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Methane flux, vertical gradient and mixing ratio measurements in a tropical forest

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Abstract. Measurements of CH_4 mixing ratio, vertical gradients and turbulent fluxes were carried out in a tropical forest (Reserva Biológica Cuieiras), about 60 km north of Manaus, Brazil. The methane mixing ratio and flux measurements were performed at a height of 53 m (canopy height 35 m). In addition, vertical CH_4 gradients were measured within the canopy using custom made air samplers at levels of 2, 16 and 36 m above ground. The methane gradients within the canopy reveal that there is a continuous methane source at the surface. No clear evidence for aerobic methane emission from the canopy was found. The methane fluxes above the canopy are small but consistently upwards with a maximum early in the morning. The measured fluxes are in agreement with the observed CH_4 gradient in the canopy. In the morning hours, a strong canopy venting peak is observed for both CH_4 and CO_2, but for CO_2 this peak is then superimposed by photosynthetic uptake, whereas the peak lasts longer for CH_4. Monthly averaged diurnal cycles of the CH_4 mixing ratio show a decrease during daytime and increase during nighttime. The magnitude of the difference in CH_4 mixing ratio between day and night gradually increases throughout the wet season. The fluxes required to explain the nighttime increase are in agreement with the nighttime fluxes measured above the canopy, which implies that the CH_4 increase in the nighttime boundary layer originates from local sources.

1 Introduction

Amazonia plays a prominent role in the global carbon and methane cycle and its land use change implies numerous modifications to the biogeochemical cycles. Several studies have been carried out to understand the role of the tropical forest in the global cycle of the main greenhouse gases (Andreae et al., 2002; de Araújo et al., 2002; Bergamaschi et al., 2009; do Carmo et al., 2006; Janssens et al., 2001; Malhi et al., 1999; Malhi and Grace, 2000; Meirink et al., 2008; Miller et al., 2007; Molion, 1988; Sanhueza and Donoso, 2006).

Methane (CH_4) is the second most important anthropogenic greenhouse gas and its mixing ratio (presently $\sim$1.8 ppm) has increased by about 150 % since pre-industrial times (Etheridge et al., 1998). It is the most predominant hydrocarbon and the most abundant organic trace gas in the Earth's atmosphere, with 25 times higher greenhouse warming potential than CO_2 resulting in a 20 % contribution to the current enhanced greenhouse effect (IPCC, 2007). CH_4 also plays a central role in atmospheric oxidation chemistry and affects stratospheric ozone and water vapor levels (Lelieveld et al., 1998).

The atmospheric CH_4 budget has been intensively studied over the past two decades using numerous techniques, including flux measurements (Bartlett and Harriss, 1993; Singh et al., 1997; Hendriks et al., 2008; Smeets et al., 2009), mixing ratio measurements in global monitoring networks (Dlugokencky et al., 1998, 2009), isotope measurements (Quay et al., 1999; Miller et al., 2002), forward inverse modeling

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(Bousquet et al., 2006; Meirink et al., 2008; Bergamaschi et al., 2009) and recently also satellite remote sensing (Frankenberg et al., 2005, 2008).

Production of CH_4 is generally believed to occur mainly in anoxic environments, such as the submerged soils of wetlands, paddy fields and rice fields, by methanogenic bacteria during the anaerobic degradation of organic matter, and gastrointestinal tract of ruminants (Itoh et al., 2009). In the tropics, CH_4 is emitted at high rates from wetlands (Bartlett and Harriss, 1993), and conversion of forest-to-pasture may transform the soils from CH_4 sinks to sources (Steudler et al., 1996). However, regional net emissions are poorly constrained.

The responses of methane emission to climate change or to forest clearing and associated agricultural development, land abandonment and ecological succession are still inadequately understood (Keller and Matson, 1994; Veldkamp et al., 1998). Megonigal and Guenther (2008) reviewed the available literature and found that the understanding of methane emissions from upland soil and vegetation was incomplete based on the few available measurements.

Using the first available global satellite dataset from SCIAMACHY, Frankenberg et al. (2005) concluded that current emission inventories considerably underestimate the magnitude of methane source in tropical areas. With improved spectroscopic parameters Frankenberg et al. (2008) noticed that the strong elevations of methane mixing ratios above the tropical rainforest regions reported in Frankenberg et al. (2005) could not be confirmed, but the data still imply a large source of CH_4 in tropical areas (Bergamaschi et al., 2009).

do Carmo et al. (2006) used closed chamber and vertical profile measurements at three forests sites in Amazonia, to estimate an annual CH_4 flux between 4 and 38 Tg yr^{-1}, which even the lowest value already represents 1 % of the total global CH_4 emissions. They also concluded that there is no clear difference between wet and dry seasons. Other experiments conducted in a tropical savanna, suggest that this type of vegetation is a large source of CH_4 with higher production during the dry than wet season (Crutzen et al., 2006; Sanhueza and Donoso, 2006). Miller et al. (2007) analyzed ground-based and airborne profiles measurements from 2000 to 2006 and found large methane emissions from the Amazon basin. They calculate emissions averaging 20 mg CH_4 m^{-2} day^{-1} from the area around Manaus.

As the underlying processes that produce CH_4 in the tropics are still not well-quantified, the goal of this study was to learn about the CH_4 budget on a local scale by in-situ measurements at a tropical forest site. We performed detailed measurements of CH_4 fluxes, vertical gradients and mixing ratios in the Amazonia forest during the period of the international measurement campaign BARCA (Balanço Atmosférico Regional de Carbono na Amazônia) in Manaus – Amazonia.

2 Methodology

2.1 Site description

The Amazonia rainforest is well known for its diverse fauna and flora and peculiar characteristics in topography (Prance, 2001). We carried out experiments at the Reserva Biológica do Cuieiras, a terra firme forest covering an area of 22 735 ha located about 60 km north of Manaus. The area is characterized by little deforestation, a canopy height around 35 m and mainly consists of vast expanses of undisturbed rainforest (de Araújo et al., 2002). The area consists of plateaus (∼40 %) and valleys (∼60 %) with maximum height differences of about 60 m. Measurements were done on a 53 m tall scaffolding flux tower called K34 (Fig. 1), which was erected in 1999. It is a 1.5×2.5 m^2 cross section aluminum tower that is located on a medium sized plateau (2°36′32.67″ S, 60°12′33.48″ W, 130 m a.s.l.) (de Araújo et al., 2002). For a topographic image of the area and the exact location of the site we refer to Fig. 2 in de Araújo et al. (2010). The site belongs to the Instituto Nacional de Pesquisas da Amazonia (INPA), and it is coordinated by the Large Scale Biosphere and Atmospheric Experiment in Amazonian – LBA project. A detailed description of the site can be found in de Araújo et al. (2002).

The topography of valleys and plateaus implies that a plateau is surrounded by a vast area with lowland-waterlogged vegetation. From plateau to valley the soil clay fraction decreases while the sand fraction increases. The valley soil is usually waterlogged during the rainy season (Chambers et al., 2004; Luizão et al., 2004), while plateau areas are characterized by well drained clay soils (de Araújo et al., 2002).

At plateau regions the microbial biomass in the first 20cm of the soil layer varies from 266 to 1460 µgC g^{-1}, which corresponds to 1.8 to 4.8 % of the total soil carbon. The turnover time of soil microbes is 0.13 to 0.17 yr (Andreae et al., 2002).

2.2 Flux measurements

Flux instruments were installed on the K34 tower (Fig. 1). The instrumentation consisted of a Fast Methane Analyzer (FMA, Los Gatos Research), a sonic anemometer (Campbell CSAT3), a Campbell FW3 Type E thermocouple and a LI-COR LI7500 open-path fast CO_2 & H_2O analyzer. Raw data were sampled at 10 Hz using a Campbell CR1000 data logger and stored on a memory card. The FMA was operated in a closed-path eddy covariance (EC) set-up that carries the air through an 11 m long PVC tube (1 cm inner diameter). The air inlet was located 53 m above the ground and ∼20 m above the canopy. The tube inlet was shielded from rain by a funnel that was mounted 0.2 m behind the sonic anemometer and close to the LI7500. Measurements were carried out between November 2008 and July 2009. Due to some technical
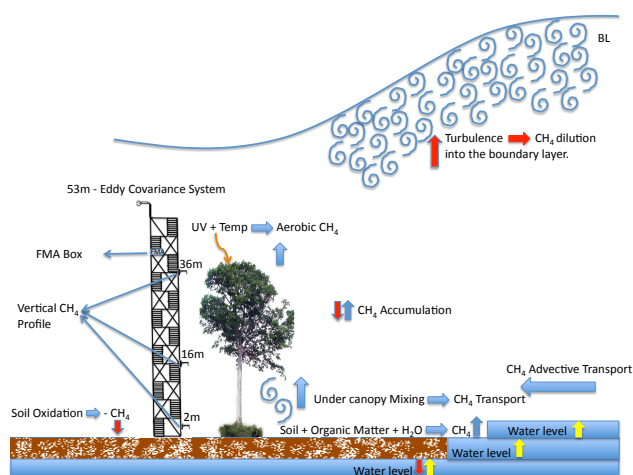
Fig. 1. Schematic picture of the measurement equipment installed at the K34 tower, in combination with processes that influence CH_4 levels below and above the canopy in the tropical forest environment. 06:00 h integrated samples are taken at levels, near the ground (2 m), close to the top of the canopy (36 m) and in the middle of the canopy (16 m). The eddy flux equipment, including the inlet to the closed path FMA, is installed at 53 m. CH_4 is formed via anaerobic decomposition of the organic matter by methanogenic bacteria in the soil, which depends strongly on soil water level. Dynamical factors also should be considered. Under canopy mixing and advection can transport CH_4 below the canopy. Since methane chemistry is rather slow, processes above the canopy is largely controlled by variations in the height of the planetary boundary layer, and by advection.

problem with the equipment, all the data from December, March and April had to be deleted.

Data processing was done in the same way as described in Smeets et al. (2009). Throughout this work we use the flux sign convention, i.e. positive flux values indicate an upward flux (from the canopy to the atmosphere), and negative values indicate a downward flux (from the atmosphere to the canopy). Details on data analysis are given in Appendices A and B. Most important was the correction of the WPL-effect (see Appendix A), which required the combination of the closed path data from the FMA and the open path H_2O data. The delay time between the raw data signal from the anemometer and the open and close path sensors were determined to correct for the longitudinal separation of sensors as well as the tube delay (2 s). As in Ibrom et al. (2007) we also found a large difference in delay time between water vapor and other scalars that strongly varied with relative humidity. In Appendix A we describe all applied corrections in detail. In addition, a correction for the recently discovered H_2O interference due to pressure broadening (Tuzson et al., 2010) was implemented. In Appendix B the detection limit for our CH_4 flux measurements is discussed.

2.3 Gradient and mixing ratio measurements

Vertical CH_4 mixing ratio gradients were measured during November and December 2008 using custom-made air samplers at 3 different levels 2 m, 16 m and 36 m (Fig. 2). Air was sampled at a constant flow rate of 11 ml min^{-1} over a period of 6 h by a metal bellows pump model MB-118E, and collected in 21 volume stainless steel canisters. The long time sampling was chosen to eliminate the short-term variability of methane mixing ratios due to turbulent mixing in the forest canopy. The canisters were changed up to four times per day. All canisters were pre-evacuated in the laboratory utilizing a high vacuum pump (TMH071P, Pfeiffer, Germany) before installation in the field. The samples were analyzed at the Atmospheric Chemistry Laboratory (LQA) of the Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, Brazil, using the MAGICC (Multiple Analyses of Gases Influence Climate Change) system developed by NOAA/GMD. Precision and accuracy have been described in Miller et al. (2007).

2.4 Calibration of the online measurements by flask samples

For a limited period (April–July 2009) we collected once a week air samples for CH_4 analysis at the top of the tower (50 m) next to the continuous CH_4 flux and mixing ratio measurements of the FMA system (see above). These samples were collected using another custom-made air-sampling unit. The sampling unit filled two 11 glass flasks in about 5 min with ambient air to an absolute pressure of up to 1.9 bar using a KNF Neuberger pump type PM22874-86. Moisture was removed using DRIERITE™ with moisture indicator, which was replaced when it was 75 % purple. The flask samples were analyzed in the IPEN laboratory, which allowed linking the FMA measurements to the international NOAA 2004 CH_4 scale (Dlugokencky et al., 2005). An average offset of -36 ± 9 ppb between the FMA data and the flask data was established. We corrected the FMA data assuming that this offset was constant throughout the campaign.

2.5 Rainfall and soil moisture measurements

In order to characterize the climatology during the experimental period and its relation to CH_4 production or absorption, soil moisture and rainfall data were analyzed. These data were obtained at the K34 automated weather station. Precipitation was collected using a rain gauge EM ARG-100, Campbell Scientific. The total precipitation values were stored every 30 min in a Campbell CR10X data logger. Soil moisture was sampled every 30 s using a Profile Probe type PR1, Delta-T Devices Ltd. The measurements were made at six different depth levels (0.05, 0.1, 0.2, 0.3, 0.5 and 1 m) and 10 min averages were stored in a Campbell Scientific CR10X data logger.
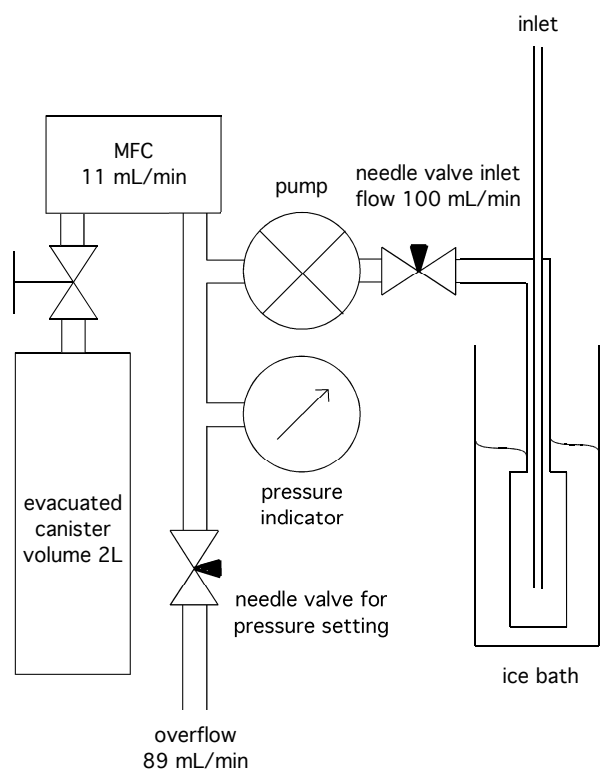
Fig. 2. Schematic drawing of the gradient air sampling units. Before filling the evacuated 2 l sample canister, the air passes through an ice bath to reduce the humidity. The sample flow is set to $11\,\mathrm{ml\,min}^{-1}$ by a Mass Flow Controller (MFC). Typically samples were taken over a period of 06:00 h.

The Climatological Normal (CN) average yearly rainfall at the site is 2400 mm with two marked seasons (November–May wet; June–October dry). Although highly variable, rainfall is present throughout the year, but typically less than 100 mm of precipitation occur from July to August (Chambers et al., 2004; de Araújo et al., 2008; Luizão et al., 2004). A comparison between the monthly rainfall in 2008/2009 and the CN is shown in Fig. 3. The study period (November 2008 to July 2009) showed some clear deviations from the CN. The months before the experiment (dry season) had precipitation higher than the CN. In particular, the first months of the measurement period (November to January) were unusually wet. The subsequent months (February, March and April), that usually mark the peak of the rain season, had slightly lower precipitation than the CN by about 30 mm. At the beginning of the dry period, June and July had 140 mm and 60 mm more rain than the CN. For the entire experiment period (November 2008–July 2009) precipitation surpasses the normal climatological mean by 523 mm.

The soil moisture for six different depths throughout the experimental period is shown in Fig. 4. The three top levels (0.01, 0.05 and 0.1 m) were directly influenced by the rainfall increase. The most significant increase happened 2 months
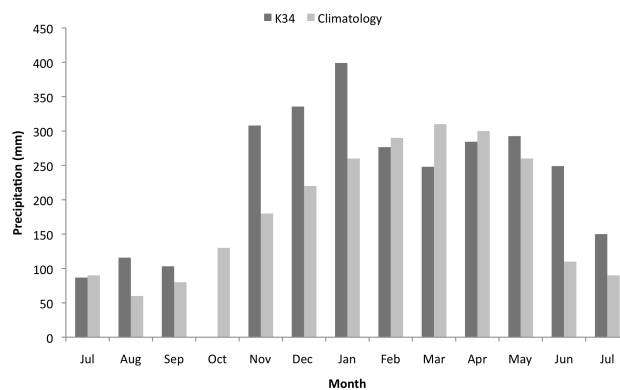

Fig. 3. Comparison between K34 rainfall data from July 2008 to July 2009 and the Manaus climatologically mean. Due to technical problems the data of October 2008 are not available.

after the rainy season starts (January). After January, the soil moisture only increases very slightly. The deeper levels show very small variability in soil moisture, with almost constant levels of 0.33, 0.27 and $0.42\,\mathrm{m}^{-3}\,\mathrm{m}^{-3}$ at 0.3, 0.5 and 1 m respectively.

3 Results

3.1 Vertical gradients

An intensive campaign to measure vertical CH_4 mixing ratio gradients in the canopy was carried out in November–December of 2008. Figure 5a and b show the raw 6 h average gradient data sampled during daytime (sampling started between 05:00 a.m. and 03:30 p.m. local time) and nighttime (sampling started after 04:00 p.m. and before 04:00 a.m.), respectively. The data show a large variability, and the mixing ratios below the canopy vary by 50 ppb. However, the changes within individual vertical gradients are much smaller and more systematic.

To obtain a better comparison of the CH_4 mixing ratio profiles we removed the offset between the different profiles by calculating the difference between the 2nd level (16 m) and the ground level (2 m) and between the 3rd level (36 m) and ground level. The results are shown in Fig. 5c and d with the average differences printed in red. During daytime, the CH_4 mixing ratio decreases ~3.2 ppb between the 2 m and the 16 m level, and ~4.3 ppb between 2 m and 36 m. During nighttime, the difference between the first two levels is ~3.4 ppb, and the difference increases to 9 ppb between the 3rd and 1st level.

3.2 Flux data

Figure 6 shows the monthly averaged diurnal cycle of CH_4 and CO_2 vertical eddy fluxes over the measurement period. The CH_4 fluxes are small, but measurable and reproducible
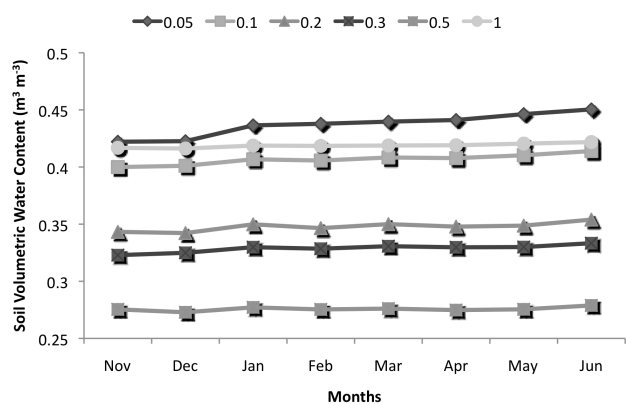
Fig. 4. Monthly average of the soil volumetric water content at six different levels below the surface (in meters) from November 2008 to June 2009.

between the months. Each morning after sunrise a peak in the CH_4 fluxes is observed above the canopy (Fig. 6a). A similar peak is observed for the CO_2 fluxes (Fig. 6b) although the duration of the peak is shorter, and in the case of CO_2 it is followed by an extended period of negative fluxes. During the afternoon and throughout the night the CH_4 fluxes are low, but on average positive, with values between 0.5 and 1.6 nmol m^{-2} s^{-1}. The size of the morning peak appears to increase from the dry season month November (maximum flux 2 nmol m^{-2} s^{-1}) to the wet season months, January, February and May (maximum flux 4–10 nmol m^{-2} s^{-1}). The positive morning peak is the most prominent and significant feature in the CH_4 flux data.

3.3 Diurnal variability of CH_4 mixing ratio

To study the diurnal evolution and its variation throughout the season, the average diurnal CH_4 mixing ratio cycle was calculated from the FMA data for each month (Fig. 7). Except for November 2008 all months clearly show a diurnal variation. Generally we observe a decrease during daytime and increase during nighttime. The diurnal amplitude increases from the beginning of the wet season (10 ppb in January) throughout the wet season to >30 ppb in the dry season (July). It should be noted that for the study region the timing of sunset and sunrise does hardly change throughout the year. The maximum nocturnal mixing ratios of CH_4 are observed in July, while November exhibited the lowest values.

4 Discussion

4.1 Vertical gradients

Absolute CH_4 mixing ratios varied from below 1790 to above 1840 ppb, and differences up to ±40 ppb were seen in subsequent sample sets separated by 6 h. This is much more

than the rather small vertical gradients shown in Fig. 5. It should be noted that it is not individual sample flasks that show these elevations, but all three samples from a certain vertical gradient, which strongly argues against contamination of individual flasks. Although our sampling resolution over a day is limited, it appears that episodes of CH_4 elevations are not confined to a certain period of the day. This suggests that such episodes are not caused by local sources, but by advection of CH_4-rich air. Tóta et al. (2008) detected a nocturnal subcanopy horizontal advection at K34 that transports a significant amount of CO_2, which is a significant term in the local budgets. It is clear that in order to further examine this feature for CH_4, high temporal resolution measurements are required. A continuous vertical gradient system is presently being installed at the K34 site. Such measurements should also reveal whether the observed negative vertical gradients (on average) can be observed year-round and whether the occasionally observed positive gradients are a robust feature and indeed occur regularly during daytime. A longer observation period is important since the vertical profile measurements presented here were limited to few weeks only (8 December–9 January). These measurements describe a snapshot only, and we do not know whether the vertical gradients vary on longer timescales, and how they vary spatially between the plateaus to the valleys.

The decrease of CH_4 mixing ratios with height inside the canopy implies that the surface on the plateau is a net source of methane in the measurement period, i.e. methane production surpasses methane uptake. The observed gradient is in agreement with measurement carried out on the ground. Soil flux chamber measurements have been initiated to investigate seasonality and spatial heterogeneity of these emissions, with the goal to link them to the gradient observations. First results (not shown here) indicate that the natural soil indeed produces CH_4, but when the litter and surface soil layer are removed, methane can be taken up by the soil.

The present data add to the growing evidence that upland forests (i.e. not only wetlands) in Amazonia have to be considered a significant methane source. A positive surface flux was also determined by do Carmo et al. (2006) from measurements in a Brazilian forest. In contrast, for dry tropical forest soils in India, Singh et al. (1997) found that uptake dominated over production. The influence of water and temperature on the competition between CH_4 uptake and production has been investigated by Itoh et al. (2009). They also observed CH_4 production at values of soil water content and temperature comparable to the conditions at our measurement site.

Recent measurements have indicated that UV irradiation can lead to CH_4 production from organic matter (McLeod et al., 2008; Vigano et al., 2008). In the tropical forest, the soil does not receive much radiation due to shielding from the canopy. Radiation is strong at the top of the canopy itself, but it was already argued that living plants should be well protected against UV radiation (Vigano et al., 2008). In
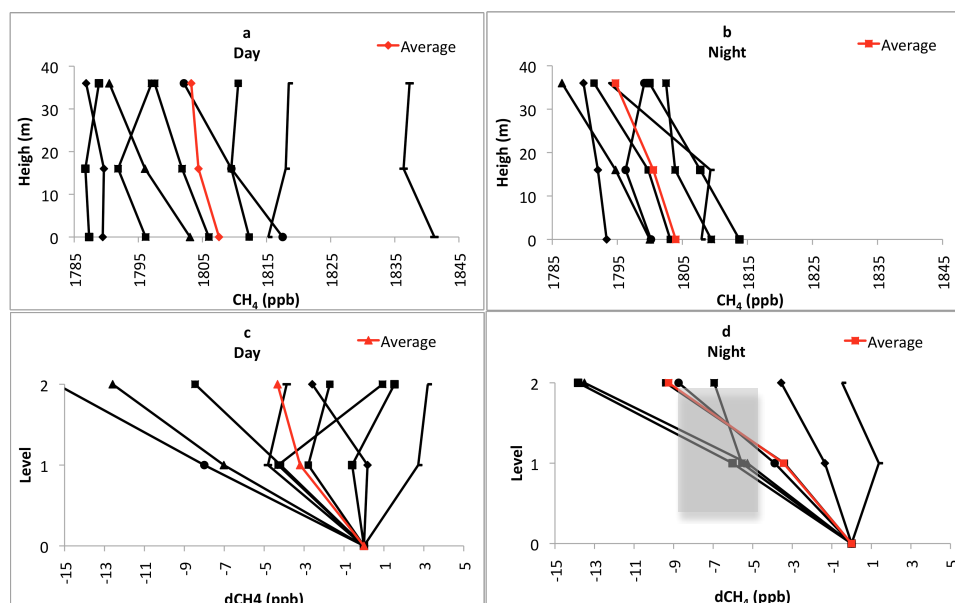
Fig. 5. Daytime and nighttime vertical gradient measurements. Panels **(a)** and **(b)** show CH_4 mixing ratios. Panels **(c)** and **(d)** show the relative difference (dCH_4) between 36 m (level 2) and 16 m (level1) to the 2 m (level 0). The grey-shaded area in **(d)** corresponds to the average CH_4 excess that is exchanged per hour from the canopy according to the calculations in Sect. 4.3.

our observations, the CH_4 mixing ratio gradient is stronger between 2 and 16 m than between 16 and 36 m. This does not suggest a significant CH_4 production in the canopy. Tóta et al. (2008) studied sub-canopy horizontal and vertical CO_2 fluxes. Results showed that nighttime advection could transport significant amounts of CO_2 in the lowest 10 m of the canopy. According to the same research advection accounted for 73 % and 71 % of the CO_2 budget during the dry and wet period. Advection could have similar relevance for CH_4. Nevertheless, if CH_4 is horizontally transported below the canopy, it also implies that production is happening close to the ground.

4.2 Turbulent fluxes above the canopy

The main feature of the eddy flux data is the clear flux peak in the morning. Coinciding with sunrise at 06:00 a.m. local time, the measured fluxes start increasing and reach a mean level of almost 6 nmol m^{-2} s^{-1} for CH_4 and $\sim$9 µmol m^{-2} s^{-1} for CO_2 between 7 and 08:00 a.m. local time. de Araújo et al. (2002), observed a similar CO_2 peak at this flux tower. They interpreted it as a canopy venting peak, where CO_2 from respiration, that has accumulated inside the canopy at night, is transported upward into the boundary layer in the morning. Accumulation occurs due to radiative cooling at the top of the canopy leading to stably stratified air that acts as a lid on top of the canopy (Tóta et al., 2008). In the case of CO_2, the venting peak is quickly superimposed by the strong CO_2 uptake signal due to photosynthesis. Our CH_4 flux data show that methane is not affected

by such a compensating process. This suggests that methane measurements allow inferring the real duration of the canopy venting period, and averaged over all months the peak has a width of about 5 h. After $\sim$12:00 p.m., the fluxes return to the low positive value around 0.5–1.6 nmol m^{-2} s^{-1} that continues throughout the rest of the day. The CO_2 fluxes remain clearly negative until sunset ($\sim$06:00 p.m. local time), as was observed by de Araújo et al. (2002) and Culf et al. (1997).

Apart from this strong flux peak, it is notable that the fluxes of CH_4 are small but positive throughout the day. During the night, this also holds for CO_2. It is known that application of the eddy flux technique is limited to periods in which turbulent mixing dominates. At night, surface cooling suppresses turbulent transport and increases horizontal advection possibly leading to an underestimate of emissions during calm and clear nights (Goulden et al., 2006). However, for CH_4, the nighttime fluxes are very similar to the fluxes measured during the afternoon, where conditions for eddy-flux measurements are more favorable. In Appendix B, we show detailed covariance spectra for the nighttime fluxes and calculated a detection limit, which implies that the small values are significantly different from zero.

The positive CH_4 gradients measured inside the canopy discussed above (Sect. 4.1 and Fig. 5) provide further support for the positive fluxes detected above the canopy throughout the day. A detailed study of the vertical dispersion of trace gas at another Amazon rainforest station in Rondonia (Simon et al., 2005) showed canopy flushing rates of one hour at 90 % canopy height. We note that the canopy at the
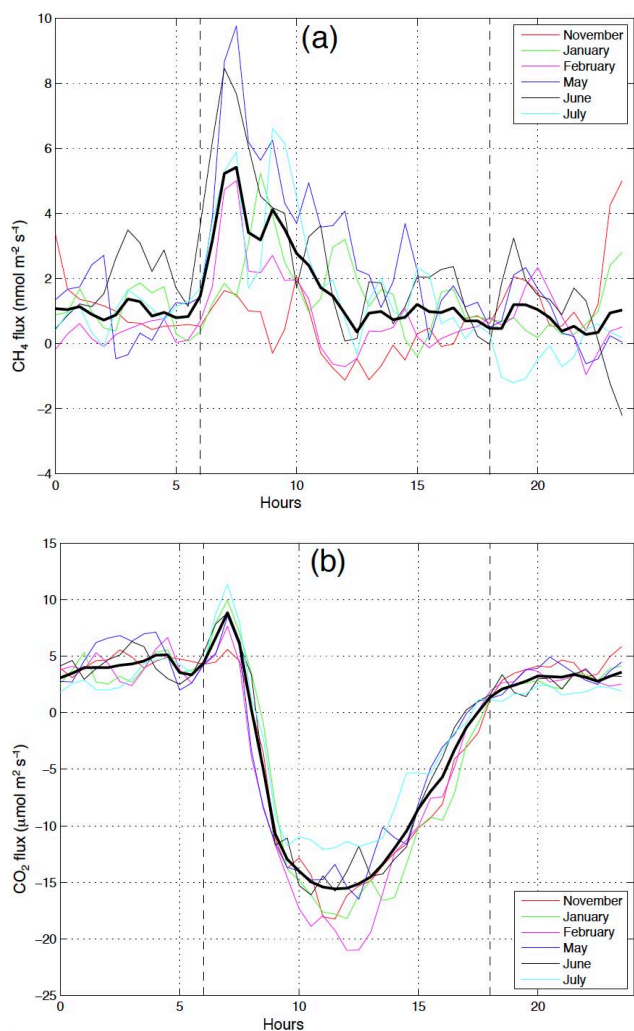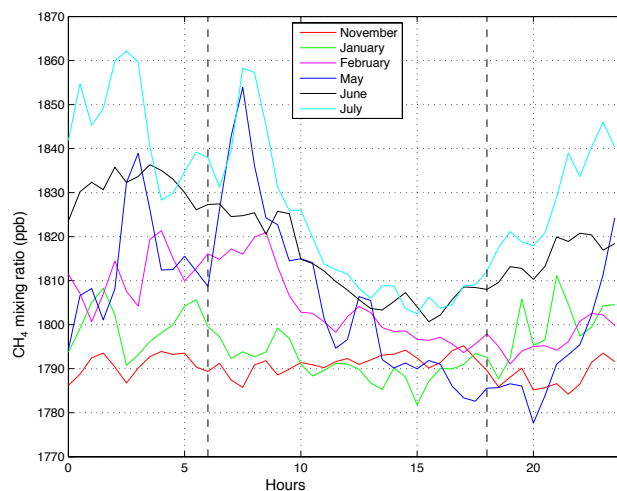
Fig. 7. Monthly averaged diurnal cycles of CH_4 mixing ratios measured with the FMA at the top of the tower K34 during six months. Vertical dashed lines indicate the time of sunrise and sunset, respectively.

Fig. 6. Monthly averaged diurnal cycles of CH_4 **(a)** and CO_2 **(b)** fluxes measured at the top of the K34 tower.

Rondonia site is higher (43 m) than at K34, and the canopy and turbulence statistics may be different at the two sites. Nevertheless, in the absence of similar data for our location, we use this flushing rate for a rough estimate. From the gradient results in Fig. 5, we estimate that a CH_4 excess of $\sim$5 ppb $\cdot$ 30 m^3 is emitted from the canopy per m^2 and per hour, which corresponds to a CH_4 flux of 40 nL m^{-2} s^{-1} or 1.6 nmol m^{-2} s^{-1}. This value is similar to the nighttime fluxes ($\sim$1 nmol m^{-2} s^{-1}) measured during the same period (November), and thus provides independent support for positive CH_4 fluxes during day and night. These two independent datasets provide an internally consistent picture and the CH_4 flux detected above the canopy can be explained by local production at the surface.

It is useful to compare the total average measured flux of $\sim$2 nmole m^{-2} s^{-1}, which corresponds to $\sim$2.8 mg CH_4 m^{-2} day^{-1} to the flux estimates from Miller et al. (2007), who deduced an average flux of 20 mg CH_4 m^{-2} day^{-1} from air-

craft flights in the Manaus Amazon basin. It follows that the measured emissions from the upland forest reported here are probably not representative for the Amazon basin as the fluxes are probably much higher in wetland areas (e.g. from the valleys). Multiplying $\sim$2.8 mg CH_4 m^{-2} day^{-1} by the total forest area in Amazonia of 5×10^6 km^2 yields an estimate for the total annual CH_4 flux of 5 Tg yr^{-1}, which is about 1 % of the total global CH_4 emissions and similar to results reported by do Carmo et al. (2006), however, this a factor of 7 lower than the total flux calculated with the emission of 20 mg CH_4 m^{-2} day^{-1} from Miller et al. (2007).

4.3 Diurnal variations above the canopy

The measurements above the canopy (53 m, top of the tower) revealed clear diurnal cycles in CH_4 mixing ratio and the amplitude of these cycles varies throughout the season from almost no diurnal variability in November to >30 ppb in July. In general, CH_4 mixing ratios above the canopy increase during night and decrease during the day. This shape of the diurnal cycle can be qualitatively explained by accumulation of surface emissions in the shallow nighttime stable boundary layer and dilution of the accumulated CH_4 into the daytime planetary boundary layer when the nocturnal layer breaks up. This has been discussed in detail in Culf et al. (1997) for the case of CO_2.

No information on the height of the nighttime boundary layer at the location of the K34 tower is available, but Culf et al. (1997) reported boundary layer heights around 100 m above the canopy during the Rondonia Boundary Layer Experiment. We can use this estimate for a back-of-the-envelope calculation to estimate which flux is required to explain the observed nighttime increase in CH_4 mixing

ratio. At 1800 ppb, a total volume of 10^5 l above $1\,m^2$ canopy surface contains 180 ml or 7.2 mmol CH_4. An increase of $0.1\,\%\,h^{-1}$ ($=1.8\,ppb\,h^{-1}$) is then required to produce the observed average nighttime increase of roughly 20 ppb. If this flux was produced locally, we should thus observe a continuous nighttime flux of $7.2\,\mu mole\,m^{-2}\,h^{-1}$, or $2\,nmole\,m^{-2}\,s^{-1}$.

This is of the order of the observed mean nighttime flux between 0.5 and $4\,nmole\,m^{-2}\,s^{-1}$ for the different months, and similar to the estimate based on the gradients and canopy mixing times as discussed above. Therefore the nighttime EC flux measured directly at the tower is sufficient to explain the increase in CH_4 mixing ratios above the canopy during the night.

5 Conclusions

The collective evidence from vertical CH_4 gradient measurements in an upland tropical forest, CH_4 fluxes above the canopy, and the diurnal cycle of CH_4 mixing ratio above the canopy, suggests that this ecosystem is a source of CH_4 to the atmosphere. CH_4 fluxes directly measured above the canopy are positive, and can explain the observed increase of methane mixing ratios in the boundary layer during the night. A canopy venting peak is observed for CH_4 around sunrise. The total duration of elevated fluxes due to canopy venting is of order of five hours. Nevertheless, this flux is not detectable as a mixing ratio increase above the canopy, since mixing with free tropospheric air due to the breakup of the nighttime boundary layer overwhelms the small flux from the canopy. No conclusive evidence for aerobic methane emissions from the canopy could be found, although some individual vertical profiles showed an increase in CH_4 mixing ratio from the middle to the top of the canopy, and the average decrease between these two levels is less during day than during night. Gradient measurements with higher temporal resolution and for a longer period will be required to address this issue in more detail. The present measurements indicate that the source of CH_4 at this site is located at the ground. Together with advective transport close to the surface all our observations can be understood.

Appendix A

The delay time of water vapor versus scalars in a closed-path system

Scalars (e.g. CH_4 mixing ratio) and water vapor can behave very differently inside the tube of a closed path system. As first shown quantitatively by Ibrom et al. (2007), the delay time of water vapor transport through a tube can be much larger than for other scalars and strongly depends on relative humidity. As a consequence, the water vapor dilution of scalars (i.e. the Webb Pearman Leuning – WPL effect) inside
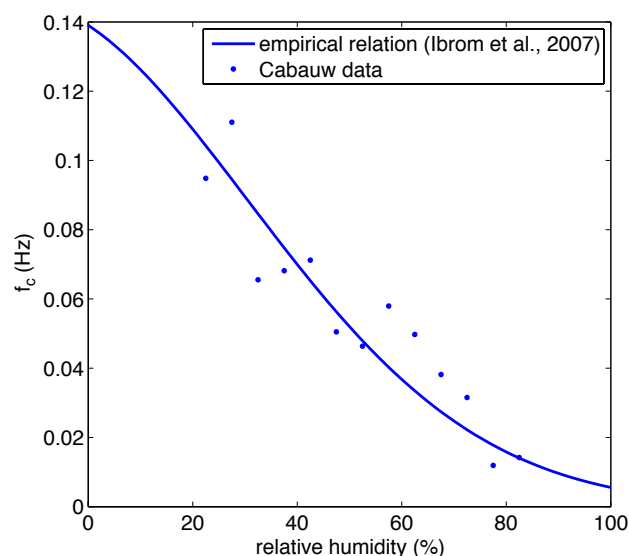

Fig. A1. Cut-off frequency for water vapor as a function of relative humidity. The symbols are the results from combining different fits to the spectra and various data selection criteria applied to the Cabauw data. The solid line represents the empirical model presented by Ibrom et al. (2007).

the closed-path system is desynchronized. Following Ibrom et al. (2007), the desynchronization of the water vapor signal can be simulated as the low pass filtering with a first-order recursive filter

$$H(f) = \frac{1}{1 + (f/f_c)} \tag{A1}$$

where f_c is the cut-off frequency (the frequency at which the filter reduces the power spectral estimates by a factor of 2). Ibrom et al. (2007) present an exponential function that predicts the increase of f_c as a function of relative humidity for their EC-system. Moreover, they also demonstrate that the same relation can be used to other EC-systems with very different tube dimensions (i.e. radius and length). We confirm their findings by using measurements performed at the CESAR observatory near Cabauw, The Netherlands, (http://www.cesar-observatory.nl) at 20 m height during the summer of 2010. The measurement system that we used was the same as at the K34 tower in Manaus with the addition of a closed path LI-COR LI6262 H_2O/CO_2 analyzer. The LI6262 and FMA were both connected to the same 20 m tube (the same as we use for the experiments at K34). The water vapor signal measured with the LI6262 is assumed to be the same as that within the measurement cell of the FMA. We used these data to calculate power spectra for the water vapor and fitted these to obtain values for the cut-off frequency. The results are plotted as a function of relative humidity in Fig. A1 together with the empirical model from Ibrom et al. (2007).

Table A1. Values for the constants used in Eq. (A4).

	c_1 (m^{-1})	c_2 (Hz)
Unstable	2.457×10^{-3}	6.342×10^{-4}
Stable	6.761×10^{-3}	2.906×10^{-3}

Our data scatter around the empirical formula from Ibrom et al. (2007) and we decided to adopt their empirical model given as

$$f_c = e^{-2.499 \mathrm{RH}^2 - 0.717 \mathrm{RH} - 1.973} \tag{A2}$$

where RH is the relative humidity. The calculation of the low pass filtering effect on the fluxes by means of a phase shift of water vapor inside the tube is performed as described in Ibrom et al. (2007)

$$F = \frac{\overline{w'C'}}{\overline{w'C'_m}} \tag{A3}$$

where $\overline{w'C'}$ and $\overline{w'C'_m}$ is the actual flux in the atmosphere and the low pass filtered flux inside the closed path system, respectively. A model for F can be described as

$$F = \frac{c_1 u}{c_2 + f_c} + 1 \tag{A4}$$

where the constants c_1 and c_2 are presented in Ibrom et al. (2007) separately for stable and unstable stratification (see Table A1).

Appendix B

The validity of the nighttime CH$_4$ fluxes

For a correct estimate of the detection limit we estimated its maximum value via a trial and error method that repeatedly calculates covariance for a range of lag times between $w\prime$ and CH$\prime_4$, i.e. the vertical velocity component and the methane mixing ratio, respectively. The flux detection limit can be estimated as the standard deviation for a range of covariances calculated in a lag-time window far away from the lag time of maximum covariance (Wienhold et al., 1995; Kroon et al., 2007). We calculated covariance for a lag-time window ranging between plus and minus 80 to 100 s. The standard deviation of the covariance within this range is an estimate for the lower detection limit of CH$_4$ fluxes for one half-hour interval. Calculating the true detection limit for CH$_4$ fluxes is however not straightforward since it includes the influence of water vapor fluxes via the WPL effect. We apply the same procedure as described in (Smeets et al., 2009) to obtain the true detection limit.

In Fig. B1 we display the averaged diurnal variation of methane fluxes and the corresponding detection limit for the
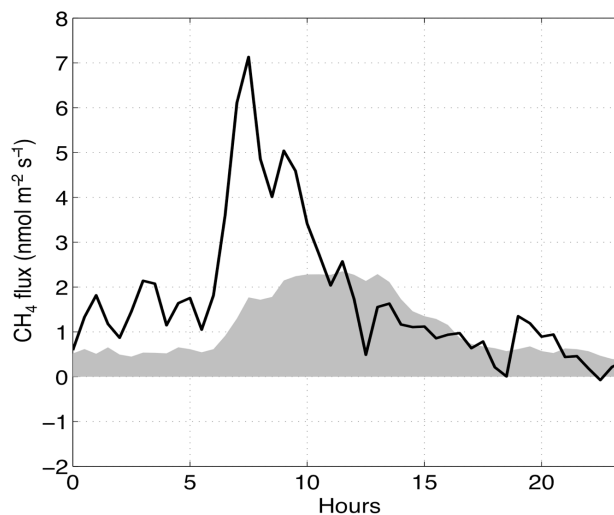

Fig. B1. Averaged diurnal variations of methane fluxes (solid line) and the corresponding detection limit (filled area) for data obtained from January to July 2009.
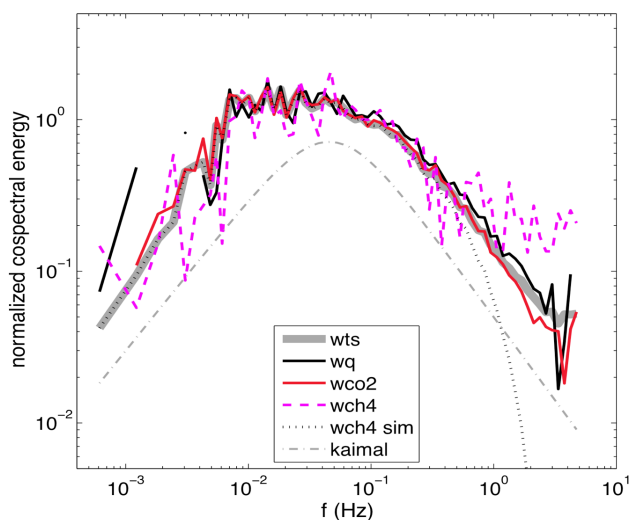

Fig. B2. Normalized averaged co-spectra from an ensemble of 109 half hour nighttime runs obtained between 20:00 h and 05:00 h from February to July 2009. The co-spectra for sonic temperature, water vapor, CO$_2$ and CH$_4$ flux are plotted as a function of natural frequency. The dotted black curve (CH$_4$ simulated) represents an estimate of the expected shape of the co-spectrum of CH$_4$ without the influence of signal noise. The dashed grey curve is the arbitrarily offset near-neutral universal co-spectrum (Kaimal et al., 1972; Kaimal, 1973). The average stability and wind speed for the ensemble are $z/L = +0.65$ and $\overline{u} = 2.2 \pm 0.6$ m s^{-1}.

whole measurement period. In particular in the second half of the night (after midnight), the measured fluxes are above the detection limit. These results illustrate that, although the methane fluxes measured become very small during the night, they are most of the time larger than the detection

limit. Consequently, our results for continuous upward directed methane fluxes during the night are realistic.

The quality of our nighttime flux data (between 20:00 h and 05:00 h) is also illustrated by the average from an ensemble of 109 normalized co-spectra as a function of the natural frequency presented in Fig. B2. Note that we did not use the dimensionless frequency (f_z/u) to average our co-spectra because the wind speed variations within the selection of 109 runs were small ($\overline{u} = 2.2 \pm 0.6\,\mathrm{m\,s^{-1}}$). The co-spectra of sensible heat and water vapor, CO_2 (C_wT_s, C_{wq} and C_wCO_2) overlap and compare very well to the universal Kansas curve for near neutral co-spectra (Kaimal et al., 1972; Kaimal, 1973). The universal curve was arbitrarily offset so that a comparison with its slope at low and high frequencies is not obscured by our co-spectra. This result is another indication for the high quality of our EC measurements.

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