Gas transfer velocities of CO₂ and CH₄ in a tropical reservoir and its river downstream

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Abstract

We have measured simultaneously the methane (CH₄) and carbon dioxide (CO₂) surface concentrations and water–air fluxes by floating chambers (FC) in the Petit-Saut Reservoir (French Guiana) and its tidal river (Sinnamary River) downstream of the dam, during the two field experiments in wet (May 2003) and dry season (December 2003). The eddy covariance (EC) technique was also used for CO₂ fluxes on the lake. The comparison of fluxes obtained by FC and EC showed little discrepancies mainly due to differences in measurements durations which resulted in different average wind speeds. When comparing the gas transfer velocity (k₆₀₀) for a given wind speed, both methods gave similar results. On the lake and excluding rainy events, we obtained an exponential relationship between k₆₀₀ and U₁₀, with a significant intercept at 1.7 cm h⁻¹, probably due to thermal effects. Gas transfer velocity was also positively related to rainfall rates reaching 26.5 cm h⁻¹ for a rainfall rate of 36 mm h⁻¹. During a 24-h experiment in dry season, rainfall accounted for as much as 25% of the k₆₀₀. In the river downstream of the dam, k₆₀₀ values were 3 to 4 times higher than on the lake, and followed a linear relationship with U₁₀.

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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 CO₂ and CH₄ contributors to the atmosphere (Galy-Lacaux et al., 1999; Saint Louis et al., 2000; Abril et al., 2005). Owing to the microbial decomposition of soil and flooded biomass composed of primary tropical forest, tropical reservoirs emit large amounts of CO₂ and CH₄ to the atmosphere (Galy-Lacaux et al., 1999; Abril et al., 2005). A large fraction of the gaseous emissions occurs as diffusive fluxes from the surface of the artificial lakes or from the rivers downstream of the dam (Abril et al., 2005).
Diffusive CO₂ and CH₄ fluxes depend on the concentration gradient between the surface water and the atmosphere, which is mainly controlled by the gas concentration in the surface water, and by the gas transfer velocity, \( k \). The diffusive CO₂ and CH₄ fluxes can either be measured directly or calculated from the surface water and air concentrations if \( k \) is known. Direct CO₂ and CH₄ fluxes measurements include three different techniques: the floating chambers (Frankignoulle et al., 1996a), the eddy correlation (McGillis et al., 2001) and the gradient flux techniques (Zappa et al., 2003). Indirect methods consist in measuring the gas concentration air–water gradient and determining \( k \) using deliberate tracers such as SF₆ (Wanninkhof et al., 1985) or SF₆/³⁷He (Clark et al., 1994). In addition, measurements must be performed at a frequency that adequately reflects the temporal variations in the gas concentrations in surface waters and fluxes at inter-annual, seasonal and daily time scales. Recently, equilibrator techniques have been developed in order to measure continuously CO₂ and CH₄ concentrations in systems with rapid temporal variations like estuaries (Frankignoulle et al., 2001) and stratified tropical lakes (Abril et al., 2006). This allows continuous monitoring of gas concentrations variations in surface waters. When combined to an adequate parameterization of \( k \), this would allow the calculation of accurate gas emission budgets.

In the present paper, we investigate the dependence of \( k \) on various meteorological parameters (wind speed, rainfall, and temperature) in an Amazonian tropical reservoir and its river downstream. We compare gas transfer velocities obtained by floating chamber and eddy covariance measurements of CO₂ and CH₄ fluxes performed at the same time on the same system. We establish experimental relationships of the gas transfer velocity against wind speed and rainfall and compared them with other studied lakes and rivers.

2. Materials and methods

2.1. Study site

The Petit-Saut dam was constructed on the Sinnamary River in the tropical forest of French Guiana 100 km upstream its mouth to the Atlantic Ocean. Relevant physical characteristics of the system are shown in Table 1. The reservoir started to be filled in January 1994 and covers 80 km of the Sinnamary River course. At its maximal level of 35 m (first reached in July 1995), 365 km² of un-cleared tropical forest are flooded. Owing to the differences between high and low water levels, the average surface of the reservoir is 300 km² (Table 1).

Average residence time of waters is 5–6 months. The reservoir water body remains stratified throughout the year with a permanent thermocline around 6–8 m depth. Downstream of the dam, the Sinnamary River has an average depth of 4 m and is influenced by the tide with average amplitude of 0.5 m (Table 1).

2.2. Field experiments

Two field experiments were carried out in the reservoir in May and December 2003 during the wet and dry seasons. Intensive measurements of diffusive CO₂ (\( n = 211 \)) and CH₄ (\( n = 89 \)) fluxes were performed with floating chambers from a small boat at different sites on the reservoir, including open waters and flooded forest, and on the Sinnamary River and Estuary downstream of the dam. At each station, wind speed and air

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Meteorology</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wind speed (m s(^{-1}))(^a)</td>
<td>1.02</td>
<td>0–11.50</td>
</tr>
<tr>
<td>Air relative humidity (%)(^b)</td>
<td>86.76</td>
<td>38–107</td>
</tr>
<tr>
<td>Annual precipitation (mm)(^c)</td>
<td>2965</td>
<td>2156–4538</td>
</tr>
<tr>
<td>Air temperature (°C)(^d)</td>
<td>25.65</td>
<td>19.00–36.00</td>
</tr>
<tr>
<td><strong>Lake</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface (km²)</td>
<td>300</td>
<td>260–365</td>
</tr>
<tr>
<td>Volume (10⁹ m³)</td>
<td>2.9</td>
<td>2.3–3.5</td>
</tr>
<tr>
<td>Water discharge (m³ s(^{-1}))</td>
<td>235</td>
<td>3–2431</td>
</tr>
<tr>
<td>Turbined water discharge (m³ s(^{-1}))</td>
<td>225</td>
<td>35–1957</td>
</tr>
<tr>
<td>Depth (m)</td>
<td>10</td>
<td>0–35</td>
</tr>
<tr>
<td>Surface water temperature (°C)(^e)</td>
<td>30.42</td>
<td>27.50–33.70</td>
</tr>
<tr>
<td>Thermocline depth (m)</td>
<td>7.5</td>
<td>7–8</td>
</tr>
<tr>
<td><strong>Downstream river and estuary</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface (km²) &lt; 40 km</td>
<td>5</td>
<td>n.a.</td>
</tr>
<tr>
<td>Surface (km²) &gt; 40 km</td>
<td>17</td>
<td>n.a.</td>
</tr>
<tr>
<td>Tidal range (m)</td>
<td>0.5</td>
<td>n.a.</td>
</tr>
<tr>
<td>Depth</td>
<td>4</td>
<td>3–5</td>
</tr>
<tr>
<td>Water temperature (°C)(^f)</td>
<td>26.8</td>
<td>24.8–28.4</td>
</tr>
</tbody>
</table>

\(^{a}\) Monthly average from August 2003 to June 2005.
\(^{b}\) Monthly average from December 2002 to June 2005.
\(^{c}\) Annual average from January 1991 to June 2005.
\(^{d}\) Daily average of the water discharge entering the reservoir from June 1994 to June 2005.
\(^{e}\) Monthly to bi-monthly average of measurements made at Roche Génipia (reference station since impoundment) from July 1995 to June 2005.
\(^{f}\) Daily average at 40 km downstream the dam from July 1995 to June 2005.
temperature were measured at 1-m height, and surface water was sampled at 10 cm below the water surface for the determination of CO$_2$ and CH$_4$ concentrations. Surface water temperature was determined at the same depth than gas concentrations. In Dec. 2003, CO$_2$ fluxes were also measured by the Eddy Covariance technique ($n=35$) a few hundred meters upstream of the dam, during a 24-hour cycle. Chamber fluxes were measured at regular intervals on the distance of 20 m from the eddy covariance mast, for validation and intercomparison. During this 24 h-survey, gas concentrations in surface waters were monitored with an equilibrator.

2.3. Floating chambers measurements

Fluxes were measured with three different plastic floating chambers (FC) that were deployed simultaneously from a small boat that was left drifting during measurement to avoid creation of artificial turbulence. An exception was the 24-h cycle near the eddy covariance mast when chambers were deployed from an anchored boat. The FCs used in this study had walls extending 2–5 cm into the water column. Two small chambers (volume 20 L, surface 0.2 m$^2$, square design), connected to gas analyzers for CO$_2$ and CH$_4$ were deployed during 5 to 10 min, on 3 to 5 replicates. CO$_2$ was detected with a Non dispersive Infra Red analyzer (CIRAS-2SC, PP System), and CH$_4$ with a Fourier Transformation Infra Red analyzer (Gasmet DX-4010, Temet Instruments). The gas analyzers were calibrated with certified CO$_2$ and CH$_4$ gas standards at the beginning of each campaign (390 and 409 ppm for CO$_2$ and 90 ppm for CH$_4$, Gaz Spéciaux MEGS). In addition, the zero was checked automatically for the CIRAS-2SC and manually, everyday, with nitrogen for the Gasmet DX-4010. In order to avoid condensation problem into the sampling tube and/or inside the IRGA, the ambient air was passed through a water trap of sodium perchlorate. Fluxes were calculated from the ambient air was passed through a water trap of sodium perchlorate. Fluxes were calculated from the slope of the partial pressure of the gas versus time, sodium perchlorate. Fluxes were calculated from the linear regression of gas content versus time and 88% of the measurements were accepted ($r^2>0.90$).

2.4. Eddy covariance technique

The eddy covariance (EC) method is considered as the reference method for vertical flux scalar measurement (Beverland et al., 1996; McGillis et al., 2001). This method is based on the direct high frequency measurement of the two components of the vertical flux of a scalar: the vertical wind speed ‘$w$’ and the scalar itself, CO$_2$ or ‘$c$’ here. Flux comes as the integral of the product of the vertical wind speed fluctuation $w'$ and of the scalar $c'$:

$$ F_c = \overline{w'c'} = \frac{1}{T} \int_0^T w'(t)c'(t) \, dt $$
$$ = \frac{1}{T} \overline{f(t)} \text{ with } f(t) = \int_0^T w'(t)c'(t) \, dt \quad (1) $$

Although this method presents a number of advantages, the processing of raw data shows that data control is necessary to guarantee their quality for further use (Foken and Wichura, 1996; Affre et al., 2000). Such a control is relatively simple since all the turbulence functions involved are available and can be verified at all post-treatment steps (Mann and Lenschow, 1994).

Turbulence stationarity is one of the fundamental hypotheses that should be fulfilled when determining turbulent fluxes. The presence of low frequencies, which usually are not of local turbulent origin, but can be induced by the constraint of large-cell circulations or meso-scale events in the Atmospheric Boundary Layer (ABL), implies longer scale processes in the turbulent fluctuations. They can yield significant disturbances in flux evaluation. For this reason, and as defined in Affre et al. (2000), the contribution to $w'c'$ covariance is studied along the sample. The evolution of the integral function $f(t)$ defined in Eq. (1) is an indication of the quality of the integral flux which is given by $(f(T)−f(0))/T$. There is a second way to calculate the flux which is based on a statistical approach. In that case, the flux is no more calculated on the integral slope, but on the statistical slope deduced from the least mean squares.

The criterion presented here defines the sample homogeneity. This is done by calculating the mean slope...
of the least mean square regression line. This slope corresponds to a statistical evaluation of the covariance \( \sigma_{\text{wrcov}}^2 \). It takes into account all the function evolution and not only the extreme points as for the “classical” variance calculation. The homogeneity is quantified by evaluating the standard deviation \( \sigma_{\text{wreg}} \) between \( f(t) \) and the regression line. The CRS expressed in percentage (Eq. (1)), is then defined as the ratio of the standard deviation \( \sigma_{\text{wreg}} \), to the \( \sigma_{\text{wstat}} \) covariance.

\[
\text{CRS} = 100 \left[ \frac{2 \sigma_{\text{wreg}}}{f(t_f) - f(t_i)} \right] = 100 \frac{2 \sigma_{\text{wreg}}}{\sigma_{\text{wstat}}^2} \tag{2}
\]

It represents the error in the variance evaluation, and the higher the CRS is, the less homogeneous the sample is, and on the opposite, CRS tends to zero (small difference between the integral function \( f(t) \) and the linear regression) for a linear \( f(t) \) function and a homogeneous sample. Based on the statistical distribution, a cut-off limit was applied for fluxes with CRS higher that 20%.

Once the quality control was made with the CRS, time lags related to the time response of the scalar analyzer (and to the transfer through the tubing) was to be taken into account. In this case, the time lag is easily estimated through the calculation of the cross-correlation between \( w \) and \( c \), as the time lag for which the cross-correlation shows a maximum. The flux is then calculated from the lagged functions. We found here a maximum correlation for a time lag of 9/5 s, consistent with the tubing length (4 m, \( 0.4 \times 10^{-2} \text{ m inner diameter} \)) and pump flow rate (10 L min\(^{-1}\)). Sampling tube effects were accounted by as proposed by Leuning and Judd (1996) and McGillis et al. (2001). We calculated a dimensionless cutoff limit proposed in the latter of these studies. This limit depends on the tubing length and inner diameter, the wind speed, the measurement height, the Reynolds number and the kinematic viscosity. We found that our system was capturing most of the turbulent flux as long as the wind speed was below about 8 m s\(^{-1}\).

CO\(_2\) fluxes were measured with the EC technique during the dry season, for a 24 h-period from December, 10 at 4:00 p.m. to December, 11 at 4:00 p.m. Experimental set up included a Gill\textsuperscript{®} R1 3D sonic anemometer, a Licor\textsuperscript{®} 6262 IR Gas analyser, calibrated, at the beginning of the experiment with certified gas standard (Air Liquide, 500 ppm), and a lab-made datalogger. 5 Hz logging of horizontal wind components \((U, V)\), vertical wind component \((W)\), temperature \((T)\), CO\(_2\) and H\(_2\)O data was performed on a 30 min basis, given, after quality control (CRS>20%), a total of 35 (over 48) fluxes for subsequent flux calculation. The Sonic anemometer and the tubing were installed 2.1 m above the reservoir water level at the tip of a small flat island located 400 m south-east of the dam. Fetch ranged from 400 to 1500 m in all directions, excepted of wind coming from the south. A wind sector analysis showed that no samples were collected in this latter direction.

### 2.5. Gas concentration gradients

At each station, CO\(_2\) surface concentration was measured by a headspace technique in 30-mL vials (headspace volume 15 mL) followed by a GC-TCD analysis. As described by Hope et al. (1995), this method is the most appropriate for acid, low ionic strength, organic rich waters as in Petit-Saut. Concentrations were computed with the solubility coefficient of Weiss (1974). CH\(_4\) surface concentration was also measured by the headspace technique followed by the GC-FID analysis and surface concentrations were computed with the solubility coefficient of Yamamoto et al. (1976). During the 24-hour survey, the surface concentrations were measured in air equilibrated with subsurface water pumped from a depth of 20 cm using an equilibrator connected to a photo-acoustic gas analyzer (Abril et al., 2006). Atmospheric concentrations were obtained by GC-FID (CH\(_4\) with FC-GC) and by the gas analyzers connected to the FCs at initial time of each flux measurements.

### 2.6. Meteorological variables

Wind speed and air temperature were measured with a portable anemometer (Kestrel 4000, accuracy: 3%) at 1-m height for all stations on the lake and the river. Wind speed at 10-m height \((U_{10})\) was recalculated using the Amorocho and DeVries (1980) formulation:

\[
U_z = U_{10} \left[ 1 - C_{10}^{1/2} \kappa^{-1} \ln(10/z) \right] \tag{3}
\]

where \(C_{10}\) equals the surface drag coefficient for wind at 10 m \((1.3 \times 10^{-3}; \text{ Stauffer, 1980})\), \(\kappa\) equals the von Karman constant (0.41), and \(z\) the height of wind speed measurements (meter) above the water surface.

During the 24-hour survey near the dam in December 2003, a meteorological station (OTT HYDROMETRY sensors) installed on the dam at 10-m height above the water surface measured, at 1-min interval, the wind speed (accuracy: 3%), the rainfall rate (accuracy: 0.01 mm min\(^{-1}\)), the air temperature and relative humidity. Wind speed and rainfall rate were averaged over the duration of the flux measurement.
2.7. Calculation of the gas transfer velocity

The flux across an air–water interface can be formulated as follows:

$$F_{g,T} = a k_{g,T} \Delta P$$

(4)

with

$$\Delta P = P_{w,g} - P_{a,g}$$

(5)

where $F_{g,T}$ is the flux at air–water interface for a given gas (g) at a given temperature ($T$), $a$ is the solubility coefficient of the considered gas, $k_{g,T}$ is the gas transfer velocity (or piston velocity) for a specific gas at a given $T$, and $\Delta P$ the partial pressure gradient between water ($P_{w,g}$) and the overlying atmosphere ($P_{a,g}$).

To compare the exchange coefficient for different gases and at different water temperatures, the gas transfer velocity was normalized to a Schmidt number of 600 ($Sc=600$, for CO2 at 20 °C) with the following equation (Jähne et al., 1987):

$$k_{600} = k_{g,T} (600/Sc_{g,T})^{\alpha}$$

(6)

where $Sc_{g,T}$ is the Schmidt number of a given gas at a given temperature (Wanninkhof, 1992). For the lake, we used $n=2/3$ for wind speed <3.7 m s⁻¹, and $n=0.5$ for higher wind speed (Liss and Merlivat, 1986; Jähne et al., 1987). In the turbulent river downstream, we used $n=0.5$ whatever the wind speed (Borges et al. 2004a).

3. Results and discussion

3.1. Description of the dataset

Three regions of the Petit-Saut system can be differentiated in terms of gas concentrations and fluxes: the reservoir surface (lake), the first section of the Sinnamary River from 0 to 40 km downstream of the dam, and the second section of the river, from 40 to 80 km, corresponding to the limit of the coast of the Atlantic Ocean. CO2 and CH4 fluxes measured at these different sites are shown in Table 2.

Surface waters of the lake were supersaturated in both studied gases with respect to the atmospheric equilibrium, with mean $\Delta pCO_2=3340±802$ μatm and $\Delta pCH_4=81±76$ μatm for both sampling periods. Resulting mean fluxes to the atmosphere were $103±82$ mmol m⁻² d⁻¹ and $4±6$ mmol m⁻² d⁻¹ for CO2 and CH4, respectively. The large range of $\Delta pCO_2$ and $\Delta pCH_4$ for a given season (Table 2) were mainly due to the variety of sampling sites (e.g., flooded forest, open waters) and meteorological conditions. The Petit-Saut Lake can be destratified during high wind speed and rainfall periods (Abril et al., 2006). These short and dynamic phenomena can cause an increase of surface concentrations and partly explains why $\Delta pCH_4$ are significantly higher in the wet season than in the dry season. For CO2, only 3 surface concentrations were measured during the May campaign. Rainfall events were only sampled in Dec. 2003, when, in addition, wind speeds were higher (Table 2).

CO2 and CH4 diffusive fluxes along the first 40 km section downstream of the dam were the highest of the Petit-Saut whole system. The $\Delta pCO_2$ were 4 to 10 times higher than at the lake surface and the resulting fluxes to the atmosphere were 10 times higher (Table 2). The $\Delta pCH_4$ were 6 to 30 times higher than in the lake and the corresponding fluxes were one order of magnitude higher (Table 2). These high CO2 and CH4 concentrations in this section of the river originate from the reservoir hypolimnion (Galy-Lacaux et al., 1999; Abril et al., 2005). The fluxes to the atmosphere were very high due to very high

---

Table 2

<table>
<thead>
<tr>
<th>Site</th>
<th>Lake</th>
<th>River downstream (&lt;40 km)</th>
<th>River downstream (&gt;40 km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling period</td>
<td>May 2003</td>
<td>December 2003</td>
<td>May 2003</td>
</tr>
<tr>
<td></td>
<td>December 2003</td>
<td></td>
<td>December 2003</td>
</tr>
<tr>
<td>F(CO2) (mmol m⁻² d⁻¹)</td>
<td>113±90 (50)</td>
<td>99±79 (117)</td>
<td>936±572 (24)</td>
</tr>
<tr>
<td>ΔpCO2 (μatm)</td>
<td>1525±564 (3)</td>
<td>3390±694 (116)</td>
<td>9275±1860 (10)</td>
</tr>
<tr>
<td>k600(CO2) (cm h⁻¹)</td>
<td>2.34±1.59 (3)</td>
<td>2.93±2.12 (116)</td>
<td>14.72±6.22 (10)</td>
</tr>
<tr>
<td>F(CH4) (mmol m⁻² d⁻¹)</td>
<td>6±7 (18)</td>
<td>2±2 (17)</td>
<td>57±27 (15)</td>
</tr>
<tr>
<td>ΔpCH4 (μatm)</td>
<td>122±86 (18)</td>
<td>37±24 (17)</td>
<td>115±59 (21)</td>
</tr>
<tr>
<td>k600(CH4) (cm h⁻¹)</td>
<td>3.13±2.29 (18)</td>
<td>5.10±6.30 (17)</td>
<td>10.06±5.60 (10)</td>
</tr>
<tr>
<td>U₁₀ (m s⁻¹)</td>
<td>2.48±2.62</td>
<td>1.84±1.28</td>
<td>2.21±0.96</td>
</tr>
</tbody>
</table>

**Note:**

- $a$ Average with 28 values during rainy event. For these data, F(CO2) range from 29.56 to 449.13 mmol m⁻² d⁻¹, $k_{600}$ from 0.81 to 13.37 cm h⁻¹ and rainfall rates from 0.6 to 25.26 mm h⁻¹.
- $b$ Average with 5 values during rainy event. For these data, F(CH4) range from 1.75 to 6.95 mmol m⁻² d⁻¹, $k_{600}$ from 2.59 to 28.35 cm h⁻¹ and rainfall rates from 2.40 to 36.00 mm h⁻¹.
concentrations, together with high gas transfer velocities in the downstream river (see Table 2 and next section).

In the second section of the river (N 40 km), ΔpCH4 and CH4 fluxes decreased rapidly (Table 2), due to the loss of CH4 by emission to the atmosphere and aerobic oxidation (Galy-Lacaux et al., 1999). In the N 40 km river section, CO2 fluxes were on average for the two campaigns 750 mmol m−2 d−1 (Table 2). Surface pCO2 and ΔpCO2 were close or higher than 10000 μatm all along the river, except at the limit of the coast, where it was around 6000 μatm. These high pCO2 along the whole estuary are attributed to an intense mineralization of organic matter originating from the reservoir (Abril et al., 2005).

3.2. Comparison of techniques

Fluxes obtained with floating chambers have been dismissed by several workers (Liss and Merlivat, 1986; Marino and Howarth, 1993; Raymond and Cole, 2001; Matthews et al., 2003). Two main contradictory critics were formulated. On one hand, FC is considered to increase the turbulence at the water surface (Marino and Howarth, 1993; Raymond and Cole, 2001). However, as described by Frankignoule et al. (1996a), drifting with the water masses, as done in our study, limits such disturbance. Artificial turbulence can also be created when the FC walls do not extend below the water surface. In such case, the chamber drifts above the water surface which can generate gas fluxes up to five times higher in comparison to FCs with wall extensions into the water (Matthews et al., 2003). This artifact becomes very important at low wind speed, as shown by Matthews et al. (2003), who compared FCs with wall not extending into the water with an SF6 addition during a period at wind speeds < 1 m s−1. Eugster et al. (2003) compared 8 one-hour measurements by FC with 16 half-an-hour EC samples in a lake, and concluded that the FC gave CO2 fluxes more than double than the EC fluxes. However, at the exception of samples taken during heating periods (3 FC fluxes), fluxes derived from FC measurements were very similar to those computed with the Cole and Caraco (1998) k-wind relationship and a surface-renewal model including the wind effect and the heat loss between the

Table 3
Comparison of the CH4 fluxes obtained by the two different floating chambers and the CO2 fluxes obtained by eddy covariance and floating chamber measurements

<table>
<thead>
<tr>
<th>Gas</th>
<th>Site</th>
<th>FC-IRGA (20L)</th>
<th>FC-GC (30L)</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>Lake</td>
<td>5.34 (0.6–29.4) n=10</td>
<td>4.64 (0.2–23.5) n=12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>River downstream (0–40 km)</td>
<td>95.1 (47.7–161.2) n=7</td>
<td>81.3 (29.5–144.4) n=7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>River downstream (40–80 km)</td>
<td>1.41 (0.15–3.3) n=4</td>
<td>0.90 (0.4–2.6) n=6</td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td>Lake</td>
<td>134.97 (21.76–49.13) n=40</td>
<td>90.76 (29.80–37.13) n=35</td>
<td></td>
</tr>
</tbody>
</table>

a Floating chamber with an Infra red gas analyzer with associate mean wind speed of 1.65 m s−1 (0.12–6.14 m s−1) and rainfall rates of 5.25 mm h−1 (1.00–25.26 mm h−1).

b Eddy covariance with associate mean wind speed of 1.52 m s−1 (0.18–3.87 m s−1) and rainfall rate of 3.40 mm h−1 (0.60–8.64 mm h−1).
water and the atmosphere (Crill et al., 1988; MacIntyre et al., 1995). The comparison of the two methods by Eugster et al. (2003) must therefore be taken with caution because it is based on few data, including net positive air-to-water CO$_2$ fluxes by EC while $p$CO$_2$ in the water was above the atmospheric concentration. These unexplained air-to-water fluxes significantly lowered the mean efflux values from EC and created most of the discrepancy between the two methods.

The second critic formulated was that FCs isolate the water surface from the influence of wind (Liss and Merlivat, 1986). However, the gas exchange is controlled by the turbulence in the aquatic boundary layer (Liss and Slater, 1974; McGillis et al., 2001; Kremer et al., 2003a) and if these conditions are determined over an area that is large enough relative to that influenced by the FC, the method could be reliable (Jähne et al., 1987). The disturbance of the FC on the wind speed boundary layer was tested experimentally by Kremer et al. (2003a), who measured O$_2$ fluxes using a FC with a fan to generate air turbulence and using a control FC in parallel. Under moderate wind conditions (1.6–3.4 m s$^{-1}$), the presence of the fan increased the fluxes by only 2% to 12%; such error is below classical sampling variability. Kremer et al. (2003a) also reported a series of experiments comparing the FC with mass balance approaches of O$_2$, $^{222}$Rn, and $^{3}$He in various experimental setting. Fluxes based on FC technique agreed with the other direct methods within 10% to 30%. Furthermore, Borges et al. (2004b) show that $k$ values determined by Frankignoulle et al. (1996b) in coral reefs fits within $k$-wind parameterizations from open ocean, hence, going against the recurrent argument that FC artificially enhances the fluxes. The recent work of Borges et al. (2004a) in tidal estuaries also indirectly validates the reliability of the floating chamber with other methods showing the strong dependency of $k_{600}$ with wind speed and water current velocity.

In the present study, the two FCs used to measure CH$_4$ fluxes were not deployed for the same duration time (30–60 min versus 5–10 min) due to differences of volume and detection sensitivity (GC-FID versus IRGA), and thus, can not be compared individually. In Table 3, we compare the CH$_4$ fluxes obtained for the lake and the river downstream with the two FCs for both campaigns. The differences between these two chambers were within 7% at the lake surface, 15% in the first 40 km river section and 33% in the second river section (>40 km) (Table 3). During the 24-h survey we measured concomitant CO$_2$ fluxes by EC and FC. The comparison of individual measurements is also difficult for two reasons: first, the fluxes are measured during 30 min for the EC and only during 5–10 min for FC which results in different average turbulent conditions; second, EC and FC measurements do not correspond to the same space scale: our EC integrates flux from a surface of 4 10$^4$ m$^2$ (Businger, 1986) compared to <1 m$^2$ for the FC. Nevertheless, average CO$_2$ fluxes during the same 24-h period were 91±73 mmol m$^{-2}$ d$^{-1}$ and 135±90 mmol m$^{-2}$ d$^{-1}$ for the EC and the FC techniques respectively (Table 3). The difference between these two mean fluxes was within 30%, in the generally accepted range of error for this type of experiment (Kremer et al., 2003a). In our case, these discrepancies can be explained by the difference of average meteorological conditions during the measurements. Respectively for the EC and FC measurements, mean wind speeds were 1.5 m s$^{-1}$ and 1.7 m s$^{-1}$, and mean rainfall rates were 3.4 mm h$^{-1}$ and 5.3 mm h$^{-1}$ (Table 3).

Table 4
Correlation function between the gas transfer velocity ($k_{600}$ cm h$^{-1}$) and the wind speed at 10 m height ($U_{10}$ m s$^{-1}$) and rainfall rates (R, mm h$^{-1}$) in the Petit-Saut Reservoir and in the tidal river downstream based on unbinned and bin-averaged data ($k_{600}$ data were averaged over wind speed bins of 1 m s$^{-1}$)
3.3. Wind effect

In the Fig. 1A the $k_{600}$ obtained on the lake with the EC and the FC are plotted versus the wind speed at 10 m ($U_{10}$). The $k_{600}$ values during rainy events are not shown in this figure. It can be seen that, besides some general scatter in the data, both methods fall within the same range for a given $U_{10}$. Similarly, the $k_{600}$(CO$_2$) and $k_{600}$(CH$_4$) obtained by FC are consistent on the lake surface. At zero wind speed was 2 to 3 times higher than in several studies in lakes (Crill et al., 1988; Cole and Caraco, 1998; McGillis et al., 2001; Borges et al., 2004a), data were averaged over wind speed bins of 1 m s$^{-1}$ (Fig. 1B). Various parameterization functions (linear, exponential, and power) have been used in the literature; based on statistical analyses ($r^2$ and $p$ values), the exponential model was the most appropriate for Petit-Saut Reservoir (Table 4). At very low wind speed ($<3.7$ m s$^{-1}$), we observe a weak dependency of $k_{600}$ with wind speed, consistent with several studies in lakes, oceans and wind tunnels (Wanninkhof et al., 1985; Liss and Merlivat, 1986; Cole and Caraco, 1998; Wanninkhof, 1992; Frost and Upstill-Goddard, 2002; Crucius and Wanninkhof, 2003). The slope of the relationship was 0.7 cm h$^{-1}$/m s$^{-1}$ for wind speed $<3.7$ m s$^{-1}$, similar to what is found in Liss and Merlivat (1986), and 1.7 cm h$^{-1}$/m s$^{-1}$ at higher wind speed. In addition, the intercept at zero wind speed was 2 to 3 times higher than in several previous studies (Wanninkhof et al., 1985; Frost and Upstill-Goddard, 2002; Crucius and Wanninkhof, 2003), except the one of Cole and Caraco (1998) on Mirror Lake determined by SF$_6$ addition. This could be due to thermal effects. The effect of evaporation (warm layer) and condensation (cool skin) on the gas transfer velocity was tested in a wind tunnel (Liss et al., 1981) and over the Pacific Ocean (Ward et al., 2004). These authors have shown that the gas transfer velocity can be enhanced by 4% to more than 30% under evaporative condition ($T_{\text{water}}-T_{\text{atm}}$) due to the destabilization of the near surface water. Frost and Upstill-Goddard (2002) measured gas transfer velocity by SF$_6$ evasion from a temperate reservoir ($\Delta T=T_{\text{water}}-T_{\text{atm}}=-1.4^\circ\text{C}$) and found a $k_{600}$ lower than 1 cm h$^{-1}$ for very low wind speed (Fig. 1B). In tropical environments, water is generally warmer than the overlying air above the water surface. In a tropical floodplain, MacIntyre et al. (1995) showed that more than 50% of the CH$_4$ fluxes observed by Crill et al. (1988) could be explained by convective cooling at very low wind speeds ($<2$ m s$^{-1}$). Anderson et al. (1999) presented $k_{600}$ values ranging from 1 to 15 cm h$^{-1}$ for wind speed ranging from 2 to 8 m s$^{-1}$ derived from CO$_2$ fluxes measured with the EC technique at a woodland lake surface. For a given wind speed, $k_{600}$ varied from 60% to 90%. They found the...
highest values of $k_{600}$ when water was warmer than air or during periods following strong winds and rapidly falling temperature. During our measurements the average $\Delta T$ between water and air was 2.1 °C ranging from $-2.2$ °C to 6.7 °C, generating a cooling of the surface water by evaporation. Like Cole and Caraco (1998), we could however not find any significant correlation between the thermal gradient and the difference between the individual $k_{600}$ and the “mean” $k_{600}$ derived from our $k_{600} – U$ relationship ($p=0.6085$). The large range of $\Delta T$ during our measurements can also explain the scatter of our low wind speed data.

In the tidal river downstream of the dam, the $k_{600}$ values were 3 to 4 times higher than at the lake surface at the same wind speed (Table 2) due to the turbulence induced by water currents (Zappa et al., 2003; Borges et al., 2004a). In addition, the relationship with wind speed was steeper than in the lake. The whole dataset (Fig. 2A) presents a large scatter probably due to rapid changes in water current, water depth and bed roughness between individual measurements. The mean $k_{600}$ in the Sinnamary Estuary was high (10.8 ±6.4 cm h$^{-1}$ $n=84$) which is consistent with previous studies in rivers and estuaries (Devol et al., 1987; Marino and Howarth, 1993; Clark et al., 1994; Frankignoulle et al., 1996a; Zappa et al., 2003; Borges et al., 2004a,b). On Fig. 2B, the whole dataset was averaged over wind speed bins of 1 m s$^{-1}$. The relation obtained is considered to be linear (Table 4) as shown in some other estuaries (Kremer et al., 2003b; Borges et al., 2004a). The difference of the formulation of the $k_{600}$-wind relationship from one site to another is still under debate. The most common hypothesis to explain these differences is that the slope of the linear regression could be due to the fetch limitation and the intercept to the contribution of water currents (Hartman and Hammond, 1984; Wanninkhof, 1992; Kremer et al., 2003b; Borges et al., 2004a). The fetch effect was shown in wind tunnel (Wanninkhof and Bliven, 1991) and in estuaries (Borges et al., 2004a). As shown in Fig. 3, the slope of the Sinnamary River $k_{600} – U_{10}$ relationship (2.7 cm h$^{-1}$/m s$^{-1}$) fitted well with the formulation as a function of surface area proposed by Borges et al. (2004a).
3.4. Rainfall effect

Rainfall falling on a water body is another mechanism creating turbulence at the water surface and leading to an enhancement of the $k_{600}$ (Banks et al., 1984; Ho et al., 1997). Quantification of this effect requires the wind influence to be removed from the data using our relationship between $k_{600}$ and wind speed (Table 4). Therefore we calculated the difference between our $k_{600}$ value during rainy events and our $k_{600}$ without rainy events at the same wind speed (Cole and Caraco, 1998; Frost and Upstill-Goddard, 2002) (Table 4). The $k_{600}$ dataset included rainfall rates from 0.6 to 36 mm h$^{-1}$ with wind speeds from 0.1 to 3.3 m s$^{-1}$. The residual $k_{600}$ was positively related to rainfall rates ($k_{600\text{-rain}} = 0.66 (±0.10) R^{-1.81}$ ($±1.52$), $R^2 = 0.84$, $p < 0.0001$, $n = 10$ for data averaged over rain rates bins of 1 mm h$^{-1}$) reaching 29 cm h$^{-1}$ for a rainfall rate of 36 mm h$^{-1}$ (Fig. 4). The fact that the effect of rainfall on $k_{600}$ is measurable by the FC confirms that this method adequately picks up the effect of turbulence in the aquatic boundary layer on the gas transfer velocity. Our relationship is not statistically different from those obtained in laboratory experiments (Banks et al., 1984; Ho et al., 1997). The relationship of Ho et al. (1997) was obtained in laboratory experiments (Banks et al., 1984; Ho et al., 1997). Quantification of this effect requires the wind speed, both methods gave similar $k_{600}$. Thus, the FC appears to be a reliable and inexpensive technique to determine the gas transfer velocity in various environments (lakes, estuaries, rivers). To avoid the creation of artificial turbulence, chambers must however have walls extending into the water and measurements must be performed while drifting. In the Petit Saut Lake, the $k_{600}$ dependence to wind speed followed an exponential model, with a significant intercept probably due to thermal effects. In addition, rainfall significantly contributes to the gas transfer velocity in such tropical environment. Finally, $k_{600}$ was significantly higher in the river downstream of the dam than in the lake, due to a contribution of water current to the turbulence in the aquatic boundary layer.

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