

# Comparison of measurements of diffusive methane fluxes and stagnant film model flux estimate on the Manso Reservoir, Mato Grosso, Brazil

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## Abstract

This work presents the methane fluxes and the used methodology in the reservoir hydroelectric power plant of (Matogrosso, Brazil) Manso were presented. Measurements of water dissolved methane (DM) in three different depths (subsuperficial, middle and near the sediments) were also made. These measurements show that the primary production of methane occurs mainly on the sediments, and the consumption on water column is important to the emission balance. The diffusive methane flux was also estimated with the stagnant film model from the DM measured on the sub superficial water. The results were compared with the measured diffusive fluxes and shows that this model gives a good first estimative and that the water turbulence and wind have an important role on the methane emission from water bodies.

# Introduction

Methane (CH<sub>4</sub>) is the most abundant hydrocarbon on atmosphere and like carbon dioxide (CO<sub>2</sub>) is an important greenhouse gas (*Seinfeld and Pandis, 1998, Ramanathan et al., 1985*). Beside this, methane have a key role on atmospheric chemistry, acting on the tropospheric OH and on the stratospheric cycles of ozone and chlorine (*Wuebbles and Hayhoe, 2002*).

The majority of atmospheric CH<sub>4</sub> is produced microbially under anaerobic conditions in such diverse environments as ruminants and termites, agricultural wetlands and a variety of natural wetlands (*Bartlett et al., 1988, Devol et al., 1988, Bartlett et al., 1990., Webbles and Hayhoe, 2002, Marani and Alvalá, 2007*).

Large dams, particularly that located in tropical areas, may constitute a considerable source of methane to the atmosphere due to the anaerobic decomposition of the original flooded vegetation (*Ramos et al., 2006, Bambace et al., 2007*). The reservoirs have an important role in the development of several nations, being responsible for drinking water supplies, river flood/drought control, irrigation and hydroelectric power generation (*Lima et al., 2007*). The reservoir of the Hydroelectric Power Plant of Manso ( $14^{9}50$ 'S;  $55^{9}45$ 'W), is located on the Mato Grosso state, Brazil, on the basin of Manso River, one of the main tributary of Cuiaba River (Figure 01). Located in a Savanna biome, Manso has a superficial area of 427 km<sup>2</sup> and 60 m of maximum depth (20 m of average depth). The annual mean temperature is 26°C. Total precipitation averages 1750 mm, concentrated during the Austral summer (wet season) (*Assireu et al, 2009*).

This work presents measurements of methane flux and water dissolved methane on the Manso reservoir during the summer of 2008. The diffusive flux was compared with estimates made with a stagnant film model and the dissolved methane measured on the subsuperficial water.

## Method

Methane fluxes were determined using the static chamber technique, described by Devol et al. (1988), Bartlett et al. (1988) and Marani and Alvalá (2007). The chambers, covered with a thermal and reflective sheet to avoid temperature variations, have an area of  $0.066 \text{ m}^2$  and a volume of 26 l. Every 5 minutes, during 15 minutes, gas samples were removed through a septum with a 60-ml polyethylene syringe equipped with a 3-way polypropylene stopcock.

Methane dissolved in water was determined by the headspace technique: 30 cm<sup>3</sup> of water were collected with a 60 cm<sup>3</sup> syringe immediately below the water surface (subsuperficial) or with a depth-selective sampler (Van Dorn bottle) at greater depths, and then the dissolved methane was stripped from the water with ambient air (loffe and Vitenberg, 1984).

The methane concentration of all samples were determined with a commercial gas chromatograph (Shimadzu, GC-14A), equipped with a flame ionization detector (FID), a 2.2 ml sample loop and two stainless steel columns that were optimized to perform methane analyses in the Ozone Laboratory at INPE, São José dos Campos, Brazil. The first column was packed with silica gel (2.5-m long and 1/8" diameter) and it was used to remove the water vapor, CO2 and other heavy organic compounds from the samples, in order to reduce the total retention time. The analysis column (3.0-m long and 1/8" diameter) was packed with a zeolite 5 Å molecular sieve. The methane standard (1749.4 ± 4.5 ppbv) used for calibration was acquired from the Climate Monitoring and Diagnostic Laboratory of the National Oceanic and Atmospheric Administration (CMDL/NOAA).



Figure 1. Study area with the sample points of 2008, March. The red points are sites were methane absorption was observed. The blue points represent the diffusive fluxes and the yellow point shows the ebullitive flux.

The CH<sub>4</sub> flux was determined from the temporal variation of its mixing ratio inside the chamber during the sampling time, following Schiller and Hastie (1994). The CH<sub>4</sub> fluxes were considered diffusive if the linear correlation between the mixing ratio change and the elapsed time had  $r^2$ greater than 0.90 (Sass et al., 1992, Marani and Alvalá, 2007). A second criterion was that the initial concentration obtained by the linear regression (at time t=0) must be close to the measured environmental air concentration. The fluxes that did not follow the first criterion above, but whose first point was near the ambient air concentration were taken as bubble fluxes.

On a diffusive flux, the methane produced on the sediments spreads gradually through the water column until it reaches the water-atmosphere interface and is emitted to atmosphere. This occurs with a near constant flux. On an ebullitive flux, the methane accumulates on the sediments and the bubbles are released when a variation on the hydrostatic pressure occurs. The methane emitted on this way reaches the atmosphere almost instantaneously and was not oxidized in the water column. The ebullitive flux is sporadic, but the amounts of methane released to the atmosphere are usually higher that in the diffusive way

Diffusive gas exchange between the water and the atmosphere can be estimated from dissolved gas concentrations using the stagnant film model (Lewis and Whitman, 1924; Liss and Slater, 1974; Barber et al., 1988; Hamilton et al., 1995). To do this, we have considered a very slow water flow with minimal water surface perturbations. Under these considerations, a boundary layer of 300  $\mu$ m can be used (Hamilton et al., 1995). This boundary layer corresponds to estimates for quiet waters in which gas exchange has been measured by several techniques (Barber et al., 1988). The coefficient of diffusivity adopted for Manso was  $3.0 \times 10^{-9}$  m<sup>2</sup>/s, for a water temperature of  $30^{\circ}$ C (Wise et al., 1966).

# Results

The sample campaign in Manso occurred during 2008, March (01 to 08). We obtained 12 valid fluxes (1 ebullitive, 3 absorption and 8 diffusive fluxes), The diffusive fluxes ranges from -4.3 to 9.5 mgCH<sub>4</sub>m<sup>-2</sup>d<sup>-1</sup>, with an average of 1.3 mgCH<sub>4</sub>m<sup>-2</sup>d<sup>-1</sup>. The ebullitive flux was higher, reaching 1440.2 mgCH<sub>4</sub>m<sup>-2</sup>d<sup>-1</sup>.

The water column profile shows that the dissolved methane is higher near the sediments and decrease along the column, as shown in Figure 02. As the production of methane is located in the sediments, and during the diffusive transport to the atmosphere, the methane is oxidized by methanetrophic bacteria. So a decrease in the concentration was observed in the water column.

There is a good correlation between the subsuperficial dissolved methane and the measured fluxes ( $R^2 = 0.98$ ). The ebullitive flux occured where the dissolved methane were higher. Correlation between diffusive fluxes and the dissolved methane near the sediment are not observed ( $R^2 = -0.15$ ), and this indicates that processes of oxidation of methane in water column are important to the methane emission. Table 01 presents the measured and estimate by model fluxes and also the dissolved methane in all sample sites.



Figure 2. Average of the dissolved methane (mg/l) along the water column.

| Data     | Time  | Depth. | Measured Flux                           | Model Flux    | Dissolved Methane (x10 <sup>-3</sup> mg/l) |        |          |
|----------|-------|--------|---|---------------|--|--------|----------|
|          | (LT)  | (m)    | (mgCH₄m <sup>-2</sup> d <sup>-1</sup> ) | (mgCH₄m⁻²d⁻¹) | Sub sup.                                   | Middle | Sediment |
| 2/3/2008 | 07:50 | 20     | -3.0                                    | -             | 0.74                                       | 0.98   | 3.74     |
| 2/3/2008 | 09:00 | 21     | 1.5                                     | 1.5           | 1.75                                       | 6.46   | 0.99     |
| 2/3/2008 | 10:25 | 23     | 1.9                                     | 0.5           | 0.54                                       | 0.87   | 1.12     |
| 2/3/2008 | 12:20 | 23     | -2.9                                    | -             | 1.27                                       | 0.80   | 3.21     |
| 3/3/2008 | 15:25 | 27     | 1.1                                     | 1,6           | 1.89                                       | -      | -        |
| 3/3/2008 | 16:35 | 17     | -4.3                                    | -             | -  | -      | -        |
| 4/3/2008 | 11:25 | 10     | 1440.2                                  | -             | 30.20                                      | -      | -        |
| 4/3/2008 | 16:40 | 17     | 4.6                                     | 1.2           | 1.39                                       | -      | -        |
| 4/3/2008 | 17:30 | 45     | 2.8                                     | 0.8           | 0.96                                       | 15.32  | 1795.98  |
| 5/3/2008 | 11:00 | 19     | 0.9                                     | 1.9           | 2.30                                       | 0.66   | 210.04   |
| 5/3/2008 | 11:45 | 23     | 9.5                                     | 4.0           | 4.65                                       | 30.15  | 6.35     |
| 5/3/2008 | 12:20 | 17     | 2.0                                     | 1.7           | 1.96                                       | 2.15   | 14.98    |

 TABLE 1. FLUXES MEASUREMENTS AND MODEL ESTIMATES FOR MANSO RESERVOIR. DISSOLVED METHANE IN THREE WATER DEPTHS (SUB

 SUPERFICIAL, MIDDLE AND NEAR SEDIMENTS), THE SITE WATER DEPTH AND TIME OF MEASUREMENT ARE ALSO PRESENTED.

The estimate of the methane fluxes using the subsuperficial dissolved methane (average 1.5  $\pm$  1.0 mgCH<sub>4</sub>m<sup>-2</sup>d<sup>-1</sup>; median: 1.4 mgCH<sub>4</sub>m<sup>-2</sup>d<sup>-1</sup>) were compared to the measured positive diffusive fluxes (average: 3.0  $\pm$ 2.8 mgCH<sub>4</sub>m<sup>-2</sup>d<sup>-1</sup>; median: 1.9 mgCH<sub>4</sub>m<sup>-2</sup>d<sup>-1</sup>). The measured fluxes were about twice the estimated fluxes, showing that the presence of wind and water turbulence act to increase the flux.

# Conclusions

The flux measurements and the water column dissolved methane profile show that the mainly production of methane in the Manso reservoir occur in the sediments, and that processes of methane consumption on the water column are significant. These processes, together with the stratification of the water column, are determinant of the final emission of methane, and could result in absorption of methane from the atmosphere by the water body in some points. The ebullitive flux was not subject of the majority of these processes, and the resultant methane emission by the ebullition way could be significant.

The comparison between the measured diffusive fluxes and the flux estimates by stagnant film model shows that this model gives a good first approximation to the methane emission. The average measured flux was about twice that was estimated by the model. This can be explained by the presence of water turbulence, waves and wind, which was not considered on this simple model.

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