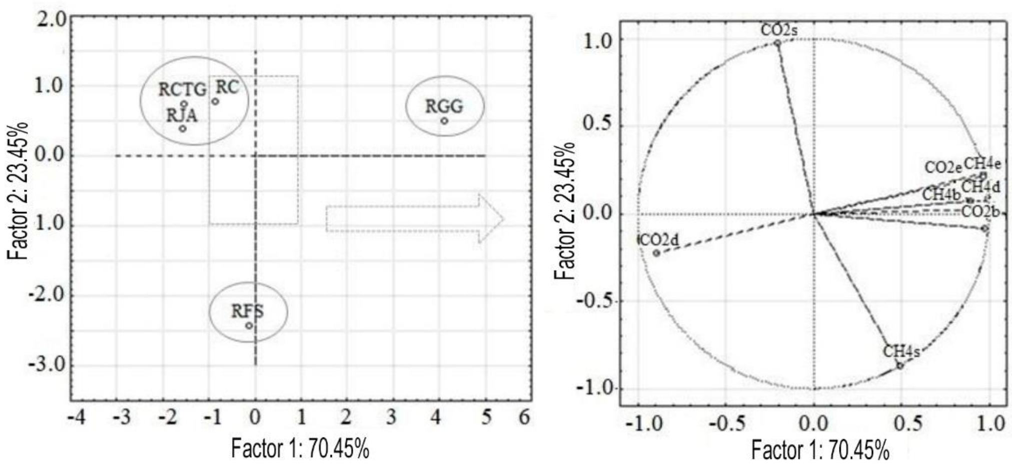

Figure 7. Principal Component Analysis performed among the regions at the Rodrigo de Freitas Lagoon with the results of diffusive and ebullitive emissions, gas concentration in surface and bottom water. RFS (Fonte da Saudade Region); RGG (General Garzon Region); RC (Central Region); RJA (Jardim de Alah Region); RCTG (Cantagalo Region); CO_2d (CO_2 diffusive flux); CO_2e (CO_2 ebullitive flux); CO_2s (CO_2 concentration in surface water); CO_2b (CO_2 concentration in bottom water); CH_4d (CH_4 diffusive flux); CH_4e (CH_4 ebullitive flux); CH_4s (CH_4 concentration in surface water); CH_4b (CH_4 concentration in bottom water).

Lagoon. The study of Martens & Val Klump (1980) at Cape Lookout Bight, a small organic-rich marine basin located on the Outer Banks of North Carolina, found a flux of approximately 400 mg CH_4 m^{-2} d^{-1} in the low tide, during summer months, values higher than that found at Rodrigo de Freitas Lagoon. Cape Lookout Bight is a system with different salinity influences than at Rodrigo de Freitas Lagoon and with sandy sediment, which may explain this higher flux. De Mello *et al*. (2017) found 780 and 316 mg CH4 m^{-2} d^{-1} at Pampulha Lagoon, a eutrophic system in the state of Minas Gerais in the southeastern region of Brazil, during summer. This system was built mainly to serve as a water source for the northern area of the city. However, the intense eutrophication and siltation processes resulted in the decay of the water quality.

Regarding the bubbling flux, no relation was found to rainfall events. On the other hand, the higher fluxes occurred in collections with higher temperatures. Although December is a month of high temperatures on the collection days, the maximum temperatures were lower than in April and October collections. Then, it is possible to establish a relation between fluxes and the temperature. As presented in other studies like Wik *et al*. (2011) and DelSontro *et al*. (2016), the ebullitive flux seems to be more sensitive to temperature influences than diffusive flux.

Temperature is an important parameter considering gas flux, since it favors the metabolism of bacteria, intensifying methanogenesis and stimulating methane production (Zeikus & Winfrey, 1976; Tranvik *et al*., 2009; Duc *et al*., 2010). Surface water temperature was also important for the correlation with flux. Short periods of higher temperatures may temporarily increase the water temperature, and also the temperature of sediment in contact, resulting in increased release of CH_4 from sediments (Duc *et al*., 2010). Another important factor is depth, which has a direct relation to pressure. Thus, the negative correlation with emissions of CH_4 and CO_2 is because the hydrostatic pressure is reduced at lower depth, decreasing the gas solubility and increasing its emission (De Mello *et al*., 2017).

The wind is an important parameter when considering the diffusive flux (Wanninkhof, 1992; Raymond & Cole, 2001). However, no relation with this parameter was found in this study. It can be a consequence of low wind speed (usually lower than 2 m s^{-1}) at Rodrigo de Freitas Lagoon. Cole *et al*. (1998) also indicate that the diffusive flux and wind are independents at low wind speeds.

The high value of gas fluxes in General Garzon Region can be explained by the presence of the mouth of Macacos and Cabeças River, and it is also the area with the lowest depths. These rivers spring in the area of the Tijuca National Park and outflow at Rodrigo de Freitas Lagoon (SMAC, 2012). However, even if they spring in preserved areas, they pass through urban areas, where they receive irregular waste from domestic sewage and become very impacted by urbanization without sanitation. General Garzon region is located at the mouth of these rivers, receiving the discharge of particulate matter in suspension, which reduces the local depth and the hydrostatic pressure by increasing temperature. Thus, it generates areas considered as hotspots for methane emissions, such as in the Pampulha reservoir studied by De Mello *et al*. (2017). The study of Rosman (2012) shows that Jardim de Alah has already been almost two months without significant inputs of seawater with no renovation of waters, intensifying the accumulation of organic matter at Rodrigo de Freitas Lagoon.

Eutrophic conditions are favorable for methane production activity. Organic matter decomposition processes can stimulate methanogenesis and dissolved oxygen consumption that promotes anaerobic processes (Marinho *et al*., 2009; Furlanetto *et al*., 2012). Palma-Silva *et al*. (2013) indicate that trophic state affects production and flux of methane to the atmosphere. Davidson *et al*. (2018) corroborate this relation and suggest that eutrophication intensifies the ebullitive flux. Also, the combination of nutrient enrichment and higher temperature increases gases emissions.

Carbon dioxide ebullitive flux was not the main route of this gas to the atmosphere and is usually less efficient than methane due to the higher CO_2 solubility in water (Casper *et al*., 2000; Poissant *et al*., 2007; Felix, 2014). In the present study, around 99% of the CO_2 was lost by diffusion and corroborated the percentage cited in Casper *et al*. (2000). Methane released into the atmosphere is generally lower in the diffusive flux, because, in that case, a part of the gas can be oxidized in the water column. Thus, is methane carbon also transferred to pelagic food networks differently from the bubbling flux where methane is released directly from the sediment without going through these oxidation pathways. (Bastviken *et al*., 2002, 2004; Duc *et al*., 2010). However, in this study, the inverse was observed, with higher values of methane in the diffusive flux.

A microhabitat formed by organic and inorganic matter harboring a rich microbial community (Soares-Gomes & Figueiredo, 2009) may explain this fact because in these aggregates of organic matter, even on the surface, methanogenic bacteria could also occur. The low levels of oxygen dissolved in some sites of the lagoon may generate anaerobic environments, allowing the activity of these bacteria. The dredging in the Rodrigo de Freitas Lagoon can also contribute to this process as it releases high rates of organic compounds from the sediment to the water column (Torres *et al*., 2009), causing anoxia or sub-anoxia in regions with a higher concentration of diffusive flux than the bubbling flux.

Another explanation may be the type of sediment in the region, which is predominantly muddy, thus having lower gas percolation (Jain & Juanes, 2009) and consequently lower sediment release into the water column. At site 14 (General Garzon Region), the sediment is predominantly sandy, and in this case, bubbling flux was greater than the diffusive flux, as expected, which corroborates this hypothesis.

In general, methane and carbon dioxide concentrations were higher in the bottom water, indicating that the bottom and probably the sediment are an important compartment to produce these gases. The accumulation of organic matter and the lower levels of oxygen are the main reason, favoring the activity of methanogenic bacteria. In December, methane values were higher in the surface water. It may be the result of a high concentration of organic matter in the waters of this lagoon due to the heavy rains in the previous days and during collections.

The analysis of main components indicated that the hydrodynamics of the Rodrigo de Freitas Lagoon is a relevant factor to determine the characteristics of each region because those close to the Jardim de Alah (that connects the lagoon with the sea, but also with sewage input) and more influenced by their waters are grouped. Sites 1, 7 and 10 have similar results from CO_2 surface and maybe the reason for this grouping. On the other hand, the General Garzon Region, which receives less influence of the sea waters and receives the discharge of the Rivers Cabeça and Macacos is more distant from the other regions. The Fonte da Saudade Region, the last to receive the sea waters, according to Rosman (2012), is also isolated. The reason can be site 16 had higher levels of CH_4 surface and CO_2 diffusive in December. Also, the characteristics of the General Garzon Region as lower depth, sandy sediment, and the discharge of the rivers help to characterize this region and generate higher ebullient flux.

CONCLUSIONS

The Rodrigo de Freitas Lagoon was considered a source of methane (135.14 t of CH_4 yr^{-1}) and a sink of carbon dioxide (-1,157 t CO_2 yr^{-1}) during the studied period. The highest values of water temperature, lower depth and higher sediment granulometry type of the region were important parameters and related to the emission of these gases to the atmosphere. Additionally, Cabeça and Macacos rivers discharge impacts the lagoon, increasing methane and carbon dioxide concentration in the water and fluxes in the region. Thus, the General Garzon Region is considered as a hotspot of methane emission.

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