

Influence of environmental variables on diffusive greenhouse gas fluxes at hydroelectric reservoirs in Brazil

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Abstract

For almost two decades, studies have been under way in Brazil, showing how hydroelectric reservoirs produce biogenic gases, mainly methane (CH₄) and carbon dioxide (CO₂), through the organic decomposition of flooded biomass. This somewhat complex phenomenon is due to a set of variables with differing levels of interdependence that directly or indirectly affect greenhouse gas (GHG) emissions. The purpose of this paper is to determine, through a statistical data analysis, the relation between CO₂, CH₄ diffusive fluxes and environmental variables at the Furnas, Itumbiara and Serra da Mesa hydroelectric reservoirs, located in the *Cerrado* biome on Brazil's high central plateau. The choice of this region was prompted by its importance in the national context, covering an area of some two million square kilometers, encompassing two major river basins (Paraná and Tocantins-Araguaia), with the largest installed power generation capacity in Brazil, together accounting for around 23% of Brazilian territory. This study shows that CH₄ presented a moderate negative correlation between CO₂ and depth. Additionally, a moderate positive correlation was noted for pH, water temperature and wind. The CO₂ presented a moderate negative correlation for pH, wind speed, water temperature and air temperature. Additionally, a moderate positive correlation was noted for CO₂ and water temperature. The complexity of the emission phenomenon is unlikely to occur through a simultaneous understanding of all the factors, due to difficulties in accessing and analyzing all the variables that have real, direct effects on GHG production and emission.

Keywords: methane, carbon dioxide, environmental variables, reservoirs.

Influência de parâmetros ambientais em fluxos difusivos de gases de efeito estufa em reservatórios hidrelétricos no Brasil

Resumo

Há quase duas décadas, no Brasil, vêm sendo realizados estudos que revelam que os reservatórios hidrelétricos produzem gases biogênicos, principalmente o metano (CH₄) e o dióxido de carbono (CO₂), provenientes da decomposição orgânica da biomassa alagada. Observa-se que esse fenômeno é bastante complexo devido a uma gama de variáveis que possuem diferentes graus de interdependência e que influenciam diretamente ou indiretamente nas emissões de gases de efeito estufa (GEE). O objetivo deste trabalho é determinar o grau de relacionamento entre os fluxos difusivos de CO₂, CH₄ e variáveis ambientais dos Reservatórios Hidrelétricos de Furnas, Itumbiara e Serra da Mesa, através da análise estatística dos dados. Os reservatórios hidrelétricos estão situados no Bioma Cerrado, localizado no Planalto Central do Brasil. A escolha da região deu-se devido a sua importância no contexto nacional, já que corresponde a uma área de aproximadamente dois milhões de quilômetros quadrados, e, nela estão inseridas duas bacias (Bacia do Paraná e Bacia do Tocantins-Araguaia), com a maior capacidade instalada de energia elétrica do país. Esta duas bacias juntas abrangem 23% do território nacional. Neste estudo os resultados revelam que o CH₄ apresentou correlação negativa, significativa e moderada com o CO₂ e com a profundidade. Observou-se ainda correlação positiva e moderada com pH, temperatura da água e velocidade do vento. O CO₂ apresentou correlação negativa, significativa e moderada com pH, com a velocidade do vento, temperatura da água e temperatura do ar. Observou-se também correlação positiva e moderada do CO₂ com a temperatura da água. A complexidade do fenômeno de emissão dificilmente ocorrerá pelo entendimento simultâneo de todos os fatores, devido às dificuldades de acessar e analisar todas as variáveis que realmente têm implicação direta nesta produção/emissão de GEE.

Palavras-chave: metano, dióxido de carbono, variáveis ambientais, reservatórios.

1. Introduction

Biogenic gases generated by the decomposition of biomass are a complex phenomenon, due to a range of variables with differing levels of interdependence, directly influencing greenhouse gas emissions from hydroelectric reservoirs.

Factors contributing to GHG emissions include the succession of microbiological communities during reservoir lifetimes (Dumestre et al., 2001), water column depth, water level variability, air temperature, water temperature, wind speed, dissolved oxygen concentration, water transparency, altitude and rainfall, among others (Kemenes, 2006; Lampert and Sommer, 2007; Tundisi, et al., 2007; Esteves, 2011; Ribeiro et al., 2011).

For almost two decades, studies have been under way of greenhouse gas emissions from hydroelectric reservoirs (Rudd et al., 1993; Rosa and Schaeffer, 1994a; Tremblay and Schetagne, 2006; Guerin et al., 2007; Weissenberger et al., 2010), presenting important observations on fluxes of CO₂, CH₄ and nitrous oxide (N₂O) from hydroelectric reservoirs, including global estimates of emissions based on the flooded areas of different reservoirs (St. Louis et al., 2000).

The GHG emission rate per unit of electricity produced varies according to reservoir characteristics, including its size and the type of landscape flooded, as well as the power generation system used (Rudd et al., 1993). Especially in tropical regions, important knowledge has been built up that fosters a better understanding of the phenomenon of these gases released from Brazilian hydroelectric reservoirs, (Sikar et al., 2005), as well as GHG emission patterns (Rosa et al., 2004), comparisons of GHG fluxes from hydroelectric and thermoelectric power plants, and carbon circulation in reservoirs (Santos et al., 2006).

Extremely complex, the GHG emission phenomenon is unlikely to be understood through the simultaneous occurrence of all the factors involved, due to difficulties in accessing and analyzing all variables with direct effects on GHG production and emission.

In order to conduct this study, three hydroelectric power plants were selected in the *Cerrado* biome, located mainly on Brazil's high central plateau that covers some two million square kilometers, equivalent to 23% of Brazilian territory. Furthermore, these reservoirs are located within two the largest river basins in Brazil. The Paraná basin has the largest installed power generation capacity in Brazil, together with the heaviest demands while the Tocantins-Araguaia basin ranks second for power generation in Brazil.

The purpose of this paper is to determine through statistical data analyses the relation levels between environmental variables and carbon dioxide (CO₂) and methane (CH₄) fluxes at the following hydroelectric reservoirs: Furnas, Itumbiara and Serra da Mesa.

2. Causal Mechanisms of Diffusive Fluxes in Hydroelectric Reservoirs

2.1. Wind effect

The relation between high wind speeds and diffusive fluxes has been explored by several authors, with the pioneering studies conducted by Liss determining the relation between water-air gas transfers (Liss, 1973).

For carbon dioxide, Liss and Merlivat (1986) examined the empirical relations between water-air diffusive fluxes and wind speeds in oceans.

According MacInyre et al. (1995) gas fluxes at water-air interfaces depend mainly on two factors: concentration gradients between surface water and air, and physical transfers or turbulent energy at this interface.

The influence of wind speed variability on gas transfer velocities has been studied in aquatic bodies as ocean, lakes and riverine ecosystems (Wannikhof, 1992). Clark and colleagues suggested that wind is the primary source of surface turbulence at the water-air interface of the tidal Hudson River (Clark et al., 1995).

Some authors conclude that CO₂ exchange coefficients in air-water interfaces are largely independent of wind at low wind speeds (Cole & Caraco, 1998).

Ho et al. (2006) indicate that there is a quadratic relation between wind speed and gas transfer velocity in water-air interfaces over oceans.

Wind may have strong effects on thermal stratification and water column stability, strongly influencing the dynamics and vertical distribution of biogenic gases (Kemenes, 2006).

2.2. Temperature effect

In surface peat, Yavitt et al. (1987) found that temperature is the main variable controlling seasonal patterns in CO₂ production.

Neue et al. (1997) showed that variations are controlled largely by soil solution temperatures and partial methane pressures. Supplementing these studies, the work of Moore & Dalva (1993) revealed marked ($p < 0.05$) differences in carbon dioxide and methane emissions from peatland soils. Emissions of these gases were correlated with peat type, temperature and water table position. The proposed correlations of diffusive fluxes with temperatures showing CO₂ and CH₄ emissions at 23 °C were 2.4 and 6.6 times higher on average respectively, than those at 10 °C.

Lessard et al. (1994) found a positive correlation between soil surface CO₂ fluxes and soil temperatures for forests ($R^2 = 0.74$, $s(y) = 1.77 \text{ g.m}^{-2}.\text{d}^{-1}$) and croplands ($R^2 = 0.48$, $s(y) = 1.10 \text{ g.m}^{-2}.\text{d}^{-1}$).

Another study demonstrated that methane fluxes were directly correlated with water levels and temperatures at all measurement locations, except two in the central part of the fen, where fluxes were lower (Rask et al., 2002).

In northern peatlands, Macdonald et al. (1998) found positive linear correlations between CH₄ emission rates and rising temperatures from pool and lawn monoliths.

2.3. pH effect

When carbon dioxide dissolves in fresh water, it lowers the pH, making it more acid. According Rice and Claypool (1981), the most important methane generation mechanism in marine sediments is the reduction of CO₂ by hydrogen (electrons) produced through the anaerobic oxidation of organic matter.

Klinger et al. (1994) conclude that there are some indications that high CH₄ fluxes cluster around pH 4 and pH 7.

2.4. Depth

Previous studies have shown that CH₄ concentrations in tropical reservoirs increase significantly at greater depths (Galy-Lacaux et al., 1999).

The depth of hydroelectric reservoirs strongly influences the vertical distribution of biogenic gases. Studies have demonstrated daily variations in these gas concentrations, which depend on gas mixtures in water columns (Kemenes, 2006; Esteves, 2011).

2.5. Dissolved organic carbon

Dissolved organic carbon (DOC) is produced by the decomposition of plants and animals and their excreta in water, with DOC decomposition caused by photochemical and microbial degradation (respiration), results in biogenic gases production (Lampert and Sommer, 2007; Esteves, 2011).

Dissolved organic carbon can decompose partially in the presence of dissolved oxygen, forming other organic or inorganic substances, such as CO₂ for example. In the absence of oxygen, organic carbon may generate methane through methanogenesis (Esteves, 2011). Lu et al. (1999) observed that the higher levels of organic carbon in sediment resulted in higher methane effluxes from water bodies.

3. Methodology

3.1. Characteristics of the reservoirs studied

Located along the mid-course of the Grande River in Minas Gerais State, the Furnas hydroelectric power complex has eight power generation plants, six of which are in operation. The Itumbiara hydroelectric power complex is located on the Rio Paranaíba river (Paraná Hydrographic Region), on the boundary between Goiás and Minas Gerais States. The Serra da Mesa hydroelectric power complex is the largest in Brazil by water volume, playing a major role in the nation's energy sector; located in the Alto Tocantins river basin (Tocantins-Araguaia Hydrographic Region) in Goiás State, it has three power generation plants. Furnas reservoir is located at Grande

river (Paraná Hydrographic Region) at Minas Gerais state (Figure 1).

The technical characteristics of the three reservoirs studied are presented in Table 1.

3.2. Sampling methods

CO₂ and CH₄ emanation were quantified using diffusion chambers of 1 liter volume and 0.05 m² covered area. There are inverted containers that hold a trapped air volume over the water surface. Gases dissolved in water emanate into this volume.

Sampling the chamber at 0, 2, 4 and 8 minutes, the volume enrichment rate was determined according to (Santos et al., 2011) by gas chromatography (Construmaq Gas Chromatograph with flame ionization detector for CH₄ analyses and thermal conductivity detector for CO₂, HayeSep D porous polymers packed columns), from which the emanation rate was calculated, dimensions were taken into account. The chambers were fitted with shields that prevent them from trapping bubbles as they rise.

The results of the gas chromatography analyses of samples taken from the floating chamber were matched to the four concentrations in order to measure the gas concentration increase (positive flux) or decrease (negative flux) in the chamber.

The following criteria were used to accept or reject the samples (UNESCO/IHA Greenhouse Gas, 2009):

1. Fluxes were accepted when the determination coefficient (R^2) of the adjustment function was greater than 0.85 and $p < 0.002$;
2. Fluxes were rejected when due to sample contamination by CH₄ rich bubbles rising from the bottoming. If this does occur in the last measurement, that point was discarded and the only the first three points were used.



Figure 1 - Location of the hydroelectric reservoirs studied.

Table 1 – Technical characteristics of the reservoirs studied.

Hydroelectric reservoir	Dam filling	Reservoir age at measurement date (years)	Volume (km ³)	Reservoir area (km ²)	Watershed area (km ²)	Installed capacity (MW)	Density capacity (W/m ²)	Water residence time (days)*
Furnas	November	1962	42	23	1,440	50,464	1,216	0.84
Itumbiara	November	1981	25	17	778	95,000	2,082	2.68
Serra da Mesa	October	1997	12	54	1,784	50,975	1,275	0.71

* Average result of field trips.

Should contamination occur before the last sample, the measurement at this point was discarded;

3. If a problem detected during the chromatograph analysis resulted in the loss of the sample, it was discarded and the flux was calculated with the remaining three samples. After the samples passed through the filters and were accepted, the flux was calculated by the following equation:

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

where Rate: growth rate of gas concentration over time (ppm.s⁻¹), given by the gradient; P: atmospheric pressure in the laboratory at the time of analysis (atm.); F1: molecular weight of the gas (44 for CO₂, 16 for CH₄); F2: conversion factor from seconds to days (86,400 s); V: air volume in the chamber (m³); SP: standard pressure at mean sea level (101.33 kPa); R: universal gas constant (0.08207 L atm. mol⁻¹.K⁻¹) A: chamber area in contact with water (m²); T: air temperature at time of laboratory analysis (K); the findings are presented in mg (gas) m⁻²d⁻¹.

3.3. Location of sampling sites

The geographical location of the sampling sites in the studied reservoirs is shown in Figures 2 to 4. The sampling sites were distributed among the reservoirs taking into account two distinct parts of these water bodies: their main channels and their branches, whose hydrodynamic processes more closely resemble stagnant water (Table 2).

The diffusive gas fluxes were measured at three hydroelectric reservoirs owned by Furnas Centrais Elétricas S.A. Each reservoir was sampled at least three times a year, covering the dry, wet and transition seasons (wet-dry) as shown in Table 3.

3.4. Statistical analysis

For statistical treatment, the mean results of the diffusive CH₄ and CO₂ fluxes were used, at the hydroelectric reservoirs. These data were obtained through collecting samples.

In order to calculate the correlation coefficients in addition to physical and chemical variables such as: wind speed, air temperature, water temperature, pH and DOC. All these variables are possibly related to the production and emission of GHGs (Figure 5).

The normality of all the variables was checked through the Kolmogorov-Smirnov D test (Wilks, 2006), with estimated dataset parameters, in order to determine whether the set is well modeled for normal distribution, thus selecting the best method for describing the data and the best way of conducting this study.

The Pearson correlation matrix was used to analyze the relations between the environmental variables and the CH₄ and CO₂ fluxes. This method was selected as it is useful for simultaneous analyses of correlations among

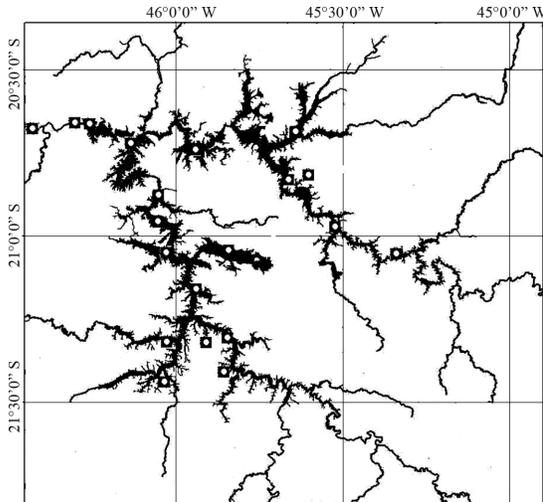


Figure 2 - Sampling sites at Furnas hydropower reservoir.

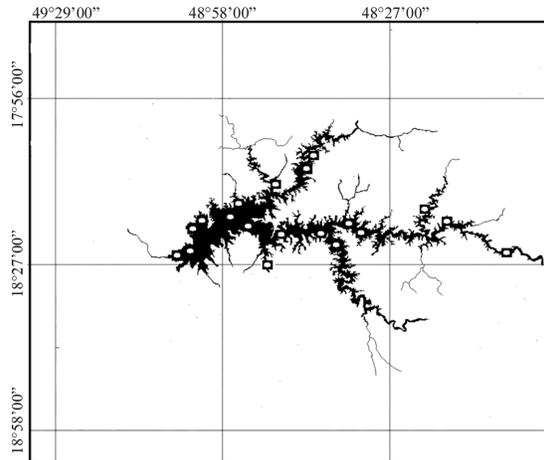


Figure 4 - Sampling sites at Itumbiara hydropower reservoir.

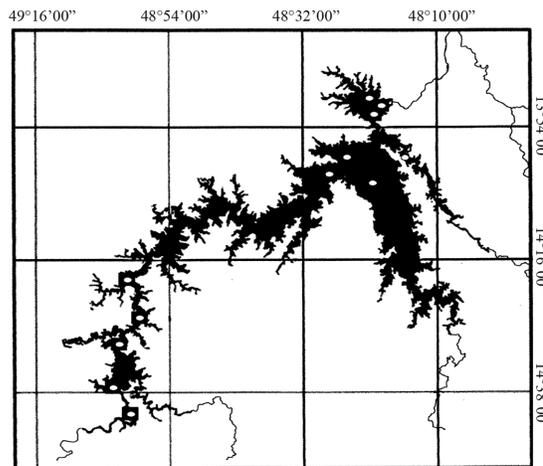


Figure 3 - Sampling sites at Serra Mesa hydropower reservoir.

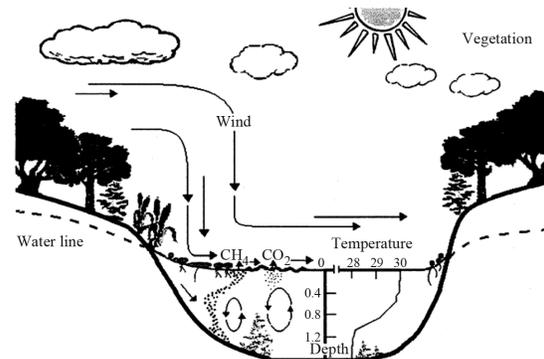


Figure 5 - Schematic diagram of greenhouse gas production and emission, and relationships with some environmental variables.

many variables. In order to conduct this study, pair deletion was used, with a significance level of 5% ($p < 0.05$).

The Kruskal-Wallis test is a nonparametric test (Helsel, 1987) used here to compare the three reservoirs studied and provide comparisons between GHGs fluxes of three sampling campaigns in each reservoir and the environmental variables. It can be used to analyse several different samples and it tests the null hypothesis.

The Mann-Whitney test (Wilks, 2006) is used to analyze data from a two different groups of results. The null hypothesis assumes that the two distributions do not differ systematically from each other. The alternative hypothesis, on the other hand, states that the two distributions differ systematically.

4. Results and Discussions

4.1. Descriptive statistics of diffusive fluxes and environmental variables

The Boxplot presents the frequency distribution of the diffusive CH_4 and CO_2 fluxes by field trip at each res-

Table 2 - Spatial localization of sampling sites in the reservoir area.

Hydropower reservoir	Main channel of reservoir (%)	Regions with poor water circulation (reservoir arms) (%)
Furnas	61	39
Itumbiara	58	42
Serra da Mesa	64	36

ervoir (Figure 6). The frequency distribution all reservoirs has similar results for the CH₄ fluxes.

The result of the Kruskal-Wallis test, at the 0.05 level, shows that the populations are not significantly different (Table 4). Results obtained for CH₄ and CO₂ fluxes, suggest that the observed differences between the three periods studied are significant (Table 5).

The Furnas reservoir presents a mean CH₄ flux for the transition period (wet-dry) that is higher than in the dry season (U = 468; Z = 2.381; Exact. Prob > |U| = 0.016; Asymp. Prob > |U| = 0.017) thus differing from the pattern found at the other reservoirs (Figure 6a). At the 0.05 level, the two distributions are significantly different.

The Mann-Whitney test shows whether the distributions between two groups are the same, with the alternative hypothesis that the populations are significantly different, or one larger than the other.

This difference might possibly be explained through the reduction recorded in wind speed (0.70 m.s⁻¹) during the sampling period (Table 6), as thermal stratification might

Table 4 - Kruskal-Wallis test statistics of the studied reservoirs.

	Chi-Square	DF	Prob > Chi-Square
CH ₄	5.430	2	0.066
CO ₂	4.046	2	0.132

At the 0.05 level, the populations are not significantly different.

Table 5 - Statistical test to compare different periods.

		Chi-Square	DF	Prob > Chi-Square
Furnas	CH ₄	11.114	2	0.003
	CO ₂	20.801	2	3.040E-5
Itumbiara	CH ₄	10.734	2	0.004
	CO ₂	8.229	2	0.016
Serra da Mesa	CH ₄	12.238	2	0.002
	CO ₂	6.762	2	0.033

At the 0.05 level, the populations are significantly different.

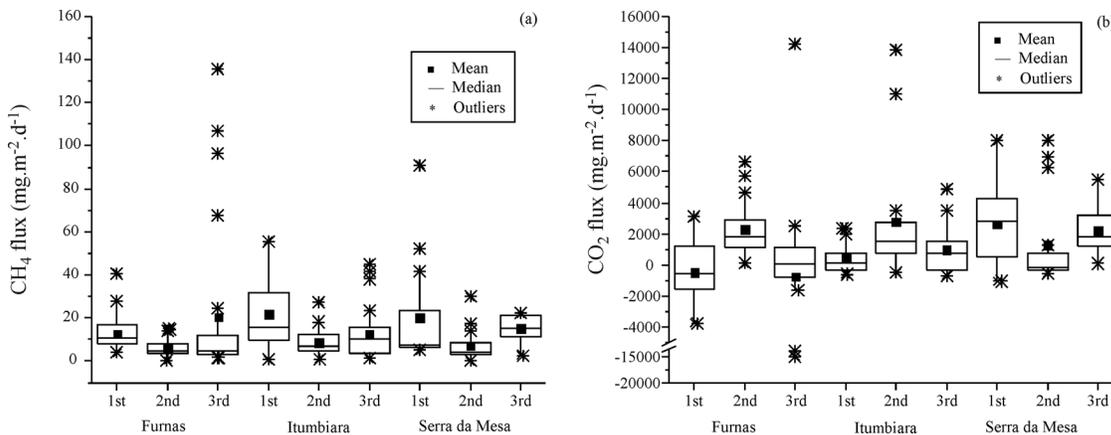


Figure 6 - Frequency distribution of the diffusive fluxes by field trips for the Furnas, Itumbiara and Serra da Mesa reservoirs (a) CH₄ flux and (b) CO₂ flux.

Table 3 - Sampling period at the studied reservoirs.

Hydroelectric reservoir	Field trip	Date	Season	Total sample
Furnas	1st.	11/2005	Dry	
	2nd.	04/2006	Wet	78 (CH ₄)
	3rd.	07-08/2006	Transition (Wet-Dry)	66 (CO ₂)
Itumbiara	1st.	11/2004	Dry	
	2nd.	03/2005	Wet	78 (CH ₄)
	3rd.	08/2005	Transition (Wet-Dry)	57 (CO ₂)
Serra da Mesa	1st.	11/2003	Dry	
	2nd.	03/2004	Wet	47 (CH ₄)
	3rd.	07/2004	Transition (Wet-Dry)	47 (CO ₂)

have increased due to this reduction, resulting in a higher accumulation of CH₄ (Lampert and Sommer, 2007).

An examination of the gap between the mean (20.28 mg.m⁻².day⁻¹) and median (4.50 mg.m⁻².day⁻¹) shows the level of deviation in the measurements dispersion, which can be explained by the spatial variability of the samples (Table 2).

Comparing the CO₂ flux frequency distribution for the three reservoirs, the Serra da Mesa reservoir posts different results. During the dry season (first field trip), the average CO₂ flux (2,617.88 mg.m⁻².day⁻¹) was similar to the rainy season values (Figure 6b), which may reflect more active aerobic bacteria due to higher oxygen availability in the water column.

Sampling in Serra da Mesa reservoir initially occurred when the reservoir had been filling for six years, with widespread decomposition of terrestrial vegetation was flooded, and huge decomposition rates, mainly anaerobic, was very intense.

During the rainy season (second field trip) the average flux (CH₄ = 7.12 and CO₂ = 1,281.68 mg.m⁻².day⁻¹) was less than expected for this period, compared to the other reservoirs. The average for this period presented characteristic values usually found for dry season (Table 6).

The Serra da Mesa Reservoir presented a higher average concentration of DOC (10.62 mg.L⁻¹) during the dry season (Table 6), which may be due to seasonal variations of autochthonous biomass production related to the nutrients inputs. The dissolved organic carbon load values are influenced by precipitation and water flows in these environments.

During the dry season, the reservoir level was five to ten meters below average, with the banks showing discoloration typical of soil appearing after flooding. It was possible to observe that during the sampling period there was heavy rainfall (157.2 mm) and an increase in the inflow (304 m³/s), which may give rise to a greater addition of organic matter and an increase in one of its main fractions, dissolved organic carbon. Studies on the DOC concentration in lakes show that it is considered indicative of partial carbon dioxide pressure (pCO₂) and consequently CO₂ flux to the atmosphere. Lennon (2004) demonstrated experimentally in mesocosms the increase of CO₂ flow with additions of dissolved organic carbon. Other authors such as Prairie et al. (2002) and Jonsson et al. (2003) also demonstrated a linear relationship between DOC and CO₂ flux in boreal and temperate lakes, respectively.

4.2. Correlation analysis of diffusive fluxes and environmental variables

The correlation coefficients (\bar{r}) between the average diffusive fluxes of CH₄ and CO₂, the DOC and the environmental variables at the reservoirs studied are shown in Tables 7 to 9.

The analysis shows a moderately positive correlation between wind speed and CH₄ fluxes at the Itumbiara Reservoir ($r = 0.322$) and Serra da Mesa ($r = 0.692$). The wind speed may have marked effects on thermal stratification and water column stability, strongly influencing the dynamics and vertical distribution of biogenic gases, which might possibly explain the correlation between these two variables. Similar effects were observed by Kemenes (2006) in Balbina Reservoir, showing that wind may exert a strong influence on gas distribution in the water column.

At the Furnas Reservoir, the CH₄ flux showed a moderate negative correlation ($r = -0.338$) with CO₂, possibly explained by CH₄ oxidation resulting from the formation of CO₂ in the presence of oxygen or an increase in its concentration (Utsumi *apud* Esteves, 2011). Additionally, a moderate positive correlation ($r = 0.508$) was noted between the CH₄ flux and the pH.

A low positive correlation ($r = 0.263$) between the CH₄ flux and the DOC may be explained by CH₄ production at the sediment-water interface, with organic carbon used in the methanogenic process.

The CH₄ flux was correlated with depth at the Itumbiara Reservoir ($r = -0.377$). Earlier studies have shown that dissolved CH₄ concentrations increased significantly at lower depths in tropical reservoirs (Galy-Lacaux et al., 1999). The possible reason for the increased flux may be related to the observed growth of gramineous plants at the bottom of the reservoir, acting as a new source of decaying organic matter.

Moderate positive correlation between CH₄ flux and water temperature was noted at the Serra da Mesa reservoir ($r = 0.397$). The water temperature directly influences the solubility of gases and therefore the phenomenon of exchange of gases in the air-water interface.

The correlation analysis showed that two of the reservoirs studied presented moderate negative correlation between CO₂ and pH, suggesting that biological processes such as primary production and mineralization have a significant effect on these variations (Chagas & Suzuki, 2004). At the Furnas Reservoir, the correlation coefficient value was equal to -0.559, reaching -0.521 at Itumbiara. In water, CO₂ tends to form carbonic acid (H₂CO₃), which could explain the moderate negative correlation with pH. Earlier studies show that carbonic acid and free carbon dioxide predominates at pH levels less than 6.4 (Lampert and Sommer, 2007; Esteves, 2011).

Negative low correlation ($r = -0.305$) between CO₂ and DOC was noted for the Furnas reservoir, which can be explained by the different metabolic processes that follow the water column profile in this ecosystem. They include the DOC photodegradation process, which consists of the absorption of sunlight and its subsequent oxidation, resulting in CO₂, which is a form of dissolved organic carbon.

The correlation analysis showed a significant correlation between CO₂ and water temperature at the two res-

Table 6 - Descriptive statistics of the hydroelectric reservoirs.

Variables	Furnas				Itumbiara				Serra da Mesa			
	N	Mean	Sd	Median	N	Mean	Sd	Median	N	Mean	Sd	Median
1st. field trip dry	25	12.77	8.35	10.54	25	21.74	16.41	15.60	17	20.08	23.10	7.54
CO ₂ ^a	18	-476.72	2,028.05	-581.50	25	453.96	937.94	148.00	17	2,617.88	2,771.09	2,834.00
DOC ^b	21	2.38	1.81	1.66	7	1.79	0.38	1.73	6	10.62	3.41	11.17
Depth ^c	29	9.44	10.35	2.50	25	13.56	9.94	10.00	17	7.44	4.42	9.00
pH	4	7.09	0.24	7.09	21	7.40	0.27	7.40	17	7.83	0.37	7.60
Wind ^d	25	2.39	0.87	2.70	23	2.49	1.34	3.00	17	0.85	0.77	1.00
Air temperature ^e	29	28.53	3.68	28.20	25	31.10	3.94	32.00	17	29.38	3.12	30.00
Water temperature ^f	29	25.99	0.81	26.20	25	28.56	1.16	29.00	17	29.50	0.95	29.00
CH ₄	26	6.38	4.37	4.69	23	8.51	6.07	6.94	16	7.12	7.67	4.30
CO ₂	25	2,275.48	1,618.99	1,786.96	16	2,763.62	3,962.04	1,506.55	16	1,281.68	2,929.29	-135.00
DOC	26	1.94	0.72	1.95	10	5.43	3.37	5.19	7	1.08	0.75	0.95
Depth	27	17.24	19.83	11.00	23	24.43	11.82	21.00	16	23.02	19.50	15.00
pH ^g												
Wind	27	1.46	1.31	1.10	22	1.35	0.85	1.30	8	0.38	0.69	0.00
Air temperature	27	26.26	1.82	26.30	23	27.71	1.32	27.90	16	28.22	2.19	28.00
Water temperature	27	26.21	0.66	26.10	23	28.10	1.05	28.10	16	29.66	1.00	30.00
CH ₄	27	20.28	36.18	4.50	30	12.73	11.63	10.16	13	15.16	6.87	15.31
CO ₂	23	-729.70	5,710.14	62.16	16	973.59	1,565.85	724.40	13	2,207.69	1,619.71	1,800.00
DOC	26	1.12	0.65	0.88	10	4.73	1.72	4.45	9	3.79	1.21	3.73
Depth	27	25.30	30.46	23.00	30	29.52	22.82	24.60	12	22.55	16.63	17.00
pH	20	7.50	0.19	7.51	7	6.65	0.32	6.48	7	7.30	1.95	8.00
Wind	27	0.86	0.70	1.10	25	1.35	1.28	1.10	7	0.21	0.57	0.00
Air temperature	26	24.55	2.39	23.60	30	28.71	2.75	28.30	12	28.46	2.34	28.25
Water temperature	24	22.05	0.69	21.90	30	24.50	1.28	24.1	12	29.88	0.88	30.00

^aCH₄ and CO₂ flux: mg.m⁻².d⁻¹; ^bDOC: mg.L⁻¹; ^cDepth: m; ^dWind: m.s⁻¹; ^eAir Temperature: °C; ^fWater Temperature: °C; ^gpH values are not presented in the second field trip because the probe was broken.

Sd: Standard deviation.

Table 7 - Correlation coefficients for the Furnas reservoir (CH₄: methane flux; CO₂: carbon dioxide flux; DOC: dissolved organic carbon carbon; Depth: lake depth; pH: potential of hydrogen; Wind: wind speed; Air Temp.: air temperature; Water Temp.: water temperature).

	CH ₄	CO ₂	DOC	Depth	pH	Wind	Air temp.	Water temp.
CH ₄	1							
CO ₂	-0.338*	1						
DOC	0.263*	-0.305*	1					
Depth	0.072	-0.016	-0.071	1				
pH	0.508*	-0.559*	0.559*	-0.047	1			
Wind	0.017	0.115	-0.081	0.008	-0.232	1		
Air temperature	0.177	-0.011	-0.050	-0.140	0.276	0.228*	1	
Water temperature	-0.180	0.338*	-0.206	-0.326*	-0.642*	0.349*	0.554*	1

*Marked correlations are significant for $p < 0.05$.

Table 8 - Correlation coefficients for the Itumbiara reservoir (CH₄: methane flux; CO₂: carbon dioxide flux; DOC: dissolved organic carbon carbon; Depth: lake depth; pH: potential of hydrogen; Wind: wind speed; Air Temp.: air temperature; Water Temp.: water temperature).

	CH ₄	CO ₂	DOC	Depth	pH	Wind	Air temp.	Water temp.
CH ₄	1							
CO ₂	-0.003	1						
DOC	-0.301	0.199	1					
Depth	-0.377*	-0.128	-0.016	1				
pH	-0.026	-0.521*	0.260	-0.293	1			
Wind	0.322*	-0.366*	-0.024	-0.162	0.290	1		
Air temperature	0.070	-0.088	-0.391*	-0.136	0.305	-0.337*	1	
Water temperature	0.041	-0.182	-0.271	-0.237*	0.819*	0.128	0.390*	1

*Marked correlations are significant for $p < 0.05$.

Table 9 - Correlation coefficients for the Serra da Mesa reservoir (CH₄: methane flux; CO₂: carbon dioxide flux; DOC: dissolved organic carbon carbon; Depth: lake depth; pH: potential of hydrogen; Wind: wind speed; Air Temp.: air temperature; Water Temp.: water temperature).

	CH ₄	CO ₂	DOC	Depth	pH	Wind	Air temp.	Water temp.
CH ₄	1							
CO ₂	-0.117	1						
DOC	0.256	0.024	1					
Depth	-0.159	-0.267	-0.347	1				
pH	-0.135	-0.286	0.193	0.216	1			
Wind	0.692*	-0.181	0.369	-0.446*	-0.312	1		
Air temperature	0.172	-0.441*	0.466*	0.251	0.249	0.181	1	
Water temperature	0.397*	-0.571*	-0.036	0.008	-0.170	0.376*	0.418*	1

*Marked correlations are significant for $p < 0.05$.

ervoirs studied. Water temperature was correlated in a positive moderate manner (0.338) with CO₂ at the Furnas reservoir, but was extremely negative (-0.571) for the Serra da Mesa reservoir, possibly due to thermal stratification. At the Serra da Mesa reservoir, moderate negative correlation (-0.441) was noted between CO₂ and air temperature. The analysis presented a significant correlation between water temperature and CO₂ for the two reservoirs under study. Daily variations were observed in the temperatures between the surface and the bottom of the reservoir, isolating its layers and resulting in higher and/or lower CO₂ concentrations. For the Furnas reservoir, there is a moderately positive correlation between the water temperature and CO₂ (0.338). In this reservoir, a negative flux of CO₂ was observed in the dry season (-476.72 mg.m⁻².d⁻¹) and in the transitional season (-729.70 mg.m⁻².d⁻¹), and low values in water temperature. According to Esteves (2011), the lower the temperature, the greater the solubility of gases in water, and the greater the rise in temperature, the greater the system's metabolism will be. For the Serra da Mesa reservoir, a negative correlation was found (-0.571) between water temperature and CO₂, possibly due to thermal stratification. Also for Serra da Mesa, a moderately negative correlation (-0.441) was found between CO₂ and air temperature, possibly influenced by oxygen concentration, a factor that is directly related to the temperature (Kemes, 2006; Esteves, 2011).

Other variables presented significant correlations with CO₂ fluxes in Itumbiara Reservoir. Wind speed showed a moderate negative correlation ($r = -0.366$) with CO₂, probably related to water mass circulation, which may have marked impacts on water column thermal structures, strongly influencing the vertical distribution of biogenic gases (Esteves, 2011), also causing water surface mixing with the underlying water (Lampert & Sommer, 2007). Wind is among the most important factors for gas transfer rates at water-air interfaces.

Comparing CO₂ flux frequency distributions at all three reservoirs, Serra da Mesa behaved differently from the others. During the dry season (first field trip), the average flux value increased (2,617.88 mg.m⁻².day⁻¹), reaching a level similar to the rainy season values.

During the rainy season (second field trip), the average CO₂ flux (1,281.68 mg.m⁻².day⁻¹) was lower than expected for this period, compared to the other two reservoirs, with values more characteristic of the dry season.

5. Conclusions

The variability of the diffusive fluxes of CH₄ was positively influenced by the environmental variables, wind and dissolved organic carbon; and negatively influenced by CO₂, depth and water temperature.

The environmental variables that negatively influenced the variability of the diffusive fluxes of CO₂ were dissolved organic carbon, air temperature and wind. The

water temperature influenced the CO₂ fluxes both positively and negatively.

Establishing the relationship between the diffusive fluxes of CH₄ and CO₂ and the environmental variables represents a contribution to greater understanding of the processes involved. Its importance is due above all to the fact that the study was carried out in a region of the *cerrado* biome, as most of the research done emphasizes the reservoirs in the Amazon region as great sources of greenhouse gas emissions.

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References

- CLARK, JF., SCHLOSSER, P., SIMPSON, HJ., STUTE, M., WANNINKHOF, R. and HO, DT., 1995. Relationship between gas transfer velocities and wind speeds in the tidal Hudson River determined by the dual tracer technique. In: *Air-Water Gas Transfer, Proceedings of the third international symposium on air-water gas transfer*, B. Jaehne and E.C. Monahan, editors, AEON Verlag & Studio, Hanau, Germany, p. 785-800.
- CHAGAS, GG. and SUZUKI, MS., 2004. Seasonal Hydrochemical Variation in a Tropical Coastal Lagoon (Açu Lagoon, Brazil). *Braz. J. Biol.*, vol. 65, no. 4, p. 597-607.
- COLE, JJ. and CARACO, NF., 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF₆. *Limnol. Oceanogr.*, vol. 43, no. 4, p. 647-656.
- DUMESTRE, JF., CASAMAYOR, EO., MASSANA, R. and PEDRÓS-ALIÓ, C., 2001. Changes in bacterial and archaeal assemblages in an equatorial river induced by the water eutrophication of Petit Saut dam reservoir (French Guiana). *Aquat. Microb. Ecol.*, vol. 26, p. 209-221.
- ESTEVES, FA., 2011. *Fundamentos de Limnologia*. Editora Interciência: Rio de Janeiro, 826p.
- FENCHEL, T., KING, GM. and BLACKBURN, TH., 1998. *Bacterial Biogeochemistry*. 2nd ed. Academic Press: California and London, 307p.
- GALY-LACAUX, C., DELMAS, R., KOUADIO, G., RICHARD, S. and GOSSE, P., 1999. Long-term Greenhouse gas emissions from hydroelectric reservoirs in tropical forest regions. *Global Biogeochem. Cycles*, vol. 13, p. 503-517.
- GUÉRIN, F., ABRIL, G., SERÇA, D., DELON, C., RICHARD, S., DELMAS, R., TREMBLAY, A. and VARFALVY, L., 2007. Gas Transfer Velocities of CO₂ and CH₄ in a Tropi-

- cal Reservoir and its River Downstream. *J. Mar. Syst.*, vol. 66, p. 161-172.
- HELSEL, DR., 1987. Advantages of Nonparametric Procedures for Analysis of Water Quality Data. *Hydrol. Sci. J.*, vol. 32, p. 179-190.
- HO, DT., LAW, CS., SMITH, MJ., SCHLOSSER, P., HARVEY, M. and HILL, P., 2006. Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: Implications for global parameterizations. *Geophys. Res. Lett.*, vol. 33, p. L16611.
- JONSSON, A., KARLSSON, J. and JANSSON, M., 2003. Sources of carbon dioxide Supersaturation in Clearwater and Humic Lakes in Northern Sweden. *Ecosystems*, vol. 6, p. 224-235.
- KEMENES, A., 2006. *Estimativa das Emissões de Gases de Efeito Estufa (CO₂ e CH₄) pela Hidrelétrica de Balbina, Amazônia Central, Brasil*. Manaus: Universidade Federal do Amazonas, 95p. Tese de Doutorado em Biologia Tropical e Recursos Naturais.
- KLINGER, LF., ZIMMERMAN, PR., GREENBERG, JP., HEIDT LE. and GUENTHER, AB., 1994. Carbon trace gas fluxes along a successional gradient in the Hudson Bay lowland. *J. Geophys. Res.*, vol. 99, no. D1, p. 1469-1494.
- LAMPERT, W. and SOMMER, U., 2007. *Limnoecology: The Ecology of Lakes and Streams*. 2nd ed. Oxford: University Press, New York, 324p.
- LENNON, JT., 2004. Experimental Evidence that Terrestrial Carbon Subsidies Increase CO₂ flux from Lake Ecosystems. *Oecologia*, vol. 138, p. 584-591.
- LESSARD, R., ROCHETTE, P., TOPP, E., PATTEY, E., DESJARDINS, RL. and BEAUMONT, G., 1994. Methane and carbon dioxide fluxes from poorly drained adjacent cultivated and forest sites. *Can. J. Soil Sci.*, vol. 74, no. 2, p. 139-146.
- LISS, PS., 1973. Processes of gas exchange across an air-water interface. *Deep Sea Res. Ocean. Abstracts*, vol. 20, no. 3, p. 221-238.
- LISS, PS. and MERLIVAT, L., 1986. Air-sea gas exchange rates: Introduction and synthesis. In: *The Role of Air-Sea Exchange. Geochemical Cycling*. P. Buat-Menard (ed), D. Reidel, Hingham, Mass., p. 113-129.
- LU, Y., WASSMANN, R., NEUE H. and HUANG, C., 1999. Dynamics of Dissolved Organic Carbon and Methane Emissions in a Flooded Rice Soil. *Soil Sci. Soc. Am. J.*, vol. 64, no. 6, p. 2011-2017.
- MACDONALD, JA., FOWLER, D., HARGREAVES, KJ., SKIBA, U., LEITH, ID. and MURRAY, MD., 1998. Methane emission rates from a northern wetland; response to temperature, water table and transport. *Atmos. Environ.*, vol. 32, no. 19, p. 3219-3227.
- MACINYRE, S., WANNINKHOF, R. and CHANTON, JP., 1995. Trace gas exchange across the air-water interface in freshwaters and coastal marine environments. In: *Biogenic Trace Gases: Measuring Emissions from Soils and Waters*, P.A. Mattson and R.C. Harris (eds), Blackwell, New York; p. 52-57.
- MARINHO, CC., PALMA SILVA, C., ALBERTONI, EF., TRINDADE, CR. and ESTEVES, FA., 2009. Seasonal Dynamics of Methane in The Water Column of Two Subtropical Lakes Differing in Trophic Status. *Braz. J. Biol.*, vol. 69, no. 2, p. 281-287.
- MOORE, TR. and DALVA, M., 1993. The influence of temperature and water table position on carbon dioxide and methane emissions from laboratory columns of peatland soils. *J. Soil Sci.*, vol. 44, no. 4, p. 651-664.
- NEUE, HU., WASSMANN, R., KLUDZE, HK., BUJUN, W. and LANTIN, RS., 1997. Factors and processes controlling methane emissions from rice fields. *Nutr. Cycl. Agroecosys.*, vol. 49, no. 1-3, p. 111-117.
- PRAIRIE, YT., BIRD, DF. and COLE, JJ., 2002. The Summer Metabolic Balance in the Epilimnion of Southeastern Quebec Lakes. *Limnol. Oceanogr.*, vol. 47, no. 1, p. 316-321.
- RICE, DD. and CLAYPOOL, GE., 1981. Generation, Accumulation, and Resource Potential of Biogenic Gas. *AAPG Bull.*, vol. 65, p. 5-25.
- RASK, H., SCHOENAU, J. and ANDERSON, D., 2002. Factors influencing methane flux from a boreal forest wetland in Saskatchewan, Canada. *Soil Biol. Biochem.*, vol. 34, no. 4, p. 435-443.
- RIBEIRO FILHO, RA., PETRERE JUNIOR, M., BENASSI, SF. and PEREIRA, JMA., 2011. Itaipu Reservoir Limnology: Eutrophication Degree and the Horizontal Distribution of its Limnological Variables. *Braz. J. Biol.*, vol. 71, no. 4, p. 889-902.
- ROSA, LP. and SCHAEFFER, R., 1994a. Greenhouse Gas Emissions from Hydroelectric Reservoirs. *Ambio*, vol. 23, p. 164-165.
- ROSA, LP., SANTOS, MA., MATVIENKO, B., SANTOS, EO. and SIKAR, E., 2004. Greenhouse Gas Emissions from Hydroelectric Reservoirs in Tropical Regions. *Climatic Change*, vol. 66, p. 9-21.
- RUDD, JWM., HARRIS R., KELLY, CA. and HECKY, RE., 1993. Are hydroelectric reservoirs significant sources of greenhouse gas? *Ambio*, vol. 22, p. 246-248.
- SANTOS, MA., ROSA, LP., MATVIENKO, B., SIKAR, E. and SANTOS, EO., 2006. Gross greenhouse gas fluxes from hydro-power reservoir compared to thermo-power plants. *Energ. Policy*, vol. 34, p. 481-488.
- SANTOS, MA., ROSA, LP., MATVIENKO, B., MADDOCK, JEL., PATHINEELAM, SR., SANTOS, EO. et al., 2011. *Monitoramento de Emissões de Gases de Efeito Estufa em Reservatórios de Usinas Hidrelétricas*. Relatório de Medições. Rio de Janeiro, 90p.
- SIKAR, E., SANTOS, MA., MATVIENKO, B., SILVA, MB., ROCHA, CHED., SANTOS, EO., BENTES, AP. and ROSA, LP., 2005. Greenhouse gases and initial findings on the carbon circulation in two reservoirs and their watersheds. *Verh. Internat. Verein Limnol.*, vol. 29, p. 573-576.
- ST LOUIS, VL., KELLY, CA., DUCHEMIN, E., RUDD, JWM. and ROSENBERG, DM., 2000. Reservoir Surfaces as Sources of Greenhouse Gases to the Atmosphere: A Global Estimate. *Bioscience*, vol. 50, p. 766-775.
- TREMBLAY, A. and SCHETAGNE, R., 2006. The Relationship between Water Quality and Greenhouse Gas Emissions in Reservoirs? *Int. J. Hydropower Dams*, vol. 13, p. 103-107.
- UNESCO/IHA GREENHOUSE GAS, 2009. *The UNESCO/IHA Measurement specification guidance for evaluating the GHG status of man-made freshwater reservoirs*, Document Track, Edition 1, 57p.
- TUNDISI, JG., MATSUMURA-TUNDISI, T. and ABE, DS., 2007. Climate Monitoring Before and During Limnological Studies: A Needed Integration. *Braz. J. Biol.*, vol. 67, no. 4, p.795-796.
- WANNIKHOF, R., 1992. Relationship between Wind Speed and Gas Exchange over the Ocean. *J. Geophys. Res.*, vol. 97, no. C5, p. 7373-7382.

- WEISSENBERGER, S., LUCOTTE, M., HOUEL, S., SOUMIS, N., DUCHEMIN, É. and CANUEL, R., 2010. Modeling the carbon dynamics of the La Grande hydroelectric complex in northern Quebec. *Ecol. Model.*, vol. 221, p. 610-620.
- WILKS, DS., 2006. *Statistical Methods in the Atmospheric Sciences*. 2nd ed. International Geophysics Series, vol. 91, Elsevier, Oxford, 627p.
- YAVITT, JB., LANG, GE. and WIEDER, RK., 1987. Control of carbon mineralization to CH₄ and CO₂ in anaerobic Sphagnum-derived peat from Big Run Bog, West Virginia, *Biogeochemistry*, vol. 4, no. 2, p. 141-157.