# Diffusive emission of methane and carbon dioxide from two hydropower reservoirs in Brazil

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Received: July 16, 2013 – Accepted: May 15, 2014 – Distributed: May 31, 2015 (With 4 figures)

### **Abstract**

The role of greenhouse gas emissions from freshwater reservoirs and their contribution to increase greenhouse gas concentrations in the atmosphere is currently under discussion in many parts of the world. We studied  $CO_2$  and  $CH_4$  diffusive fluxes from two large neotropical hydropower reservoirs with different climate conditions. We used floating closed-chambers to estimate diffusive fluxes of these gaseous species. Sampling campaigns showed that the reservoirs studied were sources of greenhouse gases to the atmosphere. In the Serra da Mesa Reservoir, the  $CH_4$  emissions ranged from 0.530 to 396.96 mg.m<sup>-2</sup>.d<sup>-1</sup> and  $CO_2$  emissions ranged from -1,738.33 to 11,166.61 mg.m<sup>-2</sup>.d<sup>-1</sup> and in Três Marias Reservoir the  $CH_4$  fluxes ranged 0.720 to 2,578.03 mg.m<sup>-2</sup>.d<sup>-1</sup> and  $CO_2$  emission ranged from -3,037.80 to 11,516.64 to mg.m<sup>-2</sup>.d<sup>-1</sup>. There were no statistically significant differences of  $CH_4$  fluxes between the reservoirs, but  $CO_2$  fluxes from the two reservoirs studied were significantly different. The  $CO_2$  emissions measured over the periods studied in Serra da Mesa showed some seasonality with distinctions between the wet and dry transition season. In Três Marias Reservoir the  $CO_2$  fluxes showed no seasonal variability. In both reservoirs,  $CH_4$  emissions showed a tendency to increase during the study periods but this was not statistically significant. These results contributed to increase knowledge about the magnitude of  $CO_2$  and  $CH_4$  emission in hydroelectric reservoirs, however due to natural variability of the data future sampling campaigns will be needed to better elucidate the seasonal influences on the fluxes of greenhouse gases.

Keywords: hydropower, dissolved organic carbon, greenhouse gas effect, lakes, reservoirs, CO, emissions.

# Emissões difusivas de metano e de dióxido de carbono oriundas de dois reservatórios hidrelétricos

# Resumo

Atualmente, em diversas partes do mundo, tem-se discutido muito sobre a contribuição das emissões de gases de efeito estufa oriundas de reservatórios hidrelétricos. Neste trabalho foram medidos fluxos difusivos de CO, e CH, em dois grandes reservatórios hidrelétricos neotropicais com diferentes condições climáticas (UHE Serra da Mesa e UHE Três Marias). Utilizamos câmaras flutuantes para estimar os fluxos difusivos de CO, e CH<sub>4</sub>. As campanhas de amostragem mostraram que os dois reservatórios estudados apresentaram-se como fontes emissoras de gases por mecanismo de difusão. No reservatório de Serra da Mesa as emissões de CH<sub>4</sub> variaram entre 0,530 e 396,96 mg.m<sup>-2</sup>.d<sup>-1</sup> e as emissões de CO, variaram entre -1.738,33 a 11.166,61 mg.m<sup>-2</sup>.d<sup>-1</sup>. No reservatório de Três Marias os fluxos de CH<sub>4</sub> variaram entre 0,720 e 2.578,03 mg.m<sup>-2</sup>.d<sup>-1</sup>. Já os fluxos de CO, variaram de -3.037,80 à 11.516,64 mg.m<sup>-2</sup>.d<sup>-1</sup>. Não houve diferença estatisticamente significativa dos fluxos de CH<sub>4</sub> entre os reservatórios estudados, entretanto os fluxos de CO, foram significativamente diferentes. As emissões de CO, medidas ao longo dos períodos estudados em Serra da Mesa mostrou certa sazonalidade, com distinções entre o período de transição seco e úmido. No reservatório de Três Marias os fluxos de CO, não apresentaram variabilidade sazonal. Em ambos os reservatórios, as emissões de CH<sub>4</sub> apresentaram aumento do fluxo ao longo dos períodos de estudo, mas isso não foi estatisticamente significativo. Estes resultados contribuíram para aumentar o conhecimento sobre a variabilidade das emissões difusivas de CO<sub>2</sub> e CH<sub>4</sub> em reservatórios de usinas hidrelétricas. Entretanto, novas campanhas de amostragem serão necessárias para melhor estudar as influências sazonais sobre os fluxos dos gases de efeito estufa.

Palavras-chave: hidrelétricas, carbono orgânico dissolvido, gases de efeito estufa, lagos, reservatórios, emissão de CO,.

# 1. Introduction

Methane ( $\mathrm{CH_4}$ ) is the most abundant organic gas in Earth's atmosphere and has an important role to tropospheric and stratospheric chemistry, affecting for example, tropospheric ozone, hydroxyl radicals and carbon monoxide concentrations, stratospheric chlorine and ozone chemistry and, through its infrared properties, Earth's energy balance (Cicerone and Oremland, 1988). Wuebbles and Hayhoe (2002) have estimated that up to 0.6 Gt of methane are emitted annually into the atmosphere; moreover about 75% of this is produced exclusively by strictly anaerobic methanogenic microorganisms present in anoxic environments (Segers, 1998; Whitman et al., 2006).

In the same way  $\mathrm{CO}_2$  plays an important role not only for atmospheric chemistry but also to the chemistry of the biosphere due to its availability as a carbon source for photosynthesis.  $\mathrm{CH}_4$  is the third most important greenhouse gas after water vapor and  $\mathrm{CO}_2$  and has a Global Warming Potential (GWP) 25 times greater than  $\mathrm{CO}_2$  on a 100 year timescale (IPCC, 2007). According Dlugokencky and Tans (2012) and IPCC (2007) global concentrations of  $\mathrm{CH}_4$  and  $\mathrm{CO}_2$  in the atmosphere were 1,775 ppb and 394 ppm while in pre-industrial era no more than 715 ppb and 280 ppm, respectively. This trend of increased concentration in the atmosphere is more and more linked to anthropogenic activities such as livestock, changes in land use and mainly energy use (IPCC, 2007).

Hydro power reservoirs as artificial aquatic systems represent an important part of the Earth's continental territory. They have an important role in the aquatic biogeochemistry and have also many effects on the environment. Recently another important negative impact of dam construction has been reported: emission of greenhouse gases generated by flooding organic matter during reservoir formation. Since the beginning of the 1990's several scientists have argued that hydropower reservoirs, as well as natural ecosystems, emit biogenic gases by bubbling and by molecular diffusion (Rudd et al., 1993; Bartlett and Harriss, 1993; Kelly et al., 1997; Hamilton et al., 1995; Abril et al., 2005).

Furthermore, several authors suggest that different environmental variables are related to greenhouse gas emission from a reservoir, such as input of carbon species by rivers and streams (Del Giorgio et al., 1999; Tranvik et al., 2009), meteorological factors (Striegl and Michmerhuizen, 1998; Cole and Caraco, 1998), and biological influences (Dumestre et al., 1999, 2002).

Knowledge of greenhouse gases emissions from hydroelectric reservoirs in Brazil becomes important since 83% of Brazilian electricity is produced by hydraulic sources (Brasil, 2012) and Brazil is the second largest producer of hydroelectricity, after China (IEA, 2012).

Research conducted by national and international teams has given successive contributions to the understanding of greenhouse gases emissions from Brazilian hydroelectric reservoirs (Rosa et al., 1994, 2003; Guerin et al., 2006; Santos et al., 2006; Roland et al., 2010).

This study presents the results of measurements of CH<sub>4</sub> and CO<sub>2</sub> diffusive emissions from two large hydroelectric reservoirs at in the Brazilian Cerrado, in an attempt to improve quantity and quality of data available.

### 1.1. Site location

The present study was carried out at the Serra da Mesa Reservoir (15° 50' 01,6" S 48° 18' 13,6" W), located in the Midwest region of Brazil in the Tocantins River – , Goiás State, and the Três Marias Reservoir (18° 12' 50,8" S 45° 15' 45,9" W) located in southeastern Brazil in the São Francisco River – Minas Gerais State, both in the Brazilian Cerrado Biome (central high plain bush country) (see Figure 1).

The Serra da Mesa Reservoir is 15 years old and is the largest by volume in Brazil with 54.4 billion m³, an average surface area of 1,784 km² and very important in the Brazilian energy scenario with 1,275 MW installed capacity. The Três Marias Reservoir has 396 MW installed capacity and 1,040 km² flooded area with 21 billion m³ volume and has been working since 1921.

Serra da Mesa is located approximately 580 km north of Três Marias. The climate in both reservoirs is classified as tropical seasonal dry winters. The average annual temperature is about 25 °C, however the monthly absolute maximum can reach 40 °C. The rains are concentrated in the period between October to March and may reach zero during the dry season which runs from May to August.

# 2. Experimental Methods

Four sampling campaigns were conducted for each reservoir in order to collect data covering all the hydrologic periods. Sampling sites was undertaken in Três Marias and Serra da Mesa in different seasons (Table 1).

In order to determine the  ${\rm CH_4}$  and  ${\rm CO_2}$  diffusive flux, a PVC chamber with a volume of 1000 mL and area of 0.047 m² was placed floating on the water surface. The method was described by Devol (1988, 1990) and Bartlett et al. (1988, 1990). All the samples were taken in vegetation-free areas both in the middle of reservoir and near the edges. One gas sample was taken from the chamber initially after 2, 4 and 8 minutes, counting from the initial moment when the chamber was placed on the water/air interface. A single sampling was used for each floating chamber point. The air samples inside the chambers (30mL) were collected by 60 mL polyethylene syringes and transferred to glass gasometric ampoules. All samples were taken between 9:00 and 17:00 h, local time.

 ${
m CH_4}$  and  ${
m CO_2}$  concentrations were determined in a field laboratory within 8 hours after collection, using a Varian CP-3800 chromatograph, with a thermal conductivity detector (TCD), FID (Flame Ionization Detector) and a PoraPLOT column. The chromatograph was calibrated using certified standards purchased from White Martins (Praxair). We use three calibration ranges for each gas: certified standard n. 2432/11 (1,98 mg/L for  ${
m CH_4}$  and 400 mg/L for  ${
m CO_2}$ ), certified standard n. 2440/11 (20,1 mg/L



Figure 1. Geographical locations of Serra da Mesa and Três Marias Reservoirs.

**Table 1.** Sampling sites of reservoirs studied.

Três Marias Reservoir	Serra da Mesa Reservoir
May, 2011 (48 sampling sites)	July, 2011 (46 sampling sites)
August, 2011 (47 sampling sites)	October, 2011 (42 sampling sites)
December, 2011 (46 sampling sites)	January, 2012 (37 sampling sites)
March, 2012 (45 sampling sites)	April, 2012 (37 sampling sites)

for  $CH_4$  and 602 mg/L for  $CO_2$ ) and certified standard n. 2442/11 (50,2 mg/L for  $CH_4$  and 998 mg/L for  $CO_2$ )

The rate of gas concentration increase within the chamber, and thus the diffusive flux, was determined by linear regression of concentration/time data sets (IEA, 2012). According to the IEA guidelines, fluxes were considered valid only when the regression coefficient (R<sup>2</sup>) was greater than 0.85 the root-mean-square error was less than 0.11 (IEA, 2012). The samples that not meet these requirements were discarded.

The Kruskal-Wallis test was used to verify possible differences in emissions between the two reservoirs and to check for differences among the sampling campaigns of each reservoir. "R statistic" software was used for statistical assessment (The R Foundation, 2012).

# 3. Results

Of 162 fluxes for each gas has measured at Serra da Mesa Reservoir, 5% of fluxes of  $CH_4$  and 9% of  $CO_2$  were discarded. Considering the whole sample period,  $CH_4$  emissions ranged from 0.530 to 396.96 mg.m<sup>-2</sup>.d<sup>-1</sup> and  $CO_2$  emissions ranged from -1,738.33 to 11,166.61mg.m<sup>-2</sup>.d<sup>-1</sup>.

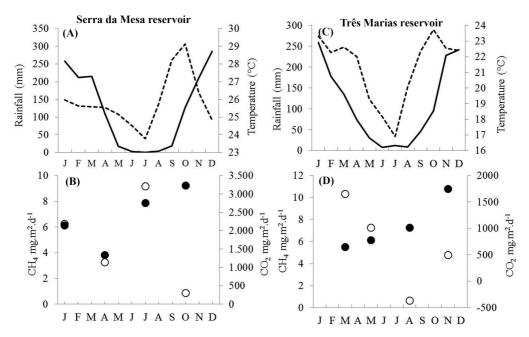
In Três Marias Reservoir we have measured 186 CH<sub>4</sub> fluxes for each gas, of which, 10% of fluxes of CH<sub>4</sub> and 13% of CO<sub>2</sub> were discarded. CH<sub>4</sub> emissions in Três Marias ranged from 0.720 to 2,578.03 mg.m<sup>-2</sup>.d<sup>-1</sup> and CO<sub>2</sub> emission ranged from –3,037.80 to 11,516.64 mg.m<sup>-2</sup>.d<sup>-1</sup>. The fluxes measurements from four field campaigns are shown in Table 2.

Figure 2 shows historical data series of the rainfall distribution 17 years (from 1975 to 1992 and 2011 to

**Table 2.** Median values of diffusive fluxes (mg.m<sup>2</sup>.d<sup>-1</sup>).

		CH <sub>4</sub> emission	Range	CO <sub>2</sub> emission	Range
Serra da Mesa	Jan/12	6.13(36)	3.82-10.88	2,185.41(32)	-1,542.51-9,526.49
Reservoir	Apr/11	3.83(37)	2.13-7.43	1,145.66(37)	-1,738.33-4,570,52
	Jul/11	7.87(42)	0.530-396.96	3,215.39(36)	870,82-11,166.61
	Out/11	9.22(39)	1.73-68.77	306,81(41)	-776,34-1,349.58
Três Marias	Mar/12	5.51(40)	1.53-172.53	1,655.21(35)	-3,037.80-11,516.64
Reservoir	May/11	6.12(43)	0.720-150.16	1,014.21 (44)	-721,29-7,860.39
	Aug/11	7.27(45)	0.890-2,578.03	-370.15 (39)	-873,46-9,776.49
	Nov/11	10.78(38)	2.73-85.81	497.62 (43)	-1,417.57-11,068.53

<sup>()</sup> The numbers in parentheses represent samples valid in each sampling campaign.



**Figure 2.** (A) and (B) refer to Serra da Mesa Reservoir while (C) and (D) Tres Marias Reservoir. In the horizontal axes are the months of the year. Solid lines represent monthly average rainfall and the lines segmented monthly average temperature. The blacks circles represent the medians of  $CH_4$  emissions and the open circles the median of  $CO_2$  emissions.

2012 of Três Marias and from 1994 to 2012 of Serra da Mesa) (ANA, 2013) and other series of 7 years (2004 to 2010 in both reservoirs) for temperature (INMET, 2013) in regions of the reservoirs as well as the median emission measurements. And as shown in Figure 3 we can see the median values and the outliers of CH<sub>4</sub> emissions in both reservoirs. The use of median results as robust description of gas fluxes and comparison of others central tendency statistical descriptors can be read in (Damazio et al., 2013).

In this current study we have made comparisons of measured fluxes among the period studied. Regarding the comparison of CH<sub>4</sub> fluxes, statistically significant distinctions between the periods studied were not found in Três Marias Reservoir (see Table 3).

We can say the same thing for the comparisons of CH<sub>4</sub> fluxes among sampling campaigns in the Serra da Mesa Reservoir. An exception was observed in the fluxes

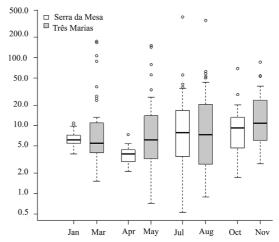


Figure 3. Box plot showing median CH<sub>4</sub> emissions from the sampling campaigns in the two reservoirs studied.

measured in April, which was particularly lower than in other periods (see Table 4).

The Figure 4 suggest a certain seasonality of  $\mathrm{CO}_2$  emission in the Serra da Mesa Reservoir', due to differences among the fluxes from rainy-transition (January vs. April and October) and dry-transition (April vs July and October). Furthermore, emissions measured in transition months are different between themselves (April vs. October). (see Table 5).

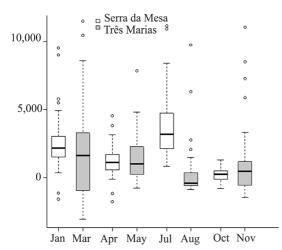
The Três Marias Reservoir showed no seasonality with regards to CO<sub>2</sub> emission, since we found no statistically significant difference, except for the emissions measured in May and August (see Table 6).

## 4. Discussion

In 1998 and 1999, Santos et al. (2006) measured diffusive emission at Serra da Mesa (range from -6,048 to 10,178 mg.m<sup>-2</sup>.d<sup>-1</sup> to CH<sub>4</sub> and -5,360 to 5,903 mg.m<sup>-2</sup>.d<sup>-1</sup> to CO<sub>2</sub>) and Três Marias Reservoir (range from 0.660 to 241 mg.m<sup>-2</sup>.d<sup>-1</sup> to CH<sub>4</sub> and -10,060 to 7,346 mg.m<sup>-2</sup>.d<sup>-1</sup> to CO<sub>2</sub>). Thus, the highest emissions that we found in the present study were higher than those found by Santos et al. (2006) in the previous study, with the exception of CH<sub>4</sub> emissions in Serra da Mesa, which in this study had lower values.

The emissions peak in the first years after filling a reservoir tends to decrease and to stabilize over the subsequent years. In older reservoirs (over 10 years) in boreal and temperate regions, emissions of greenhouse gases are similar to natural lakes. However, in the tropics, the time to return to natural values may be longer, depending on the water quality (Tremblay et al., 2005). We suggest that both the natural variations and external anthropogenic factors, such as the organic material supply, are contributing to maintain high value in the Serra da Mesa Reservoir and Três Marias Reservoir, even 13 years after these early studies (Santos et al., 2009; Fonseca, 2010; Chandrasekera, 2000).

The results shown in Figure 2 suggest that there is a general trend of increase in median values of CH<sub>4</sub> emissions



**Figure 4.** Box plot showing CO<sub>2</sub> emissions along the sampling campaigns in the two reservoirs studied.

in both reservoirs throughout the year, recording the lowest in April and highest in October despite being in the same hydrologic period and confirmed by the statistically significant differences in the flow of CH<sub>4</sub>. However in Três Marias Reservoir, the lowest value was recorded in March (end of the rainy season and very close to the rainy-dry transition season) and the highest in November (beginning of the rainy season and the end of the period of dry-rainy transition). We suggest that this trend of emissions are somehow related to transitional periods due to changes in the pattern of temperature and rainfall.

When we compare the  $\mathrm{CH_4}$  emission shown in Figure 3, considering the significance level of <0.05, we found no statistically significant difference between the two reservoirs studied (Kruskal-Wallis chi-squared = 3.8217, df = 1, p-value = 0.0509). However, this value was considered borderline for the test, since the observed value of the test statistic is slightly smaller than the critical value and this must be exceeded to be considered a statistically significant difference (SMR-TMR Difference observed = 20.4066 critical difference = 20.45932 Result = There are difference). On the other hand the  $\mathrm{CO_2}$  fluxes between the reservoirs studied showed statistically significant differences (Kruskal-Wallis chi-squared = 21.7085, df = 1, p-value

**Table 3.** Results of comparisons of CH<sub>4</sub> fluxes between the sampling campaigns conducted in Três Marias Reservoir. P-value 0.06.

Três Marias Reservoir - Kruskal-Wallis multiple comparison test

comparison test				
Period	Difference observed	critical difference	Result	
Aug-Marc	1.288889	27.53579	No difference	
Aug-May	6.317829	27.85413	No difference	
Aug-Nov	21.425439	28.77596	No difference	
Mar-May	5.02894	27.85413	No difference	
Mar-Nov	22.714327	28.77596	No difference	
May-Nov	27.743268	29.08073	No difference	

**Table 4.** Results of comparisons of  ${\rm CH_4}$  fluxes among the sampling campaigns in the Serra da Mesa Reservoir. P-value < 0.05.

Kruskal-Wallis multiple comparison test to CH <sub>4</sub>
emission fromSerra da Mesa Reservoir

Period	Difference observed	critical difference	Result
Apr-Jan	45.507132	27.54622	There are difference
Apr-Jul	52.398005	26.53021	There are difference
Apr-Oct	56.525295	27.00389	There are difference
Jan-Jul	6.890873	26.72540	No difference
Jan-Oct	11.018162	27.19567	No difference
Jul-Oct	4.127289	26.16606	No difference

**Table 5.** Comparison of  $CO_2$  emissions among sampling campaigns from Serra da Mesa Reservoir. p-value < 0.05.

Kruskal-Wallis multiple comparison test to CO, emissions from Serra da Mesa Reservoir

Period	Difference observed	critical difference	Result
Apr-Jan	28.74662	26.9345	There are differences
Apr-Jul	49.26051	26.11987	There are differences
Apr-Oct	33.20765	25.29974	There are differences
Jan-Jul	20.51389	27.10752	No difference
Jan-Oct	61.95427	26.31820	There are differences
Jul-Oct	82.46816	25.48378	There are differences

**Table 6.** Comparison of CO<sub>2</sub> emissions among sampling campaigns from Três Marias Reservoir. P-value < 0.05.

# Kruskal-Wallis multiple comparison test to CO<sub>2</sub> emissions from Três Marias Reservoir

Period	Difference observed	critical difference	Result
Aug-Mar	18.08718	28.63825	No difference
Aug-May	34.28263	27.05063	There are
			differences
Aug-Nov	11.92904	27.19802	No difference
Mar-May	16.19545	27.85801	No difference
Mar-Nov	6.15814	28.00116	No difference
May-Nov	22.35359	26.37522	No difference

= 3.17-6) possibly due to the median values obtained in the months of August in Três Marias Reservoir and July in Serra da Mesa reservoir (Table 2).

Greenhouse gases fluxes from both hydroelectric reservoirs and natural lakes showed great variability in their values. For example, Galy-Lacaux et al. (1997) measured CH<sub>4</sub> diffusive fluxes in Petit Saut (French Guiana) that ranged from 120 to 3.230 mg.m<sup>-2</sup>.d<sup>-1</sup>; Roehm and Tremblay (2006), measured CO<sub>2</sub> fluxes two large dams in Canada (La Grande 2 and La Grande 3) with ranges between 80 and 1,800 mg.m<sup>-2</sup>.d<sup>-1</sup> and 400 and 1,500 mg.m<sup>-2</sup>.d<sup>-1</sup>; Therrien et al. (2005) measured CO<sub>2</sub> flux in Arizona – USA that ranged between –1,116 and 3,104mg.m<sup>-2</sup>.d<sup>-1</sup> and Duchemim et al. (2001) measured CH<sub>4</sub> fluxes in the range 12 to 65 mg.m<sup>-2</sup>.d<sup>-1</sup> in an old reservoir in the Amazon region, Brazil.

In the present study, the  $\rm CO_2$  fluxes measured in January (rainy season) and July (dry season) in Serra Mesa Reservoir (as shown in Figure 4) proved to be indistinguishable from each other, but they are different when compared to April and October which are transition months from wet to dry and from dry to wet season, respectively. Moreover, the

CO<sub>2</sub> emission measured in April and October also showed differences between themselves. We attribute this large natural range of data as well as specific characteristics of each study period, for example, by the fact that it rains more in October than in April, even though these two months are in transition periods.

Thus, we believe that this natural variability of the phenomenon of gas emissions in the air-water interface contributes to find results that are discordant at first glance, like an apparent lack of seasonality of  $\mathrm{CH_4}$  emission in both reservoirs, even though they almost doubled over the months analyzed. Also relevant was the fact that the Serra da Mesa reservoir and the Três Marias Resevoir showed negative  $\mathrm{CO_2}$  emissions by 3 of the 4 campaigns in Serra da Mesa and all periods in Três Marias (Table 2). This fact is linked to the intense metabolism of  $\mathrm{CO_2}$  convert it to organic matter by photosynthetic organisms and thus they influence the chemical gradient of  $\mathrm{CO_2}$  in the air-water interface.

# 5. Conclusion

We concluded that the CH<sub>4</sub> fluxes were statistically indistinguishable in all analyzed hydrological periods, although the median have increased over the periods studied in both reservoirs. However during the month of April, which is a transition period in Serra da Mesa, fluxes were shown to be distinct from other periods studied, suggesting that there may be some component in this period that somehow influences the changes in CO<sub>2</sub> emissions standards.

Corroborating with this idea, the CO<sub>2</sub> fluxes measured in Serra da Mesa reservoir were distinct when comparing the periods of transition versus rainy and dry periods. We believe that perhaps this is due to seasonal influences changes in rainfall and temperatures.

Finally, the hydropower reservoirs are emitters or absorbers of carbon as CO<sub>2</sub>, which may in the long term balance the positive emissions beginning of the filling period. We believe that further measurements in greenhouse gas emissions are needed in order to better understand the variability of emissions.

In addition, other factors must be better analyzed as the input of different carbon fractions and their concentrations in the lake, the influence of meteorological factors, the human interventions such as land use basin which can exert influence and contribution with this allocthonus organic matter on greenhouse gases emissions.

# Acknowledgements

CHESF, which financed this research study through the Project Greenhouse Gas Emission Monitoring from for Hydropower Reservoirs and the National Council for Scientific and Technological Development (CNPq) for awarding a doctoral study grant to the first author of this paper. We thank the National Council for Scientific and Technological Development (CNPq) for the research

productivity grant awarded to the second author of this paper. We thank the National Science and Technology Institute (INCT – Climate Change – Emissions from Lakes and Reservoirs Sub-Project) for awarding a grant to the fifth and sixth authors of this paper. We thank Dr. John Edmund Lewis Maddock for his important discussion on this paper.

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