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# In situ measurements of dissolved gases ($CO_2$ and $CH_4$) in a wide range of concentrations in a tropical reservoir using an equilibrator

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**Abstract**

An equilibrator system connected to an infrared photo acoustic gas analyzer was used in order to measure directly in situ the concentrations of dissolved $CO_2$ and $CH_4$ in waters of a tropical reservoir (Petit Saut, French Guiana). The performance of the system was tested both on a vertical profile in the stratified water body of the reservoir and in the surface waters of the river downstream the dam. Results agreed with conventional GC analysis at ±15% in a wide range of concentrations ($CO_2$:50–400 μmol $l^{-1}$ and $CH_4$:0.5–350 μmol $l^{-1}$ corresponding to gas partial pressures of respectively 1700–13,000 and 12–8800 μatm). The time needed for in situ measurements was equivalent to water sampling, time for GC analysis in the laboratory being suppressed. The continuous monitoring of gas concentrations for 24 h in the reservoir surface waters revealed rapid changes in concentrations highly significant in the daily emission budget. The system opens new perspectives for the monitoring of gas concentrations in highly dynamic systems like tropical reservoirs.


*Keywords:* Carbon dioxide; Methane; Reservoir; In situ monitoring

## 1. Introduction

In the context of global warming, the quantification of greenhouse gases emissions from the Earth surface is recognized as a priority. Recently, artificial reservoirs particularly in the tropics have been identified as significant $CO_2$ and $CH_4$ contributors to the atmosphere (Galy-Lacaux et al., 1997, 1999; Saint Louis et al., 2000; Rosa et al., 2003). The Petit Saut hydroelectric reservoir on the Sinnamary River in French Guiana, impounded in 1994, is a typical example of a man-induced modification of the continental surface that has drastically changed the $CO_2$ and $CH_4$ exchanges with the atmosphere. Owing to the microbial decomposition of flooded biomass composed of primary tropical forest, this reservoir emits large amounts of $CO_2$ and $CH_4$ to the atmosphere (Galy-Lacaux et al., 1997, 1999). Gaseous emissions in the

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Petit Saut system occur through four major pathways (Galy-Lacaux et al., 1999; Delmas et al., 2001): (1) the bubbling flux, which occurred mainly during the first 2 years after impounding in the reservoir areas shallower than 10 m; (2) the diffusive flux from the reservoir surface; (3) the degassing at the aerating weir downstream the dam, when bottom anoxic waters rich in $CO_2$ and $CH_4$ pass through the turbines and get in contact with the atmosphere; (4) the diffusive flux from the Sinnamary River downstream the dam.

Diffusive $CO_2$ and $CH_4$ fluxes depend on the concentration gradient between the surface water and the atmosphere, which is controlled by the gas concentration in the surface water and on the gas transfer velocity. Fluxes can either be measured directly using floating chambers or be calculated using a gas transfer velocity parameterized as a function of wind speed (Cole and Caraco, 1998). Both techniques generally show good agreement (e.g. Kelly et al., 1997). Degassing fluxes can be computed from the difference in depth integrated water column concentrations upstream and downstream the dam. The quantification of $CO_2$ and $CH_4$ emissions from reservoirs thus requires accurate measurements of dissolved gas concentrations. In addition, measurements must be performed at a frequency that adequately reflects the temporal variations of concentrations and fluxes at inter-annual, seasonal and daily time scales. In a tropical reservoir like Petit Saut, gas concentrations may vary rapidly: from daytime to nighttime due to intense photosynthetic activity; throughout a single day due to storms and/or thermal wind events that may partly destratify the water body; in a few days at the beginning of the rainy season when river discharge rapidly increases and residence time of water in the reservoir decreases. This variability is difficult to apprehend with classical sampling/analysis techniques. Recently, new techniques have been developed in order to measure continuously $CO_2$ concentrations in systems with rapid temporal variations like estuaries (Frankignoulle et al., 2001) and with large spatial variations like stratified lakes (Browne, 2004). Here we describe the performance tests of an equilibrator which allows a continuous (2 min interval) recording of the concentrations of both dissolved $CO_2$ and dissolved $CH_4$ in the water. Tests were performed in the Petit Saut reservoir, a system where gas concentrations vary over a wide range from low values in the epilimnion, to extremely high ones in the hypolimnion and in the river downstream the dam. Compared to previous studies with this type of equipment (Frankignoulle et al., 2001; Middelburg et al., 2002), the originalities of our results are the simultaneous measurements of $CO_2$ and $CH_4$ in a very wide range of concentrations and the performance of vertical profiles in the water column. An example of a 24 h record is finally presented and illustrates the potentiality of the equilibrator system.

## 2. Material and methods

The equilibrator system is similar to the one of Frankignoulle et al. (2001) with few differences. It consists of a 3 l Plexiglas cylinder (diameter 8 cm, height 60 cm) filled with glass marbles, where water flows at 1.5 l $min^{-1}$ from the top to the bottom. Due to the presence of the marbles, the air volume in the equilibrator is minimized to 0.5 l, whereas the surface gas exchange is maximized to ~1.2 $m^2$. The water inlet is connected to a submerged pump at 10 cm below the water surface when performing surface measurements and to a peristaltic pump with a 20 m tygon tube when performing vertical profiles in the water column. The air inlet at the bottom of the cylinder is connected to an aquarium air pump, which maintains a slight overpressure (1.5 bar) at the equilibrator bottom. The air outlet is connected to a gas analyzer (Brüel and Kjaer type 1312), which allows $CH_4$ and $CO_2$ measurements every 2 min. The analyzer is based on the photoacoustic infrared detection method as described in Middelburg et al. (1996). The analyzer is equipped with an air pump that operates at a flow of 1.8 l $min^{-1}$. Prior to analysis, the gas circuit is purged during 40 s, which allows the renewal of all the gas contained in the equilibrator. The gas sample is then trapped in the measurement chamber for 60 s for analysis. The analyzer was calibrated before the cruise by comparison with GC analysis. It was set on a closed circuit containing 1 l of gas and equipped with a rubber septum which allowed sampling and injection of pure $CH_4$ and $CO_2$ with a syringe in order to obtain different concentrations. The calibration was linear on ranges of 0–25,000 μatm for $CO_2$ and 0–10,000 for $CH_4$. Gas concentrations were calculated from partial pressures using the solubilities given by Weiss (1974) for $CO_2$ and Yamamoto et al. (1976) for $CH_4$.

The performance of the system was tested on December 2003 on a vertical profile in the Petit Saut reservoir and in surface waters every 10 km along a 90 km transect on the Sinnamary river and estuary downstream the dam. Results of the equilibrator were compared to sampling and GC analysis. Note that the headspace–CG/TCD technique is appropriate to measure dissolved $CO_2$ in this system because waters are acidic (5<pH<6) and have low alkalinity (<0.2 mmol $l^{-1}$) (Hope et al., 1995). Finally, the equilibrator was used to monitor continuously the surface $CO_2$ and $CH_4$ concentrations during a complete 24 h cycle.

## 3. Results and discussion

Fig. 1 shows the $CO_2$ and $CH_4$ partial pressures recorded by the equilibrator system on the Sinnamary River and estuary downstream the dam. The 0–40 km section was sampled every 10 km the first day and the 60–90 km section the day after. The boat was sailing between stations but was left drifting during measure-

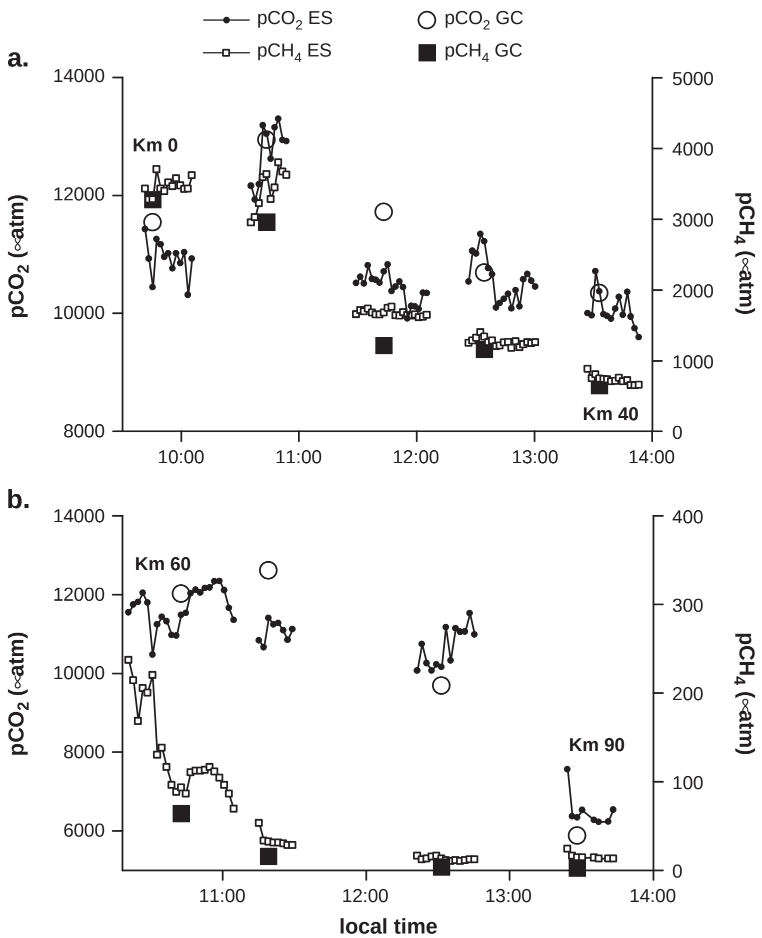


Fig. 1. Partial pressures (in μatm) of $CO_2$ (circles) and $CH_4$ (squares) recorded by the equilibrator system (small symbols) and measured by standard sampling GC analysis (large symbols) in surface waters, while sailing downstream the Sinnamary River and estuary. Measurements were performed every 10 km on December 4, 2003 on the 0–40 km section (panel a) and on December 5, 2003 on the 60–90 km section (panel b). The boat was left drifting during measurements every 10 km. Note the different scales for $CH_4$ on the right axis.

ments. $CH_4$ decreased downstream the dam from 138 to 0.5 μmol $l^{-1}$ ($pCH_4$ 3400 to 12 μatm); $CO_2$ remained extremely high at around 300 μmol $l^{-1}$ ($pCO_2$ around 10,000 μatm), except at the estuarine station (204 μmol $l^{-1}$; 6500 μatm). At all stations the stabilization of the equilibrator was fast (1–2 measurements in 2–4 min) even when concentrations were very different from one station to the other. The equilibrator also revealed rapid changes in concentrations while drifting, which would be difficult to apprehend by discrete sampling. In particular, at the 60 km station, $CH_4$ decreased very suddenly during the 15 min measurements, for a boat drift of approximately 500 m (Fig. 1b.). Fig. 2 shows the $pCO_2$ and $pCH_4$ record while performing a vertical profile in the reservoir water body. The water column is partitioned into an oxic epilimnion with moderate gas concentrations and an anoxic hypolimnion highly enriched in $CO_2$ and $CH_4$. An oxygen probe set at the tube end allowed us to localize the oxycline at 6 m depth. The use of a peristaltic pump with a tube 20 m long increased the response time of the system. Nevertheless, the maximum response time was 12 min at 7 m depth. The system thus allows us to obtain a $CO_2$ and $CH_4$ complete profile in about 2 h, i.e. the time generally needed for sampling for GC analysis and performing an oxygen profile with the probe. The comparison of results from the equilibrator with those from GC analysis showed slopes of $0.92 \pm 0.17$ for $CO_2$ and $1.11 \pm 0.15$ for $CH_4$ with no significant intercept. Owing to the very large range of concentrations the consistency of the two methods can be considered as very good. The agreement was not as good in the very low concentration range for $CH_4$ (<20 μatm) at the most downstream stations on the Sinnamary river. There, the equilibrator gave $CH_4$ concentrations about 50–70% higher than GC analysis. This must be attributed to a memory effect in the equilibrator, traces of $CH_4$ from the upstream stations probably remaining bound on the marble and/or Plexiglas surfaces. Nevertheless, the equilibrator system is largely accurate enough for monitoring programs and for computations of gas budgets in hydrosystems with high concentrations like tropical reservoirs. In addition, it suppresses a large part of the laboratory work (though weekly calibration of the gas analyzer is recommended) and allows continuous monitoring.

In order to illustrate the potentiality of our system in terms of monitoring, we show in Fig. 3 a continuous 24 h record in surface waters of the Petit Saut reservoir, at a station located just upstream the dam. The first day was very sunny with high insolation and relatively low wind. The night was characterized by heavy tropical storms with wind speeds often exceeding 6 m $s^{-1}$ and rainfall reaching

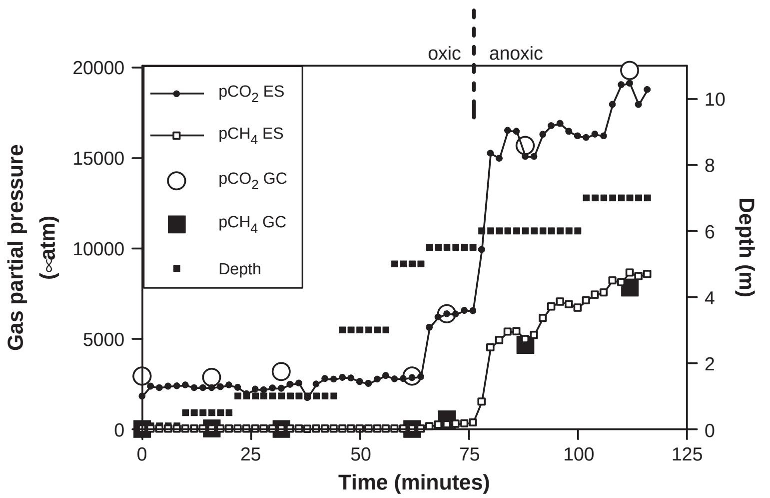


Fig. 2. Partial pressures (in μatm) of $CO_2$ (circles) and $CH_4$ (squares) recorded by the equilibrator system (small symbols) and measured by standard sampling GC analysis (large symbols), while performing a vertical profile in the Petit Saut reservoir. Sampled depths were surface, 0.5, 1, 3, 5, 5.5, 6 and 7 m. The depth of the oxycline was localized with an oxygen probe. The response times of the equilibrator are schematized by the dotted vertical lines.

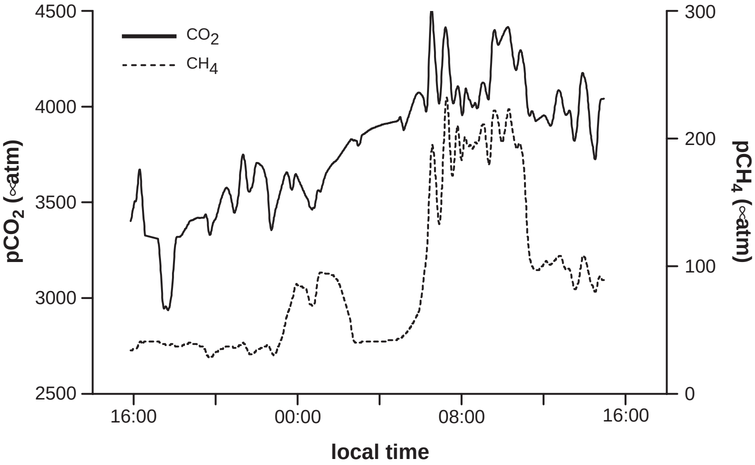


Fig. 3. A 24 h record of pCO2 (full line) and pCH4 (dotted line) in the surface waters of the Petit Saut reservoir (December 10–11, 2003).

36 mm $h^{-1}$. The second day was cloudy with several storms in the morning. $CO_2$ showed a general diel trend with higher concentrations at night, which might be explained by changes both in the photosynthesis/respiration balance and in convective and turbulent vertical mixing. $CH_4$ showed higher concentrations during storm periods (around 00:00 and 08:00) due to a partial destratification of the water column and upward transport of deeper $CH_4$ rich waters. There was also a short-term variability in gas surface concentrations, particularly in the morning during storm events, with a net parallelism for both gases. It thus appears that short meteorological events like storms and thermal winds play a crucial role in the gaseous emissions budget of the reservoir, having a multiplicative effect on the instantaneous atmospheric fluxes: an increase in surface concentrations by vertical mixing and an increase in the gas exchange rate by wind and rain stress at the water surface. Diel monitoring of gas concentrations at the water surface together with meteorological parameters are therefore necessary to adequately integrate $CO_2$ and $CH_4$ fluxes. In this context, the equilibrator system offers a great potential of applications.

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