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# **BIOGENIC GASES (CH<sub>4</sub>, CO<sub>2</sub> AND O<sub>2</sub>) DISTRIBUTION IN A RIVERINE WETLAND SYSTEM**

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## **Resumo**

A análise da distribuição de gases biogênicos na planície de inundação do rio Mogi Guaçu (São Paulo, Brasil) possibilitou o estabelecimento de um gradiente redox para os sistemas aquáticos, em que o canal principal do rio foi o ambiente mais oxidado, seguido da Lagoa do Diogo, com a Lagoa do Infernão apresentando as condições mais redutoras dos ambientes aquáticos avaliados. A Lagoa do Diogo exporta um total ao redor de 853,4 g C.m<sup>-2</sup>.ano<sup>-1</sup>, do qual 14,6% é produzido via metanogênese e 36,7% pela respiração aeróbia. Para a Lagoa do Infernão estes valores foram 2.016 g C.m<sup>-2</sup>.ano<sup>-1</sup>, 1,8% e 41,5%, respectivamente. O carbono exportado por estes sistemas está predominantemente na forma de CO<sub>2</sub> que é responsável pela liberação de 728,78 g C.m<sup>-2</sup>.ano<sup>-1</sup> para a Lagoa do Diogo e de 1.979,72 g C.m<sup>-2</sup>.ano<sup>-1</sup> para a Lagoa do Infernão. Estes padrões são resultantes da natureza das condições hidrológicas, da ação do hidroperíodo e das características morfológicas do ambiente.

Palavras-chave: Gases biogênicos; metanogênese; respiração aeróbia; produção de CO<sub>2</sub>.

## **Abstract**

Analysis of the distribution of biogenic gases in the floodplain of the Mogi-Guaçu River (São Paulo, Brazil) allowed for the establishment of a "redox hierarchy", in which the main channel is the most oxidizing environment, followed by Diogo Lake, with Infernão Lake having the most reducing conditions of the subsystems evaluated. Diogo Lake exports about 853.4 g C.m<sup>-2</sup>.year<sup>-1</sup>, of which, 14.6% is generated from methanogenesis and 36.7% by aerobic respiration. For Infernão Lake, these values were 2016 g C.m<sup>-2</sup>.year<sup>-1</sup>, 1.8 % and 41.5 %, respectively. Carbon export by these systems is predominantly in the form of CO<sub>2</sub>, which was responsible for the release of 728.78 g C.m<sup>-2</sup>.year<sup>-1</sup> at Diogo Lake, and 1979.72 g C.m<sup>-2</sup>.year<sup>-1</sup> at Infernão Lake. Such patterns may result from the nature of the hydrological conditions, the action of the hydroperiod, and morphological characteristics of the environment.

Key-words: Biogenic gases; methanogenesis; aerobic respiration; CO<sub>2</sub> production.

## Introduction

Floodplain rivers are considered important sources and/or sinks of many carbon species (Hedges *et al.*, 1986). In these environments, rates of organic production are high and anoxic conditions very frequent. Because of these characteristics, such rivers are regarded as important sources of reduced gases to the atmosphere; decomposition by methanogenic bacteria can be an important pathway for carbon remineralization, and significant methane emissions to the atmosphere can take place (Crill *et al.*, 1988; Devol *et al.*, 1994). However, there is still little information about the terminal carbon processing in this type of wetland, especially considering the role of anaerobic processes (Pulliam, 1993), the regulatory mechanisms, and detailed seasonal variations in fluxes. Richey *et al.* (1988), analyzing the distribution of biogenic gases in a series of habitats in the Amazon river floodplain found that an oxi-reduction sequence could be established, ranging from oxidizing (high O<sub>2</sub> and low CO<sub>2</sub> and CH<sub>4</sub> concentrations) to highly reducing (with high CO<sub>2</sub> and CH<sub>4</sub> levels and depletion of O<sub>2</sub>) environments, and that such distributions could be useful in understanding organic matter production and consumption in aquatic

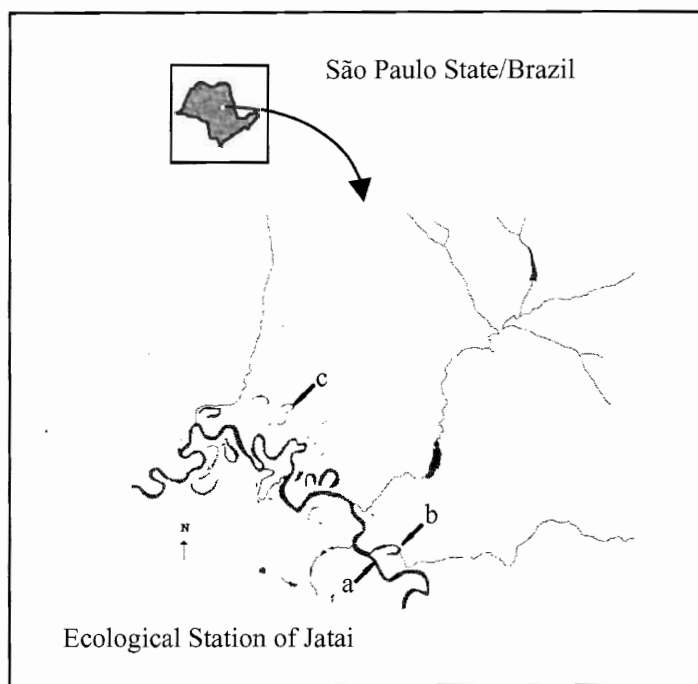


Figure 1. Localization of the Ecological Station of Jatai and sampling locations: a) main channel (Mogi-Guaçu River); b) Diogo Lake and c) Infernã Lake.

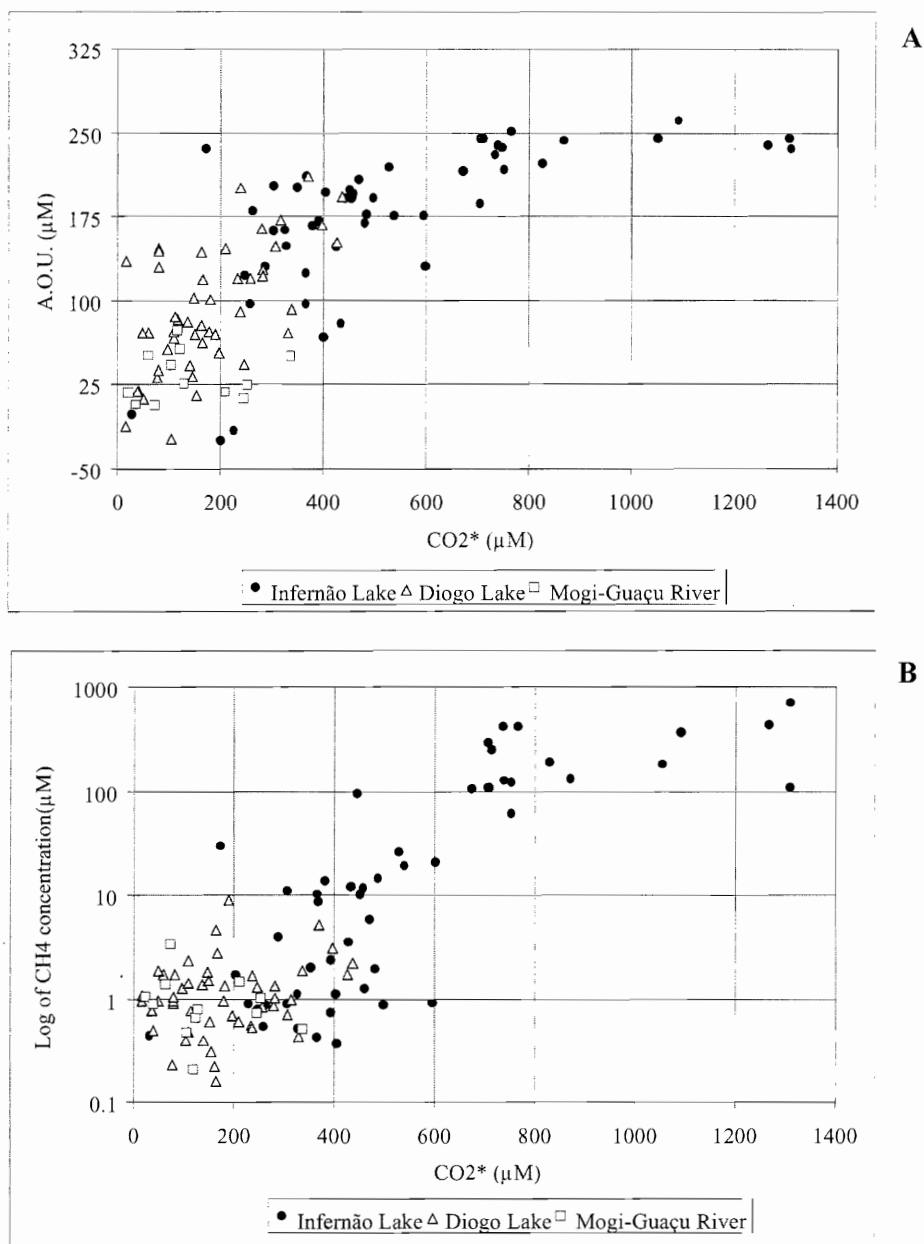
ecosystems. One of the most important factors controlling the biogeochemical and ecological characteristics in floodplain rivers is the hydroperiod (Lugo *et al.*, 1990), which regulates primary production and decomposition processes, and the extent to which aerobic and anaerobic microbial processes take place. The main objective of the present study was to examine the carbon oxidation-reduction processes using biogenic gas distribution analysis, as well as to evaluate the influence of the hydroperiod on the seasonal distributions.

### Study area and sampling collection

Dissolved gases were determined in the main channel and in two oxbows lakes (Diogo and Infern o) of the Mogi-Gua u river floodplain (Fig. 1). This area has been the object of many biogeochemical and ecological studies and detailed descriptions of the geographical, physical and ecological characteristics can be found elsewhere (Santos *et al.*, 1995). The annual mean values of temperature and precipitation of the study area are 21.7°C and 1550mm, respectively. The year can be divided in two different periods: the wet season, with frequent rain and high temperatures (November to April) and the dry season, with lower amounts of rain and lower temperatures (May to October). The Mogi-Gua u River has a unimodal inundation regime, i.e., potential conditions of inundation only once a year, during the wet season (Krusche, 1989). Floodplain inundation occurs as pulses of rapid duration, ranging from ca 2 to 31 days. The water level of the lakes shows a simultaneous but not necessarily direct variation with the river discharge increase. Diogo Lake, a drainage system, has a permanent connection with the main river channel. Changes in the river discharge are reflected directly in the depth of the water column of the lake, which increases and decreases linearly as a function of the river level. Infern o Lake, a seepage system, is 600m away from the main channel and only communicates with the latter through the floodplain during the wet season.

### Material and Methods

Water samples were collected for one year, using a Van Dorn bottle (January 1991 to February 1992). In the river, samples were collected in the middle of the channel at the surface. In the lakes, surface and bottom (0.5m above the bottom sediment) samples were taken in two different habitats: open water and macrophyte beds, dominated by *Eichhornia azurea*, *Panicum pernambucense* and *Scirpus cubensis*. The Van Dorn bottle was subsampled for measurements of: pH, water temperature, dissolved oxygen, total carbon dioxide ( $\square\text{CO}_2$ ) and dissolved methane. Dissolved oxygen content was determined by the Winkler method (Golterman *et al.*, 1978) and  $\square\text{CO}_2$  by conductivity in a Flow Injection Analysis system (Jardim & Rohwedder, 1990).



Concentrations of free dissolved  $\text{CO}_2$  were calculated from pH and  $\square\text{CO}_2$  (Skirrow, 1975). Water samples for dissolved methane were analysed using the multiple phase equilibration method (McAuliffe, 1971) for gas extraction. Gas samples were returned to the laboratory, and, after 12 hours, analyzed for  $\text{CH}_4$  in a flame ionization detection gas chromatograph, using the external standard method. Methane fluxes to the atmosphere were determined by changes in the concentrations of floating chambers (Ballester, 1994) placed over the water or vegetated surface.  $\text{CO}_2$  and  $\text{O}_2$  fluxes to the atmosphere were calculated using the boundary-layer model (Liss, 1973; Broecker & Peng, 1974). Apparent Oxygen Utilization (A.O.U.) and Apparent  $\text{CO}_2$  Production ( $\text{CO}_2^*$ ) were calculated as proposed by Richey *et al.* (1988). Data is presented as means  $\pm$  1 SD unless otherwise stated.

Table 1. Means values ( $\pm$  1 SD) of  $\text{CO}_2^*$ , A.O.U. and  $\text{CH}_4$ .

Sampling Station	$\text{CO}_2^*$ ( $\mu\text{M}$ )	A.O.U. ( $\mu\text{M}$ )	$\text{CH}_4$ ( $\mu\text{M}$ )
Main Channel	147.48 ( $\pm$ 97.56)	29.68 ( $\pm$ 21.74)	0.94 ( $\pm$ 0.785)
Diogo Lake, Open Water, Surface	174.91 ( $\pm$ 25.2)	61.77 ( $\pm$ 10.62)	0.73 ( $\pm$ 0.51)
Diogo Lake, Open Water, Bottom	263.65 ( $\pm$ 35.8)	135.04 ( $\pm$ 11.98)	1.35 ( $\pm$ 0.71)
Diogo Lake, Macrophytes, Surface	144.06 ( $\pm$ 25.87)	48.8 ( $\pm$ 11.39)	0.84 ( $\pm$ 0.501)
Diogo Lake, Macrophytes, Bottom	138.64 ( $\pm$ 27.98)	127.49 ( $\pm$ 13.14)	2.60 ( $\pm$ 2.372)
Infernao Lake, Open Water, Surface	453.25 ( $\pm$ 25.72)	178.88 ( $\pm$ 5.4)	7.40 ( $\pm$ 8.103)
Infernao Lake, Open Water, Bottom	720.03 ( $\pm$ 96.74)	224.4 ( $\pm$ 6.66)	166.45 ( $\pm$ 151.31)
Infernao Lake, Macrophytes, Surface	327.88 ( $\pm$ 38.9)	85.97 ( $\pm$ 18.74)	4.70 ( $\pm$ 6.181)
Infernao Lake, Macrophytes, Bottom	687.69 ( $\pm$ 81.79)	211.91 ( $\pm$ 8.52)	148.86 ( $\pm$ 193.06)

SD: Standard Deviation

$\text{CO}_2^*$ : Apparent  $\text{CO}_2$  Production

A.O.U.: Apparent Oxygen Utilization

## Results and Discussion

The aquatic environments of the Mogi-Guau River floodplain were characterized by positive values of  $\text{CO}_2^*$  and A.O.U. (Table 1), indicating an excess of respiration over photosynthesis. There was also a general association between high levels of  $\text{CO}_2^*$ , A.O.U. and  $\text{CH}_4$  (Fig. 2). However, negative values of A.O.U. were found in some of the macrophyte bed water samples of the lakes. Dissolved methane was found in concentrations supersaturated with respect to the atmospheric equilibrium in all habitats sampled. Higher levels were observed in the stagnant, anoxic bottom water of Infernao Lake, with concentrations up to 100 times higher than those observed in Diogo Lake and the main channel.

Main channel values of  $\text{CO}_2^*$  were about 4 to 30 times greater, and dissolved oxygen content about 13% lower, than the expected levels at atmospheric equilibrium. Methane concentrations (Table 1) were similar to those reported for tropical regions (Bartlett *et al.*, 1990; Devol *et al.*, 1994). These findings do not necessarily mean that methane is produced in the main channel, where such generation is probably limited due to the sandy and well-oxygenated characteristics of the sediments. As has been observed in similar systems (Pulliam, 1993; Richey *et al.*, 1988), methane could be produced in the marginal zones or even on the floodplain. In the oxbows lakes, the lowest values for the dissolved gases were observed for Diogo Lake. Levels of  $\text{CO}_2^*$  and A.O.U. in the open water were, in general, higher at the bottom. In the macrophyte bed,  $\text{CO}_2^*$  had a varying seasonal distribution, with higher levels occurring alternatively at the surface and at the bottom.  $\text{CH}_4$  concentrations were constant during the year in both sampling habitats, with slightly higher levels at the bottom.  $\text{CO}_2^*$  and A.O.U. levels at Infern o Lake were higher than those observed in the other subsystems. For this lake, anoxic conditions were found at the bottom of both sampling habitats. Levels of dissolved oxygen higher than those expected at atmospheric equilibrium were found only at the surface of the macrophyte beds. For dissolved methane concentrations, there was a significant difference between wet and dry seasons, with higher levels during the former. The macrophyte bed showed a similar pattern.

The highest levels of A.O.U. and  $\text{CO}_2^*$  for both lakes were observed during the wet season, although seasonal distributions differed. In this period, the organic matter contribution from surrounding areas in the form of detritus could have been responsible for the sharp decrease in oxygen content and the increase of dissolved  $\text{CO}_2$ . This pattern of greater  $\text{O}_2$  consumption and  $\text{CO}_2$  production observed during the rainy season can be the result of the increase in water column temperature and a higher availability of organic material. An additional factor influencing the observed reduction in aerobic conditions is an increase in the quantity of suspended material in the water column (Albuquerque & Mozeto, 1997), which can be responsible for decreases in water transparency and primary production. At Infern o Lake, the more anoxic conditions and thermal stratification of the water column (Nogueira *et al.*, 1996) could have been responsible for methane accumulation in the hypolimnium. In lakes, the oxygen content of the water column is closely related to the processes of circulation and stratification; these processes seem to be very different for the two lakes studied. The higher oxygen levels observed in Diogo Lake could have been the result of the constant supply of well-oxygenated water coming from the Cafund o stream influencing mainly the bottom layers and the macrophyte bed, where the stream mouth is situated. These results

should have been expected, since the Cafundó stream has been identified as an important determinant of the chemical composition of the lake, primarily during the dry season (Krusche, 1989) and, therefore, could be responsible for the absence of anoxic conditions and methane accumulation in the hypolimnion. In addition, Diogo Lake can be regarded as an exposed system, more susceptible to wind action, leading to water column circulation, mainly during the dry season when the water level is very low (~1.5 m). This kind of action seems to be less strong at Infernão Lake, a more sheltered system which maintains a deeper water column (~3.5 m) throughout the whole year. This fact, associated to the absence of a continuous input of running water richer in oxygen, could be responsible for the lower levels of oxygen in the latter lake. However, these lower values could also be an indication that more intense decomposition processes are taking place in this lake, where the respiratory rates are slightly higher (Ballester, 1994).

The fact that the  $\text{CO}_2^*$  values exceeded the levels expected for atmospheric equilibrium could be the result of *in situ* organic matter oxidation (Martins & Probst, 1991) resulting from a chain of aerobic and anaerobic respiration and fermentation processes (Nedwell, 1984), suggesting that the Mogi-Guaçu River floodplain could be a source of atmospheric  $\text{CO}_2$ . Similar results of high values of dissolved  $\text{CO}_2$  have been reported for tropical lakes (Richey *et al.*, 1991). In deeper zones, anoxic conditions are common and  $\text{CO}_2$  and  $\text{CH}_4$  accumulate (Devol *et al.*, 1994); this was observed at Infernão Lake.

The flux of biogenic gases at the water-atmosphere interface can be used as an indicator of the contributions of aerobic and anaerobic decomposition processes in the carbon remineralization (Richey *et al.*, 1988). Using this approach, and assuming that the sum of the fluxes of  $\text{CO}_2$  and  $\text{CH}_4$  ( $F_C = F_{\text{CO}_2} + F_{\text{CH}_4}$ ) represents the total decomposition of organic carbon, it could be calculated that Diogo Lake exports about  $853.4 \text{ gC}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ , 14.6% generated from methanogenesis and 36.7% from aerobic respiration. For Infernão Lake, these values were  $2016 \text{ gC}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ , 1.8% and 41.5%, respectively. Carbon exportation as  $\text{CO}_2$  was responsible for the release of  $728.78 \text{ gC}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  at Diogo Lake and  $1979.72 \text{ gC}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  at Infernão Lake (Fig. 3). The methane contribution is in the same range of variation reported for similar wetlands (Pullian, 1993; Richey *et al.*, 1988), with the Diogo Lake values being relatively high. Infernão Lake releases about 2.4 times more carbon than Diogo Lake. Nevertheless, the contribution of aerobic respiration to the total carbon flux is almost the same (~40%); this suggests that other processes of anaerobic respiration and the microbial consumption of methane could be responsible for those differences.

The observed differences between the lakes in the role of methanogenesis in the total carbon flux to the atmosphere could be the result of differences in the intensity and relative importance of methane production, consumption and emission mechanisms, which seem to occur at different rates in each lake. Oxbows lakes can be regarded as important potential sources of reduced gases to the atmosphere with a significant contribution of methane production to the carbon

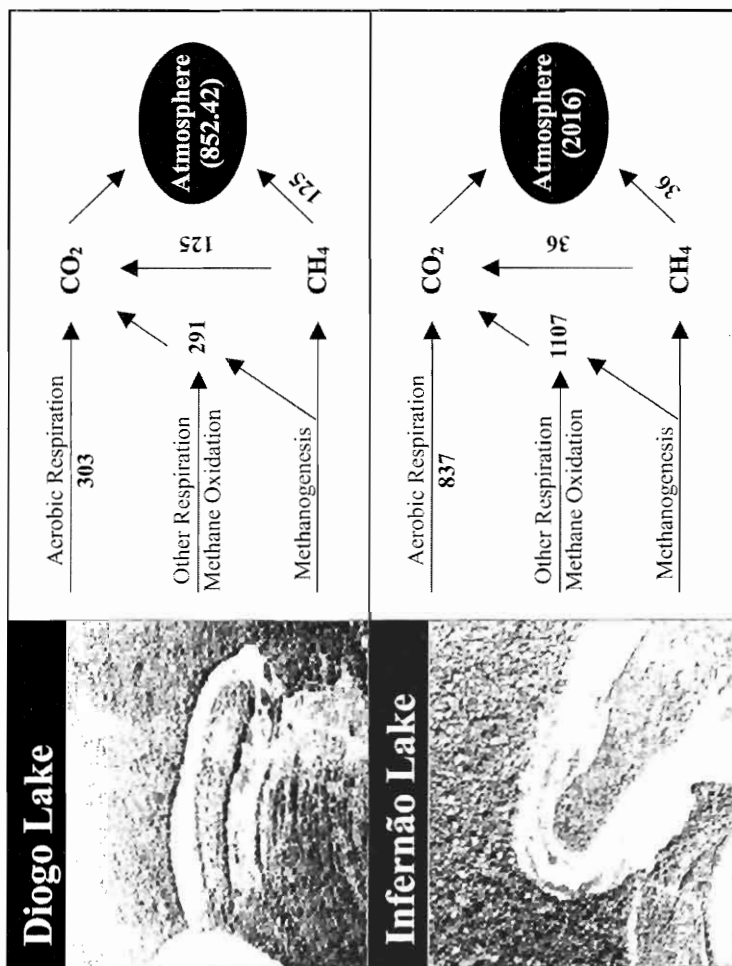


Figure 3. Rates and pathways of terminal respiration at Diogo and Infern o Lakes. Numbers on arrows show estimated carbon fluxes in  $\text{g.m}^{-2}.\text{year}^{-1}$ .



reminerzalization. The analysis of the distribution of biogenic gases in the Mogi-Guaçu River floodplain river has enabled the recognition of a "redox hierarchy" of the subsystems evaluated, where the main channel is the most oxidizing environment, followed by Diogo Lake, with Infernão Lake having the most reducing conditions. This distribution pattern may be the result of the hydrological conditions and the diverse effects of the hydroperiod. For oxbow lakes, their position on the floodplain, as well as their morphological characteristics, are additional factors that must be considered.

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