



## Methane emissions from lakes in Pantanal – Methodology and preliminaries results

Luciano Marani<sup>1</sup> e Plínio C. Alvalá, Instituto Nacional de Pesquisas Espaciais (INPE)

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### Abstract

The methodology and the preliminaries results of a study to evaluate the methane (CH<sub>4</sub>) emissions from lakes and floodplains in Pantanal are presented. The sample sites are chosen to represent different environmental characteristics on the region. The methane fluxes are obtained by the technique of static chamber. The work had begun in 2004 and extends for 2005, with sampling campaigns every 3-month (March, June, September and December of each year). The preliminaries results obtained during 2004 (March, June and September) shows a overall average flux of  $79.3 \pm 227.1 \text{ mgCH}_4 \text{ m}^{-2} \text{ d}^{-1}$ , ranged -8.7 to 1983.1  $\text{mgCH}_4 \text{ m}^{-2} \text{ d}^{-1}$  and also indicates that methane fluxes are influenced by the water depth and by the presence of aquatic vegetation. The fluxes could be divided in terms of the way of methane transport through the water column in diffusive and bubble fluxes, and each one are influenced by water depth and vegetation in different ways.

### Introduction

Methane (CH<sub>4</sub>) has an important role in the atmosphere chemistry, been one of the major sinks to OH radical and plays a role in the atmospheric cycles of O<sub>2</sub> and Cl, and in radiation transfer (Ramanathan *et al.*, 1985), with a relative contribution of almost 15% of all greenhouse effect observed in the past two decades (Krupa, 1997).

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.*, 1885, Bartlett *et al.*, 1988, Devol *et al.*, 1988, Bartlett *et al.*, 1990; Wuebbles and Hayhoe, 2002).

Since the beginning of the industrial age, the CH<sub>4</sub> atmospheric mixing ratios was increased by 2.5, and reach 1750 ppbv (parts per billion by volume) in 2001, and the continuous monitoring in past two decades showed that the mixing ratio has increase with no interruption (CMDL, 2002; Wuebbles and Hayhoe, 2002). Over this trend, there are considerable interannual variations. The continuous trend of increase in the CH<sub>4</sub> mixing ratios may be due to the human activities, while the interannual variation must have a considerable contribution of the wetlands (Walter *et al.*, 2001).

In flooded freshwater, such as those of riverine floodplains, the decomposition by methanogenic bacteria can result in significant emissions of CH<sub>4</sub> to the atmosphere. Estimates assessing the global distribution of wetlands and using published wetlands emission rates calculate the wetland methane source at approximately 100 Tg/yr ( $100 \times 10^{12}$  grams per year), or about 25% of the global biogenic source (Wuebbles e Hayhoe, 2002)

Calculations of the magnitude of the global wetlands contribution to atmosphere methane are difficult due to the temporal and spatial variability of sources. Emissions are influenced by a wide array of site-specific environmental factors and change on time scales varying from diurnal through seasonal (Bartlett *et al.*, 1988; Devol *et al.*, 1988; Bartlett *et al.*, 1990). The extrapolation of this variability to global-scale emissions requires extensive field measurements on the appropriate scale. Such data are available for only a limited number of environments. There are some works in tropical, mainly in the Amazonian Floodplain ((Bartlett *et al.*, 1885, Bartlett *et al.*, 1988, Devol *et al.*, 1988, Bartlett *et al.*, 1990), while in others tropical wetlands, like Pantanal, there are few works.

Pantanal is one of the most important wetland region in Brazil. It's a tropical ecosystem consisting of a savanna kind environment which is flooded seasonally. The flood in this region shows a clear seasonal cycle, with the maximum flooded area in December. Alvalá and Kirchhoff (2000) showed the existence of a seasonal pattern in the CH<sub>4</sub> flux from measurements performed in a lake near Miranda River.

In this work, we present the methodology used to obtain CH<sub>4</sub> flux, and the first observation results of CH<sub>4</sub> emission in various lakes at the region of the *Pantanal Sul-Matogrossense*. This will be an attempt to increase the tropical wetland data set, and so increasing the accuracy of the estimative of methane emission in the tropical wetland regions.

### Methodology

#### Site Location

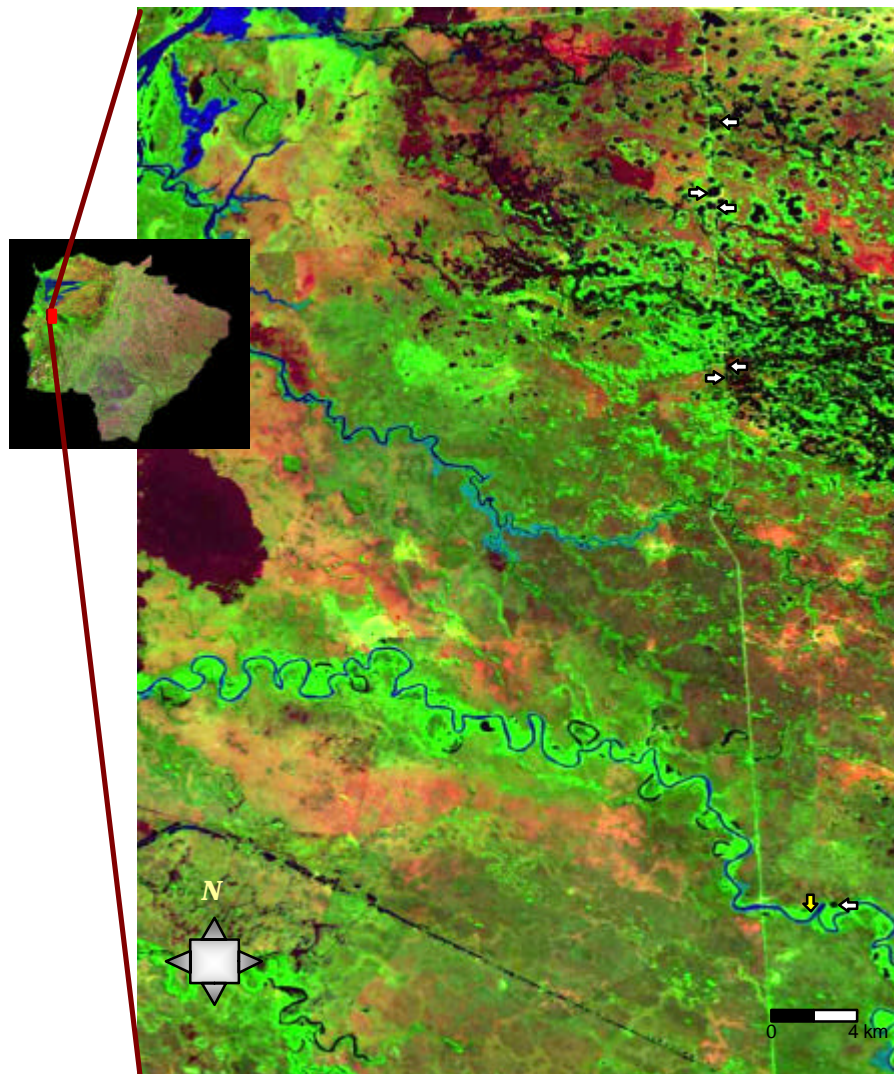
The Pantanal is a complex plain, flooded by Paraguay River and his tributaries, in a large sedimentary basin, with altitudes varying between 80 to 120 meters. The Pantanal area is estimate in 138,183 km<sup>2</sup>, in Brazil, with small areas in Paraguay and Bolivia. The Paraguay River and its tributaries flood the region seasonally, bringing organic material which is spread during the flood stage become the most important source of nutrients to the methanogenic bacteria primary methane production.

The total area under inundation conditions, including floodplain, lakes, rivers and canals, that link lakes and

river, was estimated by *Hamilton et al.* (2002) in 130,920 km<sup>2</sup>, and is the major floodplain in South America. Between 1979 and 1987, the largest flooded area was estimated in 109,920 km<sup>2</sup>, with open areas (lakes and rivers) representing 3,120 km<sup>2</sup>. The average flooded area in this period was 52,710 km<sup>2</sup>, with an observed variability of 46%. *Hamilton et al.* (2002), using a data set of Paraguay River level on the period of 1900 and 1999, estimated an average flooded area of 34,880 km<sup>2</sup>. Normally, the period that a half of the maximum-flooded area stay flooded is of 172 days, and there are a lag between the rain cycle and the flood stage, due the slow

flow of the water through of the Pantanal plain. The minimum in the flooded area occur in September, and his maximum, in December.

Methane flux measurements were made at a series of sites along a vicinal road at the vicinity of the Base de Estudos do Pantanal (BEP), a logistic support facility from Universidade Federal do Matogrosso do Sul (UFMS), in Matogrosso do Sul State, Brazil (19°34'S; 57°01'W). The sampling sites used in this work cover a distance of approximately 30 km and are show in Figure 1.



**Figure 1.** Localization of the sampling sites (white arrows) and BEP (yellow arrow).  
Source: Miranda e Coutinho (2005).

#### Flux measurements

Methane emissions were measured by the technique of static chamber, placed over the water or vegetated surfaces, such as used by *Devol et al.* (1988) and *Bartlett et al.* (1990). The flux measurements were made by taking periodic samples from the chamber using a syringe.

In this work, a chamber with a volume of 26 liters covered with a thermal and reflective sheet to avoid temperature variations was used. The samples were taken from the chamber every 6 minutes, over an 18 minutes measurement period, in 60-ml polyethylene syringes, equipped with a 3-way polypropylene stopcock. In some fluxes, a sample was taken in the first minute after the

chamber was placed. Inside the chamber, a little fan was installed, to break any air stratification.

The chambers were placed in the sampling point using a boat. We take care to avoid perturbations in water surface and surrounded vegetation. All samples were taken between 11:00 and 16:00 hours (local time).

The variables that can affect the methane emissions, such as water depth, water and air temperature, pH and vegetation inside chamber were taken and will be used with the fluxes results to study their relationships.

All samples taken in the site were carried to the Laboratório de Ozônio, at INPE, São José dos Campos, Brazil, where were analyzed with gas chromatography (GC) technique. A commercial chromatograph (Shimadzu, GC-14A) was optimized to methane analyses using two columns. The first column (2.5-m long and a diameter of 1/8 inch), filled with silica gel, was used to remove the sample water vapor, CO<sub>2</sub> and others heavy organics compounds reducing the total retention time. The analyses column (3,0-m long and diameter of 1/8 inch) was fill with molecular sieve (5Å), followed by a flame ionization detector (FID).

#### Flux Determination and Validation

The determination of the methane flux was made from the temporal variation of your mixing ratio inside the chamber during the sampling interval.

The methane emissions in a floodplain can be due to diffusive transport and due CH<sub>4</sub> bubbles (Bartlett et al., 1990). Diffusive transport represents a linear increase in the chamber mixing ratios. Always that an intense increase in mixing ratios was observed the measurement was classified like a bubble flux.

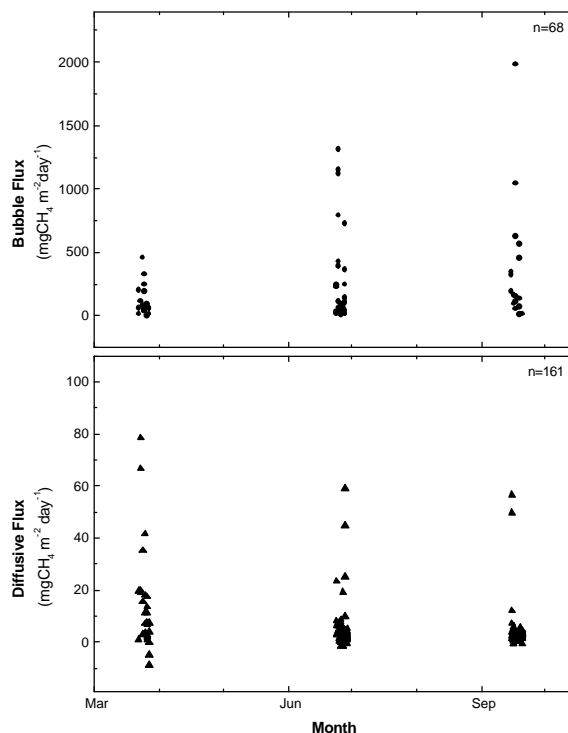
To the flux classified as diffusive, the temporal variation of methane mixing ratio was taken from the angular coefficient of the linear regression. The linear regression also gives two criteria to the validation of a diffusive flux, described by *Khalil et al.* (1998b): the regression linear coefficient (*R*) and the initial mixing ratio *C*<sub>0</sub> (*t*=0 min in the linear regression). In this work, a flux was considered diffusive when *R*<sup>2</sup> was equal or greater that 0.95. Besides, the flux is valid only with *C*<sub>0</sub> is near the ambient air mixing ratio obtained over the lake. If *R*<sup>2</sup> is small that 0.95 and the initial mixing ratio measure is around the ambient mixing ratio and there is no other perturbation, the flux is taken was a bubble flux, and so is determinate by the average variation of the mixing ratio in the measurement time interval.

#### Results and Discussion

From three sampling campaigns, 229 valid methane flux measurements were obtained. Fluxes ranged from -8.7 to 1983.1 mgCH<sub>4</sub> m<sup>-2</sup>d<sup>-1</sup>, a range similar to that reported in Amazon River Floodplain by *Bartlett et al.* (1990). The overall average was 79.3 ± 227.1 mgCH<sub>4</sub> m<sup>-2</sup>d<sup>-1</sup>. The

individual CH<sub>4</sub> flux measurements, separated between diffusive and bubble fluxes are presented in Figure 2.

Figure 2 shows that the diffusive flux and their spread decrease from March to September. This agrees with the seasonal variation of the inundation in this region, which the minimum occur in September and the maximum in December. Differently, the bubbles fluxes had higher values that the observed in the diffusive fluxes in the three campaigns.



**Figure 02.** Individual methane flux measurements in March, June and September. The fluxes were separated in diffusive and bubbles.

The average diffusive and bubble fluxes for each campaign in 2004 (March, June and September) are presented in Table 1, that also shows the number of fluxes measurements and the averages for water depth, air and water temperatures and the average flux for all campaigns.

For individual campaigns, the average diffusive flux showed a decrease from March to September, while the average bubble flux showed an increase. The magnitude and the spread of the bubble fluxes were higher in September, reflecting the fact that the water depth could be an important factor in determination of the kind of methane transport from the substrate to the water surface.

TABLE 1. AVERAGES FOR FLUX, WATER DEPTH, WATER TEMPERATURE AND AIR TEMPERATURE.

	DIFFUSIVE TRANSPORT				BUBBLE TRANSPORT			
	March	June	September	All	March	June	September	All
# of Measurements	28	65	68	161	18	33	17	68
Flux (mgCH <sub>4</sub> m <sup>-2</sup> d <sup>-1</sup> )	14.4 ± 19.8	5.4 ± 9.8	4.4 ± 8.8	6.5 ± 12.2	118.7 ± 121.9	261.1 ± 358.2	373.1 ± 496.2	251.4 ± 363.8
Water Depth (m)	1.18 ± 0.57	1.07 ± 1.08	0.78 ± 0.35	1.17 ± 0.84	1.07 ± 0.40	0.71 ± 0.55	0.52 ± 0.30	0.76 ± 0.50
Water Temp. (°C)	31.5 ± 2.7	24.9 ± 2.2	23.8 ± 1.6	25.6 ± 3.4	31.3 ± 2.6	26.6 ± 1.7	23.8 ± 1.2	30.2 ± 3.1
Air Temp. (°C)	32.5 ± 2.1	29.5 ± 2.4	31.7 ± 3.8	31.0 ± 3.3	32.8 ± 2.3	29.9 ± 2.9	30.8 ± 3.3	27.6 ± 3.8

The Figure 3, present the bubble and diffusive fluxes as a function of the water depth. The higher fluxes occur at small water depth in both cases. But to diffusive flux, they were more spread, and a greater number of them occur in deeper points, while the bubble fluxes were concentrated in shallow waters, with depth less 1 meter.

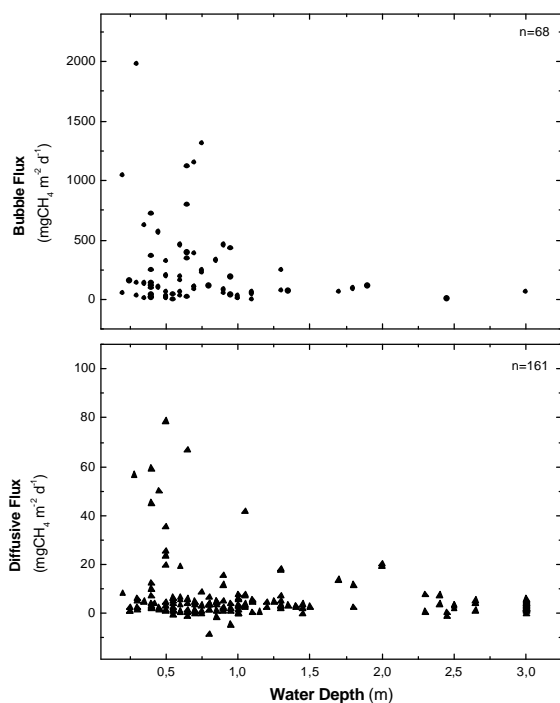


Figure 03. Influence of water depth in bubble and diffusive flux.

Other important factor in the determination of the transport is the presence of vegetation, as showed by *Bartlett et al.* (1988), *Devol et al.* (1988), *Bartlett et al.* (1990) and *Khalil et al.* (1998a). The presence of vegetation makes a way to transport the methane from substrate to the atmosphere. *Bartlett et al.* (1990) shows that if this transport is constant over the measurement period, it could not be distinguished from the diffusive transport, and was grouped with the diffusive flux. The diffusive and bubble fluxes from open water and

vegetated areas obtained for the three sample campaigns are presented in Table 2 and 3, respectively.

TABLE 2. FLUX FROM OPEN WATER

	DIFFUSIVE	BUBBLE
March	9.8±9.8	130.6±140.1
June	4.3±8.4	259.4±380.7
September	4.9±10.0	409.5±727.0
<b>Total</b>	5.3±9.3	248.7±408.6

TABLE 3. FLUX FROM VEGETATED AREAS

	DIFFUSIVE	BUBBLE
March	22.8±29.5	94.8±79.3
June	12.7±14.3	268.9±259.1
September	2.2±2.0	347.7±289.2
<b>Total</b>	11.3±29.4	257.2±254.6

As also observed by *Bartlett et al.* (1990) in the Amazon River Floodplain, the comparison between Table 2 and Table 3 indicates the influence of the vegetation in the methane emissions in Pantanal. The diffusive fluxes were higher in the presence of vegetation while the bubble fluxes were smaller. The transport through the vegetation makes possible the continuous liberation of the methane made in the substrate, so that the formation and liberation of the bubbles becomes more difficult, as observed by *Bartlett et al.* (1990) in measurements in the Amazon River Floodplain.

## Conclusions

We presented the methodology used to measure methane fluxes in the Pantanal region and the first results obtained in the three campaigns made in 2004 (March, June and September). The overall average flux was  $79.3 \pm 227.1$  mgCH<sub>4</sub> m<sup>-2</sup>d<sup>-1</sup>, with fluxes ranging from -8.7 to 1983.1 mgCH<sub>4</sub> m<sup>-2</sup>d<sup>-1</sup>, a range similar to that reported in others works in tropical wetlands.

To study the seasonal methane emission variation, the fluxes were divided in two kinds, according with their way of transport from substrate to water surface: diffusive and bubble fluxes. The average diffusive flux for each

campaign showed a decrease from March to September, while the bubble flux showed an increase. Changes in the relative importance of bubble and diffusive fluxes are therefore critical to understanding seasonal changes in total flux in Pantanal.

The magnitude and the spread of the bubble fluxes were higher in September, reflecting the fact that the water depth could be an important factor in determination of the kind of methane transport from the substrate to the atmosphere.

The influence of the aquatic vegetation was also evaluated showing that the more intense diffusive fluxes appear to occur over the vegetated water, while the more intense bubble fluxes appear to occur over the open water areas.

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