

Photoacoustic/dynamic chamber method for measuring greenhouse gas fluxes in hydroreservoirs

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Introduction

In the last years hydroelectric reservoirs have been highlighted as anthropogenic inducers of global climatic changes by emitting greenhouse gases (GHG) to the atmosphere. Due to the great variance in flux data (NOVO & TUNDISI 1994, DUCHEMIN et al. 1995, DUCHEMIN et al. 2000, ST-LOUIS et al. 2000, LIMA 2005), an appropriate study ought to consider the dynamical behavior of GHG fluxes. The present article deals with this perspective to evaluate GHG fluxes at the water-air interface of reservoirs in the Brazilian Cerrado.

Key words: biogeochemistry, hydroelectricity, climate change, continuous measurement

Study sites

The hydroelectric reservoir Serra da Mesa is located at the head of the Tocantins River basin in an arenite area. The multiple purpose reservoir Manso is formed by the confluence of the Casca (sand area) and Manso (arenite area) rivers. The Serra da Mesa reservoir has an average depth of 30 m, and some locations can reach deeper than 100 m. Manso reservoir has an average depth of 17 m and a maximum depth of 65 m.

Material and methods

Flux sampling and quantification

Measurements were made in an arenite area of Serra da Mesa (13°47'31" S, 48°18'18" W) and in a sand area of Manso (14°57'34" S, 55°45'24" W). Fluxes of CH₄, CO₂ and N₂O at the water-air interface were determined based on open dynamic chambers (FANG & MONCRIEFF 1998, FANG & MONCRIEFF 2001). Four rubber cylindric chambers adapted with floating collars were placed at four different water depths, from near the shoreline toward deeper locations. Water depths were 5.6 m, 14.8 m, 25.5 m, 32.5 m in Serra da

Mesa, and 0.7 m, 1.4 m, 2.1 m, 3 m in Manso. A quick-connection valve was fitted in the top plate to pump shoreline atmospheric air into the chamber, with a chimney allowing exit air to flow ashore to measuring instrumentation. Such design allows continuous airflow inside the chamber, minimizing temperature (increase) and pressure (decrease) effects. Two Charles Austen Capex-V2 pumps connected to four 90-m nylon tubes were used to drive shoreline atmospheric air into the chambers at a constant flow rate of ca. 0.3 L min⁻¹. A photoacoustic trace gas analyzer (TGA; Innova 1312) was used to determine trace gas concentrations. The instrument was calibrated, including a correction for water vapor (which was also measured) and appropriate cross interference calibrations. Accuracies in concentration analysis were ±2.07%, ±0.37% and ±0.09% for CH₄, CO₂ and N₂O, respectively, for a sample integration time of 5 s. A multisampler (Innova 1309) automatically switched the outlet (inlet) air from the chambers through other 90-m nylon tubes to the TGA. The gas flux was calculated by $\phi = f(C_o - C_i)/A$, where A corresponds to the gas exchange water surface area, C_o and C_i to the outlet and inlet concentrations (ppm), respectively, and f to the molar air flow given by $f = v/22.4 \times 273.5 / (273.5 + T) \times p / 1013.2$, where v is the air flow (L min⁻¹), T the temperature (°C) and p the atmospheric pressure (mbar). Constant values of T and p were assumed in the calculations.

Results

GHG flux dynamics in Serra da Mesa during two consecutive days in the middle of March 2004 are illustrated in Fig. 1A. Because the multisampler failed, sampling was conducted every 4 hours, for a 1.5-hour duration, by manually switching the valves. Fluxes were highly variable for the three gas species, sometimes negative (sink) and in other times positive (source). CO₂ fluxes were positive, especially

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Table 1. Greenhouse gas fluxes at the water-air interface in Serra da Mesa and Manso reservoirs acquired in March 2004. Presented data are mean \pm standard deviation, minimum and maximum values in parenthesis, and the number of samples. Data were stratified according to measured depth and time period.

Serra da Mesa reservoir	CO ₂ mg m ⁻² d ⁻¹	N ₂ O mg m ⁻² d ⁻¹	CH ₄ mg m ⁻² d ⁻¹
32.5 m	-99.6 \pm 668.0 (-3785.5, 2143.5) n = 90	-0.2 \pm 1.1 (-4.6, 2.5) n = 90	0.2 \pm 4.5 (-8.9, 17.7) n = 90
25.5 m	-57.0 \pm 705.2 (-3779.3, 1637.1) n = 90	-0.2 \pm 1.4 (-7.2, 3.1) n = 90	0.4 \pm 4.6 (-18.1, 14.1) n = 90
14.8 m	128.8 \pm 703.6 (-3450.2, 1807.7) n = 83	-0.4 \pm 1.3 (-5.9, 3.0) n = 83	0.7 \pm 5.4 (-15.1, 15.5) n = 83
5.6 m	332.3 \pm 849.8 (-1867.8, 5054.0) n = 90	-0.2 \pm 1.4 (-6.1, 4.7) n = 90	-0.6 \pm 7.8 (-21.9, 23.3) n = 90
00h-06h	48.3 \pm 660.0 (-1275.9, 1637.1) n = 65	0.2 \pm 0.9 (-1.6, 4.7) n = 65	1.4 \pm 7.2 (-21.9, 17.7) n = 65
06h-12h	128.7 \pm 333.4 (-799.7, 1154.6) n = 72	-0.1 \pm 0.6 (-1.1, 3.1) n = 72	1.1 \pm 2.7 (-5.4, 7.4) n = 72
12h-18h	182.8 \pm 422.1 (-736.2, 2143.5) n = 140	-0.7 \pm 1.8 (-7.2, 2.5) n = 140	-1.5 \pm 5.3 (-18.2, 14.1) n = 140
18h-00h	-151.2 \pm 1331.9 (-3785.5, 5054.0) n = 76	0.01 \pm 0.5 (-1, 1.3) n = 76	1.3 \pm 6.4 (-8.9, 23.3) n = 76
Manso reservoir	CO ₂ mg m ⁻² d ⁻¹	N ₂ O mg m ⁻² d ⁻¹	CH ₄ mg m ⁻² d ⁻¹
3.0 m	-4.8 \pm 195.6 (-588.9, 952.6) n = 710	-1.2 \pm 2.3 (-11.4, 1.3) n = 710	8.3 \pm 11.9 (-2.9, 183.9) n = 710
2.1 m	5.9 \pm 235.3 (-742.9, 971.3) n = 544	-1.1 \pm 2.4 (-13.2, 1.4) n = 544	7.2 \pm 5.6 (-3.2, 81.6) n = 544
1.4 m	-0.4 \pm 229.7 (-749.1, 973.7) n = 711	-2.0 \pm 3.3 (-14.5, 1.3) n = 711	5.3 \pm 5.4 (-7.2, 70.3) n = 711
0.7 m	-2.4 \pm 227.3 (-720.8, 1009.7) n = 713	-2.3 \pm 3.7 (-16.8, 0.9) n = 713	8.2 \pm 24.3 (-7.1, 247.9) n = 713
00h-06h	53.7 \pm 235.9 (-705.6, 1009.7) n = 811	-0.1 \pm 0.3 (-1.7, 1.4) n = 811	4.8 \pm 11.7 (-1.9, 202.3) n = 811
06h-12h	-3.7 \pm 190.6 (-469.4, 651.9) n = 603	-3.2 \pm 3.6 (-16.8, 1.1) n = 603	2.6 \pm 20.2 (-7.2, 247.9) n = 603
12h-18h	-7.3 \pm 197.1 (-389.7, 971.3) n = 505	-2.3 \pm 3.8 (-15.8, 1.4) n = 505	6.6 \pm 18.3 (-3.2, 220.5) n = 505
18h-00h	-45.5 \pm 232.7 (-749.1, 952.6) n = 759	-0.1 \pm 0.5 (-1.7, 1.3) n = 759	5.7 \pm 6.5 (-1.8, 70.3) n = 759

during daytime and in shallow areas (Table 1). N₂O showed pronounced negative fluxes around midday and positive or slightly negative in the other periods (Fig. 1A). N₂O fluxes showed small differences with respect to the water column depths (Table 1). CH₄ fluxes, however, were predominantly positive, except during midday, and tended to decrease on average with increasing depth from 14.8 to 32.5 m (Table 1).

GHG flux dynamics in Manso during approximately three successive days in the end of March 2004 are illustrated in Fig. 1B. At this time the multisampler was fixed and continuous data were acquired. At about midday fluxes notably drop to negative values for all gases. Fluxes of CO₂ presented both negative and positive values, increasing on average from 0.7 m to 2.4 m water depth, and falling to -4.8 mg-CO₂m⁻²d⁻¹ at 3 m depth (Table 1). Mean CO₂ fluxes were often positive during the nighttime, while carbon dioxide absorption was common place throughout the sampling period (Table 1).

Daylight N₂O fluxes were considerably negative and became more negative as depth decreased (Fig. 1B).

Methane fluxes in Manso were typically positive, with an unclear relation to water depth (depth range was perhaps negligible). Even so, CH₄ fluxes tended to be elevated during the daylight time (Table 1), where emissions greater than ca. 15 mgCH₄m⁻²d⁻¹ were certainly mediated by episodic bubble events. The shallowest site (0.7 m) presented bubble fluxes with values as high as 250 mgCH₄m⁻²d⁻¹. Note also three large bubble methane fluxes occurring at a relative constant time interval of 18 hours (Fig. 1B), a possible result of gas supersaturation under continuous methanogenesis, followed by sediment disruption due to the excess of a certain bubble-size threshold within the flooded sand soil.

Differences between the two reservoirs may rely essentially on the depth range of measurements (less than 3 m at Manso and 33 m at Serra da Mesa), and on the drainage basin struc-

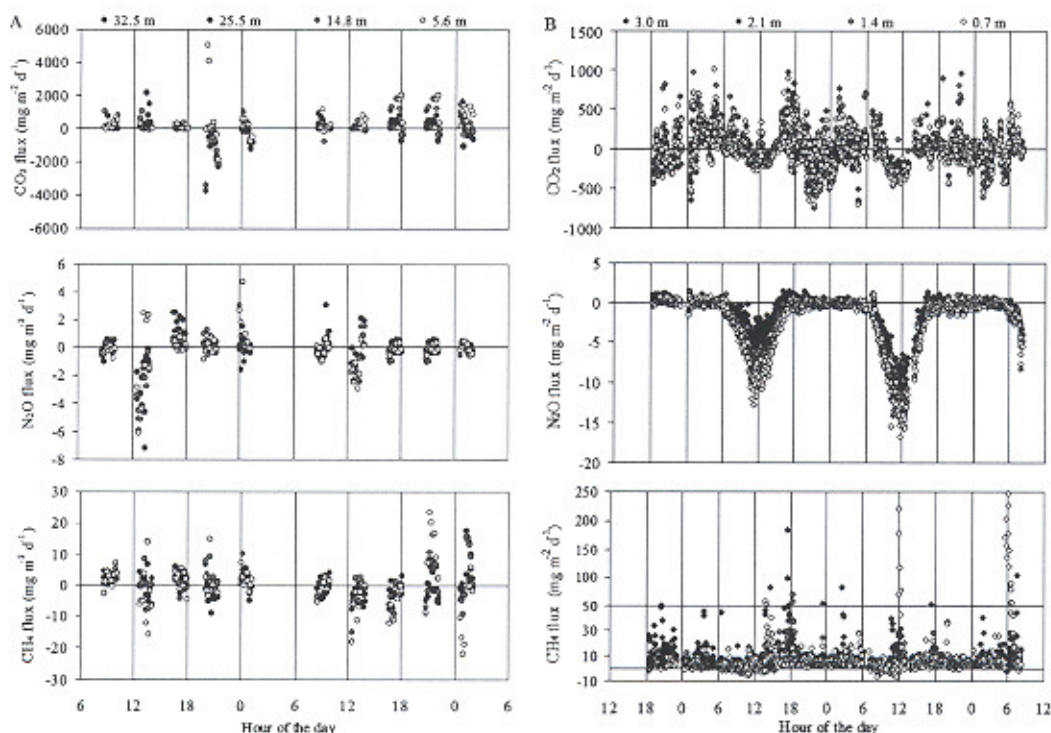


Fig. 1. Continuous GHG fluxes measured at the water-air interface at four distinct depths from Serra da Mesa (A) and Manso (B) reservoirs. Gray levels in the legend correspond to measurements over a specific water depth. The discontinuity in Serra da Mesa was due to multisampler failure.

ture. In arenite areas, methanogenesis may be lower (no bubbles were observed by disturbing the bottom of the reservoir) than in sand areas (many bubbles were verified), making bubble and diffusive methane fluxes greater in Manso, particularly in the shallow areas of the Casca River. The CO_2 absorption in Manso might rely on photosynthetic processes or on the preferential methane production via CO_2 reduction, while CO_2 emissions verified in Serra da Mesa may result from oxidative processes taking place within the aquatic ecosystem. Nonetheless, it is very difficult to generalize if these reservoirs behaved as a sink or source of CO_2 to the atmosphere due to the great flux variability in a time scale of minutes and also to the small spatial coverage. Measurements of dissolved nitrogen species with a Yellow Spring Instrument 6200 sonde showed that nitrate and ammonia concentrations in the water of both reservoirs were below detection limit of the

ion-selective probe. Consequently, the prevailing N_2O absorption (negative fluxes) in the two reservoirs may result from simple diffusion due to very low concentration of dissolved nitrogen species and/or from an intense bacterial metabolism in the water column under very nitrogen-demanding waters.

Concluding remarks

The first results of GHG flux using photoacoustic TGA and dynamic floating chambers illustrate the potential increase of the knowledge regarding the underlying GHG flux dynamics at the water-air interface of aquatic ecosystems. For the measured period, Serra da Mesa Reservoir behaved as a sink of nitrous oxide, a small source of methane and a considerable source of carbon dioxide. On the other hand, Manso Reservoir acted as a sink of both carbon dioxide and nitrous oxide and a source of methane.

This experiment showed a convenient way to evaluate trace gas flux dynamics in the water-air interface

using a TGA and dynamic chambers. The methane flux data presented a large water vapor influence because correlations of water vapor versus CH₄ concentration were beyond 0.93. Using nafion® tubes for drying gas samples prior to TGA analysis, another study verified that only methane concentration measurement is affected by humidity (unpublished results); therefore, an unavoidable recommendation is using a gas dryer previously to TGA analysis. An additional suggestion is to use a single and sufficiently large dead-volume between the pump and the chamber inlets for decreasing inlet air concentration fluctuations.

Recent data acquired in other Cerrado Reservoir (Corumbá) with TGA and dynamic chambers also suggest that the observations of large flux variances may result from natural complex fluctuations, more specifically exhibiting multifractal behavior (LIMA et al., in prep.). Dynamic chambers and TGA are thus fairly suitable for studying and evaluating GHG flux dynamics in the water-air interface of aquatic environments instead of traditional techniques such as static chambers and funnels, which provide only a glimpse of the whole process, as can be noted by comparing data obtained in Serra da Mesa (undersampling, fragmented data) and Manso (continuous sampling) reservoirs.

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